CHAPTER 26

The Effects of Sediment-Bound Heavy Metals on Algae and Importance of Salinity

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A bioassay has been carried out to determine the uptake of selected heavy metals from freshwater sediments by *Ankistrodesmus bibraianus* Korshikov and *Entermorpha intestinalis* Link. An apparatus was used in which a 0.45 μm pore diameter membrane separated the algae and sediments. When used with freshwater and sediments, this method indirectly demonstrated biological uptake from resuspended sediments. The amounts of metals accumulated in the test algae were compared to chemical associations of metals in sediments, but there were no clear relationships with geochemical phases. The observed relationships between growth and metal content of the algae indicated, based on biomass, that Cu reduced algal growth during the 96-h test period. The distributions of metals in water, sediments, and algae were influenced by salinity, and marked differences were apparent among the six elements studied.

Introduction

Algal assays are widely utilized in eutrophication and toxicity assessments (Miller et al., 1978). Most of these studies have shown that there is an enrichment of heavy metals in biological species, in comparison to the surrounding water (Ahlf et al., 1980). More recently, it has become apparent that bioaccumulation and toxicity are dependent on the chemical forms of metals in solution (Petersen, 1982). Luoma et al. (1982) found significant correlations between estuarine sediments and the tissues of benthic algae, and suggested that sediment-bound metals could provide an important source for uptake by algae. While numerous studies have shown that sediments generally act as sinks for heavy metals (e.g., Salomons and Förstner, 1984), the relative importance of contaminated sediments in the processes of bioaccumulation and their toxicity to biota remain less certain. This may be due to the experimental difficulties arising from the need to provide an interacting system of sediments and algae, while retaining the ability to analyze each system separately. An early proposal to overcome these problems was made by Laube et al. (1979), who used a laboratory system to investigate the accumulation of Cd and Cu from sediment by freshwater algae within enclosed dialysis bags. The use of elutriates prepared from sediments, instead of the sediments themselves, was described in detail by Prater and Hoke (1980). Munawar et al. (1983) applied this technique to study the impact of sediment-associated contaminants on different-size fractions of phytoplankton. Since dredging operations and subsequent disposal cause resuspension of sediments in the water column, it is important to simulate such effects during experiments and to investigate the influence on phytoplankton growth. In the present study, we used an apparatus to investigate both suppression and stimulation of algal growth caused by heavy metals; but there was no direct contact between the algae and sediments. The objective of the bioassay study was to determine the impact of some sediment-bound heavy metals on algae at various levels of salinity in an aqueous medium.

Materials and Methods

Laboratory experiments were performed with the freshwater green alga *Ankistrodesmus bibraianus* Korshikov (*Selenastrum capricornutum*), and with the seawater alga *Enteromorpha intestinalis* Link. Biological tests were carried out in a modified two-chambered device, which was described by DePinto (1982). The two vessels were separated by a

Table 26.1. Bulk sediment analysis (ranges in μg/g dry weight).

River sediment	Cd	Cu	Pb	Mn	Ni	Zn
1. Geesthacht	2.4	99.3	56.1	241	22.6	645
2. Zollenspieker	2.1	32.5	35.2	225	10.7	279
3. Heuckenlock	3.4	79.3	71.5	413	18.9	442
4. Harbor I	16.3	321.0	290.0	1267	59.7	1690
5. Harbor II	2.5	9620.0	163.0	232	30.5	340
6. Wedel	1.9	34.9	36.5	848	15.2	242

0.45-μm pore diameter membrane that permitted diffusion of dissolved trace metals from one side to the other, but prevented mixing of the algae and sediments. The inoculum contained 0.5% (weight/volume) suspended solids and 5×10^5 cells $\times$ ml^{-1} of *A. bibraianus*. The alga *E. intestinalis* was cultured in brackish water (Schlösser, 1982), and experimental samples were selected from young portions of thallus (1 g fresh weight). The bioassays were terminated when the assay cultures showed no measurable increase in heavy metal content. This was always attained within a 96-h incubation period. Chlorophyll a content was determined spectrophotometrically, following extraction with methanol (Iwamura et al., 1970). Surface water from the Elbe River was passed through a 0.45-μm (porosity) membrane filter and used as a test medium with *A. bibrainus*. A test medium for assays with *E. intestinalis* was prepared by mixing filtered seawater with filtered Elbe River water. Experiments were conducted in triplicate.

The following extraction scheme was used for the assessment of chemical forms of heavy metals associated with the particulates (Calmano et al., 1982).

1. Exchangeable cations;
2. Carbonate fraction and easily reducible phases (Mn oxides, amorphous Fe oxides);
3. Moderately reducible phases (amorphous and poorly crystallized Fe oxides);
4. Metals bound to organic matter and sulfides;
5. Residual fraction (e.g., detrital silicates).

