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Accumulation of Copper, Zinc, Cadmium and Lead from Two Contaminated Sediments by Three Marine Invertebrates—A Laboratory Study

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Ocean disposal of dredged estuarine sediments can result in the release of toxic constituents to the aquatic environment (ANDREN & HARRISS 1973; WOLFE & RICE 1972) which, in turn, may lead to the accumulation of some of the constituents in aquatic organisms. Animals from areas with contaminated sediments have been shown in some cases to contain high levels of trace metals (RATKOWSKI et al. 1974; AYLING 1974; BRYAN 1974; BRYAN & UYSAL 1978). In other cases, the tissue levels of contaminants were relatively constant regardless of the metal contents of the sediments (BRYAN 1974; RAY et al. 1979a). The availability of sediment-bound metals to bottom-dwelling organisms has been the subject of a few studies (JENNE & LOUMA 1977; NEFF et al. 1978; RAY et al. 1980). In an extensive laboratory study, NEFF et al. (1978) found that, out of 136 combinations (3 sediments, 5 invertebrates, 8 heavy metals and 3 salinities), only 36% of the combinations demonstrated a statistically significant relationship between heavy metal concentrations in the sediment and in the tissues of the exposed animals.

This study describes the uptake of copper, zinc, cadmium and lead from natural, highly contaminated sediments by three marine invertebrates: *Nereis virens*, *Macoma balthica* and *Crangon septemspinosa*.

MATERIALS AND METHODS

Two sediment samples were collected from stations about 200 m apart in Dalhousie Harbour, N.B., Canada, and were frozen immediately. The particle size of sediments used for exposure studies was <0.5 mm. On examination, 16 clams, *Macoma balthica*, were found in one of the sediment samples.

Test animals were collected from uncontaminated areas near St. Andrews, N. B., and were acclimated at 10 ± 0.5°C for at least a week before testing. The animals were selected to be within a narrow size range since metal contents in tissues of several invertebrates have been shown to depend on animal size (BOYDEN 1977; RAY et al. 1980). Experimental details have been described earlier (RAY et al. 1980). In brief, the animals were exposed to each of the sediments for 30 days and were sampled periodically. After sampling, the animals were kept in uncontaminated sea water for 24 hours to clear the gut of contaminated sediment. During exposure, the animals were not fed, although *Nereis* and *Macoma* would get some food from the sediment. Overlying water was aerated

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gently but not changed during the experiment. Individual whole Nereis (1.3-3.4 g) and Crangon (2.0-4.0 g) and pooled, soft tissues of five to seven Macoma (approximately 1 cm length) were analysed. Cadmium, lead, and copper at low concentrations, were measured by graphite furnace atomic absorption spectroscopy. Zinc, and copper at high concentrations, were analyzed using flame technique. Organic carbon content of the sediment was determined by modified Walkley-Black oxidation of the dried sample (Akagi & Wildish, 1975). The digestion technique for determination of metals in sediment has been described (RAY et al. 1980). Cold extraction of the metals from the sediments by an aqueous solution of the disodium salt of ethylenediaminetetraacetic acid (EDTA) was done accoring to AGEMIAN & CHAU (1976). Student's *t* test was used to determine the differences between the initial metal concentrations in the animals and the concentrations at 30 days.

RESULTS AND DISCUSSION

Particle size distribution, organic carbon and metal contents of the sediments, determined by selective extractions, are given in Table 1. Except for Cu, determined by the EDTA technique, the concentrations of the metals are lower in sediment A than in sediment B. Also, sediment A was coarser than sediment B, the sand contents being 48 and 33%, respectively.

Concentrations of Cu, Zn and Pb in the overlying waters at the end of the experiment were 0.06, 0.02 and 0.0002 µg/mL, respectively, for sediment A tests and 0.06, 0.02 and 0.0008 µg/mL, respectively, for sediment B. Cadmium was not detectable in water overlying sediment A but was present in trace amounts (<0.00001 µg/mL) in that over sediment B.