The leaching procedure can identify the amounts of various elements that are released from natural particles upon changes in ionic strength, pH, or redox conditions, and it provides a rough estimate of metal bonding strength. Heavy metals were analyzed using flame and carbon furnace atomic absorption spectrometry (AAS) (Hitachi, model 180–70).

Results

Six sediment samples from the Elbe River were analyzed for heavy metals and used in bioassays (Table 26.1). The concentration of heavy metals in the algae are given in Table 26.2. The data from 96-h sediment bioassays indicated an increase in trace metal uptake by *A. bribraianus* in the sediment-water system, in comparison to the control system without sediment.

No statistically significant relationship was found between bulk sediment composition and algal uptake for the six elements studied. We expected that only certain forms of heavy metals would be available to

Table 26.2. Concentrations of metals in *A. bibraianus* (μg/g dry weight) from a 96-h sediment bioassay).

River sediment	Cd	Cu	Pb	Mn	Ni	Zn
1. Geesthacht	4.43	79.0	25.5	1055.0	60.0	733.0
2. Zollenspieker	4.88	78.1	41.6	1727.5	51.6	714.5
3. Heuckenlock	7.65	127.6	19.8	3172.7	51.7	490.7
4. Harbor I	3.60	48.9	57.7	2261.0	40.1	556.0
5. Harbor II	3.20	3288.0	18.8	256.3	29.1	122.0
6. Wedel	2.32	108.7	11.3	664.0	47.0	210.3
Without sediment	0.30	46.0	3.6	141.0	3.5	172.0

Table 26.3. Concentration of cadmium in geochemical phases (μg/g dry weight) and correlation of Cd in *A. bibraianus* with geochemical phases.

River sediment	Adsorbed	Carbonate + easily reducible	Moderately reducible	Organic + sulfide	Residual	Bulk
1. Geesthacht	0.77	0.53	0.43	0.36	0.04	2.42
2. Zollenspieker	0.60	0.92	0.21	0.22	0.02	2.09
3. Heuckenlock	0.93	1.32	0.24	0.56	0.03	3.37
4. Harbor I	1.53	7.27	5.01	0.99	1.74	16.27
5. Harbor II	0.83	0.89	0.08	0.22	0.03	2.51
6. Wedel	0.33	0.91	0.06	0.49	0.03	1.92
Correlation coefficients	0.204	−0.120	−0.09	−0.149	−0.140	−0.09

algae (e.g., adsorbed/exchangeable species), but none of the concentrations in algae nor in any of the five phases of sequential extractions were significantly correlated. As an example, the concentrations of Cd in different geochemical phases and their correlations with algal concentrations are given in Table 26.3. These data suggest that even if sediments are controlling solute concentrations of heavy metals in our system, their biological uptake cannot be determined directly from chemical extraction experiments.

Algal assays were used to study the effects of sediment resuspension. The amount of growth was determined after 96 h by measuring the parameters: dry weight, cell number, and chlorophyll a (Fig. 26.1). Sediments 4 (harbor I) and 5 (Harbor II) (Table 26.3) had a significant effect upon algal growth; sediment 4 had a stimulative effect and sediment 5 reduced growth. The results of algal growth and bioaccumulation were analyzed statistically to seek possible correlations (Table 26.4). The only significant relationship detected was a negative correlation between Cu and chlorophyll a.

In a second series of experiments, the effect of a range of salinities on metal content was investigated using the saltwater alga *E. intestinalis*. Based on these algal bioassay experiments, the data suggest that uptake is predominantly due to cation exchange within the cell wall matrix, as demonstrated for short-term accumulation of metals in *A. bibraianus* (Reed and Darrig, 1983). Figure 26.2 shows the effects of increasing salinity on heavy metal uptake from harbor I sediment. Cadmium uptake was highest at intermediate salinity. Uptake of Pb was high in fresh water, but it became substantially less as salinity increased. The amount of Cu sorbed by

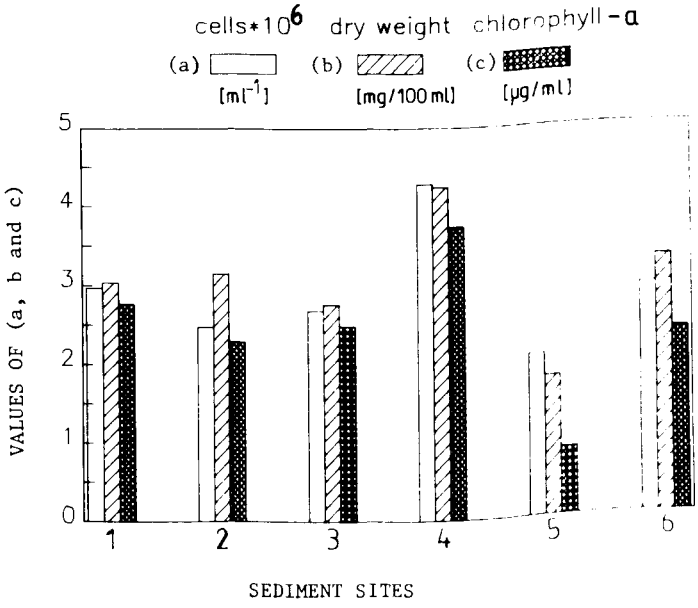

Fig. 26.1. Cell number, (a) dry weight (b) and chlorophyll a (c) of *Ankistrodesmus bibraianus* at the end of a 96-h sediment bioassay. Sediment sites 1–6 correspond to the sites in Table 26.1.

Table 26.4. Correlation coefficients from correlation analyses of bioaccumulation data and algal growth data from 96-h sediment bioassays with *A. bibraianus*.

River sediment	Cd	Cu	Pb	Mn	Ni	Zn	Sum
Chlorophyll a	0.0490	−0.8330[a]	0.5857	0.5245	0.4375	0.5421	−0.4577
Dry weight	−0.1071	−0.7837	0.6827	0.4287	0.3096	0.4886	−0.4928
Cells × ml^{-1}	−0.1207	−0.6290	0.8037	0.4275	0.1429	0.4640	−0.3007

[a] $p < 0.05$ (r_4; 0.05 = 0.811).

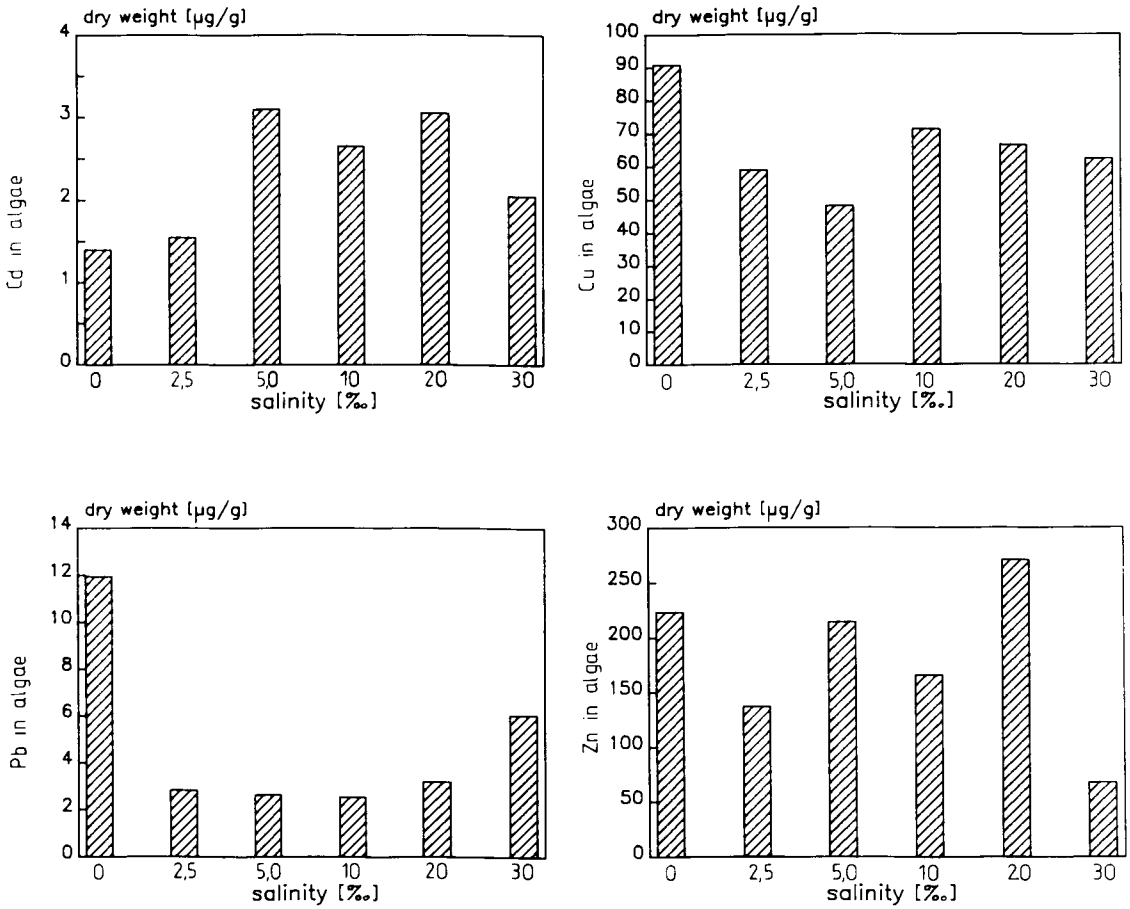

Fig. 26.2. Effect of salinity on metal contents in *Enteromorpha intestinalis* grown for 96-h with sediment from harbor site I.