Initial metal concentrations in the animals are given in Table 2. The sixteen Macoma found in sediment B had mean Cu, Zn, Cd and Pb concentrations of 50.2, 1962, 5.8 and 94.6 µg/g (dry), respectively.

Nereis virens

The copper and zinc concentrations (Fig. 1a, 1b) in Nereis virens exposed to the sediments showed no significant changes from initial values (Table 2). Cadmium concentration in N. virens exposed to sediment A did not differ from the initial value but, for those exposed to sediment B, it was 57% higher ($p < 0.05$) than the initial values after 30 days (Fig. 1c). Lead concentration in N. virens exposed to sediment A did not change but was elevated ($p < 0.05$) at 20 and 30 days for those exposed to sediment B (Fig. 1d).

RAY et al. (1979a) did not find a correlation between the concentrations of copper or zinc in polychaete tissues and in sediments. Maintenance of a constant concentraion of zinc by N. virens exposed to water containing up to 1.0 mg Zn/L has been documented (RAY et al. 1979b). In laboratory studies with Cd-spiked sediment, the

TABLE 1. Particle size distribution and heavy metal contents of sediments used for uptake studies.

Sediment	Org. carbon %	Size distribution[a] (%)	Method of extraction	Heavy metal concentration ($\mu g/g$ air dry)			
				Copper	Zinc	Lead	Cadmium
A	5.2	Sand 48, Silt 52	HCl+HNO	37.4	926.0	96.2	2.2
			EDTA (0.05 N)	9.7	41.9	81.2	0.24
B	4.6	Sand 33, Silt 67	HCl+HNO	55.5	4033.0	243.9	6.7
			EDTA (0.05 N)	6.9	96.0	176.1	0.28

[a]Sand (0.031-0.5 mm); Silt (0.031 mm)

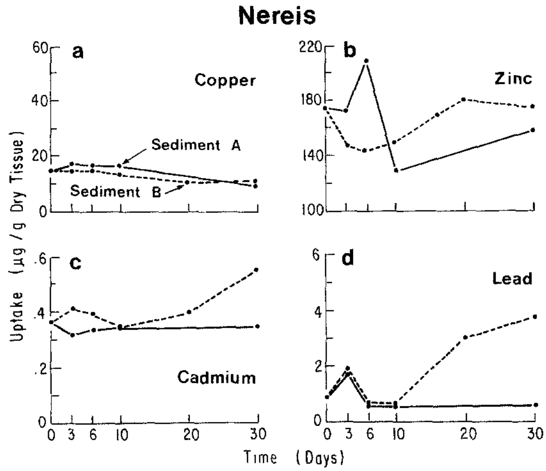

Fig. 1. Mean Cu, Zn, Cd and Pb concentrations in Nereis virens exposed to two sediments. Each point represents mean of three analyses.

TABLE 2. Initial mean (range) background levels of metal in the tissues of the experimental animals.

Invertebrate (sample size)	Concentration in animal tissues (μg/g dry)			
	Copper	Zinc	Lead	Cadmium
N. virens (n = 10)	14.7 (9.6-16.4)	175.8 (131.6-254.6)	0.89 (0.42-2.06)	0.37 (0.26-0.48)
C. septemspinosa (n = 12)	79.7 (58.0-100.8)	66.9 (50.4-81.3)	0.23 (0.04-0.47)	0.47 (0.17-0.77)
M. balthica (n = 15)	15.8 (12.1-18.3)	199.4 (178.6-218.8)	2.85 (2.07-3.94)	0.24 (0.19-0.29)

concentration of Cd within N. virens is related to the concentration of Cd in the sediment which in turn is related to the concentration of Cd leached into water (RAY et al. 1980). Similarly with sediment A, there was no detectable amount of Cd in the overlying water and no uptake of Cd by N. virens. Sediment B tests had trace amounts of Cd in the water and an elevated Cd level in N. virens at 30 days.

BRYAN (1974) found that copper, cadmium and lead concentrations in N. diversicolor were correlated with their concentrations in the sediments from which the worms were collected. His values for copper and lead in the sediments are several orders of magnitude higher than values reported by RAY et al. (1979a) and in the present study, which may explain the different relationships observed by him. BRYAN (1976) reported that the essential trace element zinc is regulated by the polychaete N. diversicolor and Nephthys.

Crangon septemspinosa

The copper concentration in C. septemspinosa exposed to the sediments showed no significant changes from the initial values (Fig. 2a), although those exposed to sediment A had slightly higher levels from 10 to 30 days. There was no change in zinc concentration (Fig. 2b). There were steep rises in cadmium concentration in the shrimp within 6 days, followed by a decline to the initial value, or below it, by 30 days (Fig. 2c). The lead concentration in shrimp exposed to sediment B at 30 days was 20 times the initial value (p 0.05) (Fig. 2d). Several shrimp exposed to sediment A were lost due to molting and subsequent cannibalism so that, for for the 30-day sample, only one animal remained.

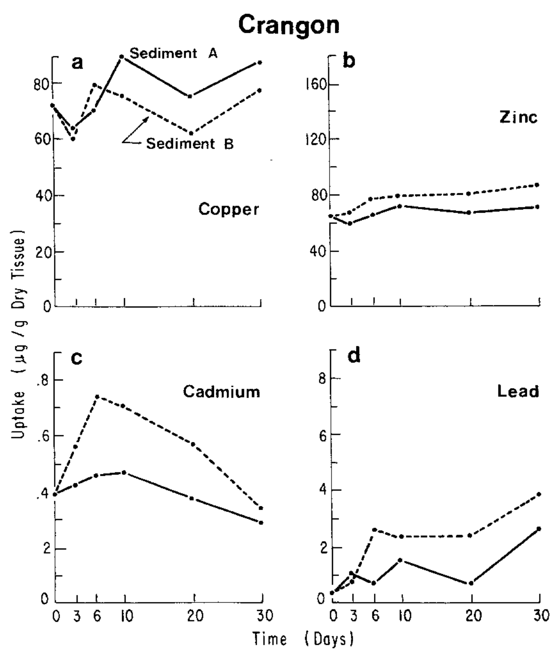

Fig. 2. Mean Cu, Zn, Cd and Pb concentrations in Crangon septemspinosa exposed to two sediments. Each point represents mean of three analyses.

RAY et al. (1979a) have shown that, under field conditions, the tissue contents of each of the four metals tend to remain constant in C. septemspinosa. Also, BRYAN (1968) showed that decapod crustaceans regulate essential trace elements like copper and zinc. However, in the present case, long-term studies might indicate whether the observed elevated lead level is of biological importance or if it would attain a steady state as observed in the field situation.

Macoma balthica

M. balthica exposed to each sediment showed a significant ($p < 0.05$) increase in copper level at 30 days (Fig. 3a). The zinc concentration showed no change in clams exposed to sediment A but increased significantly ($p < 0.01$) by 30 days in clams exposed to sediment B (Fig. 3b). Clams exposed to sediment A maintained the initial levels for cadmium but those exposed to sediment B showed an increase ($p < 0.01$) at 30 days (Fig. 3c) similar to the pattern observed with N. virens. Lead levels in M. balthica exposed to sediments A and B rose fairly rapidly to equilibrium levels which were 2.5 and 4.6 times higher, respectively, than the initial value ($p < 0.05$) (Fig. 3d).