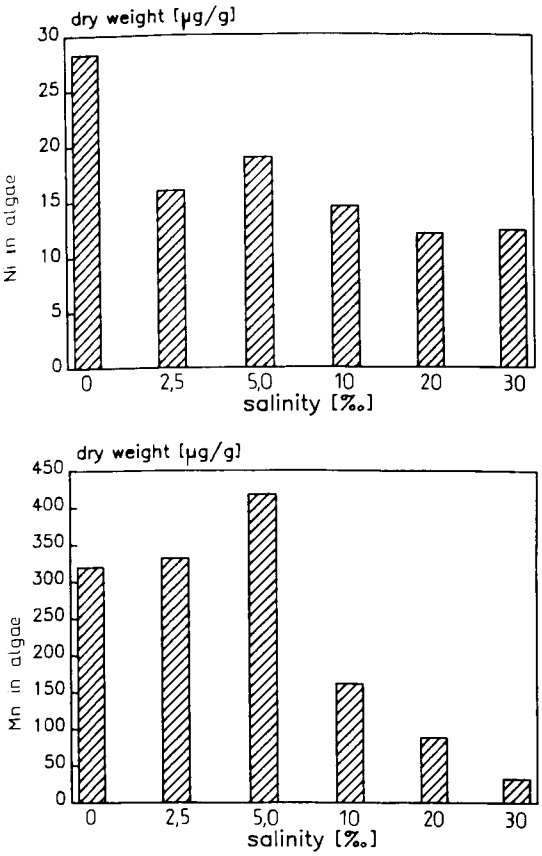

Fig. 26.2. *Continued.*

E. intestinalis was greatest in fresh water; it decreased between 0–5% salinity, but remained more elevated at higher salinities. The uptake of Zn was very irregular, being highest at 20% salinity. The uptake of Ni showed a fairly consistent decline with increasing salinity. The accumulation of Mn peaked at about 5%, but was much reduced with increasing salinity; the lowest value occurred at 30%.

Discussion

We believe that algal assays are a useful means of quantifying the behavior of sediments acting as either a source or a sink for heavy metals in different aquatic environments, and that their use is necessary because existing chemical extraction techniques do not necessarily quantify the amounts of metals that become accumulated within the algae. Since *A. hibraianus* accumulated heavy metals to a considerable extent, the data suggest that remobilization of metals from the surface of resuspended sediments made a considerable contribution to the body burden of metals in algae. Better correlations between metal concentrations in algal tissues and concentrations in sediments might result if metals were scavenged by algal tissues in contact with particulate surfaces (Luoma et al., 1982). Thus, the apparatus used in this study does not simulate the entire range of natural sediment-algal interactions. In addition, the distributions of metals in sediments, water, and algae vary widely in response to different levels of salinity.

Bioaccumulation of metals should occur for metal species whose strength of binding to algal tissues exceeds their strength of binding to sediment; but this can occur only if metals are released from the sediments. The surface effects vary from element to element (and particle type), and are significantly influenced by salinity. Under such conditions, release of metals from sediment depends on complexation with chloride ions or on competition with calcium and magnesium ions for sorption sites. The effect of salinity on metal speciation can be estimated, as a first approximation, by comparison of the respective stability constants of hydroxo- and chloro-complexes. Cadmium forms relatively stable chloro-complexes, while hydrolysis is enhanced for Zn, Pb, and Mn; the respective chloro-complexes are particularly weak for the latter metals. Cadmium is most concentrated in algae at salinities of 5–20%. There is less Cd in *E. intestinalis* at 30%. A complexing ligand (chloride) is not adsorbed onto the particulate components; thus, it competes with the surfaces for coordination of metal ions. A high concentration of the ligand likely causes a decrease in algal uptake.

The use of algal assays, based on exposure of algae to natural sediments and waters, may indicate toxicity where there is evidence of decreased rates of algal growth. The inverse relationship between algal growth and the algal Cu content largely conforms to this interpretation. In *Chlorella* spp. and presumably other species, Cu inhibits electron transport in the photosynthetic system (Cedeno-Maldonado and Swader, 1974). The toxicity data from the 96-h sediment bioassays indicate that in short-term experiments, chlorophyll a content is a sensitive indicator of Cu toxicity to algae.

Although bioassays have focused on heavy metal effects to predict sediment-algae interactions, they do not include the interactive effects of available

nutrients. More refined tests should incorporate the effects of nutrient interactions, and they should also address the significance of soluble organic compounds and the role of microbial processes in natural waters.

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