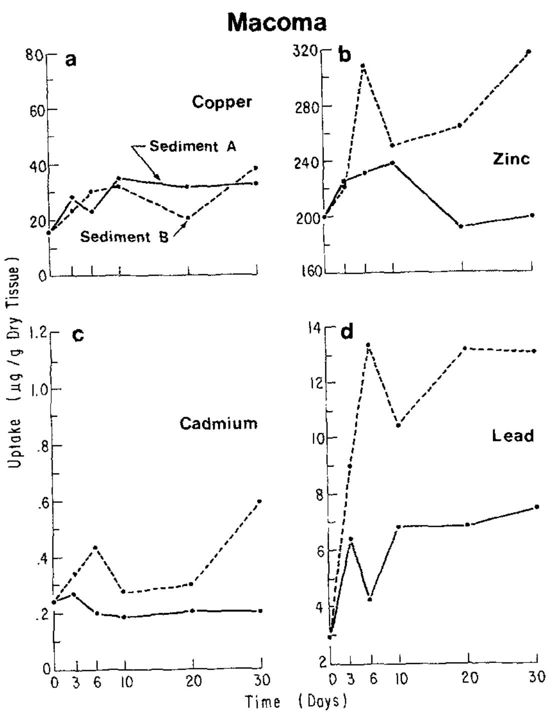

Fig. 3. Mean Cu, Zn, Cd and Pb concentrations in Macoma balthica exposed to two sediments. Each point represents mean of two analyses.

In field conditions, M. balthica maintained relatively constant concentrations of Cu, Zn and Cd but not Pb and it was suggested that the animal may be a suitable indicator for bioavailability of lead (RAY et al. 1979a) in sediment samples. The cadmium and lead levels in the sediments are of the same order of magnitude as the levels in the previous study, but copper and zinc are considerably higher.

In a similar bivalve, Scrobicularia plana, correlations between zinc, cadmium and lead levels in the soft tissues with the metal contents in the sediments were observed (BRYAN & UYSAL 1978). Also, it was shown (BRYAN & HUMMERSTONE 1978) that, when animals from two estuaries having different metal contents in the sediments were interchanged, changes in the tissue metal contents could be detected within a month. The transposed animals attained the tissue concentrations of the local animals in about a year.

In the M. balthica found in the sediment B sample, the concentration factors for copper and cadmium are close to 1.0, possibly indicating that these elements are regulated as observed earlier by RAY et al. (1979a). The concentration factors for lead and zinc were 0.39 and 0.49, respectively, indicating either saturation conditions for the number of binding sites for these metals in the animals or that the levels within the clams are controlled or regulated by metabolic processes.

CONCLUSIONS

It has been suggested that availability of sediment-bound metals to aquatic biota depends on the chemical forms and leachability of the metals (LUOMA & JENNE 1976; LUOMA & BRYAN 1978). The EDTA extraction value is considered to be a measure of adsorbed, precipitated and complexed metals (AGEMIAN & CHAU 1976). It is apparent that the bioavailability of the elements in the sediments to the animals is generally related to the EDTA extraction values for the metals. The animals accumulate more Pb, Zn and Cd from sediment B and more Cu from sediment A as reflected by the EDTA extraction values for the elements (Table 1).

In almost all cases where there was a change in metal concentrations within the animal tissues, the initial uptake was rapid, and either followed by a slow decline to the initial level or altered by attainment of new steady state levels. The exceptions were cadmium and lead in N. virens and M. balthica exposed to sediment B, and C. septemspinosa exposed to sediment A, where the increases in metal concentration in the tissues were apparent only at 30 days. The former patterns may indicate that initial uptake is controlled by physico-chemical adsorption onto the body surfaces followed by a passive diffusion (BRYAN 1976) to the tissue binding sites. The bioavailability of the metals to the animals exposed to two contaminated sediments differed widely and is controlled by factors other than the total extractable metal contents of the sediments. The observations also indicate interspecies differences in the bioavailability of the sediment-bound metals, possibly influenced by feeding habits and habitat. Only M. balthica is of any practical use for short-term testing for bioavailability test of Cu, Zn, Cd and Pb. N. virens may be useful for testing for cadmium and lead bioavailability.

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