

Scavenging of Heavy Metals from Particulates by Brown Seaweed

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Concentrations of Cu, As, Pb, Zn and Ag (but not Cd, Co, Fe, Mn and Hg) in the tissues of benthic algae (*Fucus vesiculosus*) correlate significantly with concentrations in sediment. Metals which complex most strongly with algal tissues show the strongest correlations of algal tissue and sediment. Scavenging these metals from particulates may be an important source of uptake by the algae. If so, concentrations of Cu, As, Pb, Zn and Ag in algal tissues may not be good indicators of concentrations of these metals in solution.

Concentrations of trace metals in seaweed (benthic macroalgae) have been employed by a number of authors as indicators of biologically available concentrations of metals in solution (Preston *et al.*, 1972; Bryan & Hummerstone, 1973; Phillips, 1977). The rationale for using seaweeds as indicators of metal contamination is logical: (1) Metal concentrations in solution are often near analytical detection limits and may be highly variable with time. Seaweeds concentrate metals from solution and integrate short-term temporal fluctuations in concentrations; (2) Empirical methods for distinguishing the biologically available fraction of total dissolved metal levels have not been developed for natural systems. By definition, seaweed will accumulate only those metals that are biologically available; (3) Since plants do not ingest particulate-bound

metals (as do animals), plants should accumulate metals only from solution.

Harvey (1937) suggested that aquatic plants may obtain some nutrients from particulates rather than from solution. This hypothesis remains controversial. If plants scavenge nutrients from particulates, however, they may also take up trace metals from that source. If so, metal concentrations in algae may not always reflect only biologically available metal in solution.

In this paper, we show that concentrations of Cu, As, Pb, Zn and Ag in seaweed (*Fucus vesiculosus*) collected from 18 estuaries in south and west England are closely correlated with total concentrations of these metals in surficial sediments. Concentrations of Cd, Co, Hg, Fe and Mn in *Fucus* are not significantly correlated with concentrations in sediments. Either total concentrations of sediment-bound As, Cu, Pb, Zn and Ag influence concentrations of these metals in solution, or a portion of the burden of these metals in the seaweed is scavenged from particulates.

Methods

Seaweed were collected from 32 stations throughout the salinity gradient in 18 estuaries described by Luoma & Bryan (1978, 1981, 1982). The samples of seaweed were collected and prepared for analysis using the methods of Bryan & Hummerstone (1973). All metal analyses were conducted by atomic absorption spectrophotometry. Sediment samples were collected from the surficial layer of sediment in the intertidal zone (Luoma & Bryan, 1981). 'Total' metal was determined by refluxing sediments in concentrated nitric acid, evaporating the resultant clear nitric acid solution and reconstituting in 1 N HCl for analysis. Extractions in 1 N HCl were conducted for 2 hr on surficial sediments, first sieved through 100 μm mesh, as described by Luoma & Bryan (1981). All data were log-transformed for the regression analyses.

Results

Concentrations of Cu in *Fucus* correlated almost perfectly ($r=0.98$; $n=32$) with concentrations in surface sediments (Fig. 1). Within estuaries, the correlation between Cu in sediments and Cu in seaweed was generally weaker than was observed over the broad data range among all estuaries. Concentrations of As and Pb in *Fucus* correlated significantly with concentrations in sediments; the correlation for Zn was weakly significant; and correla-

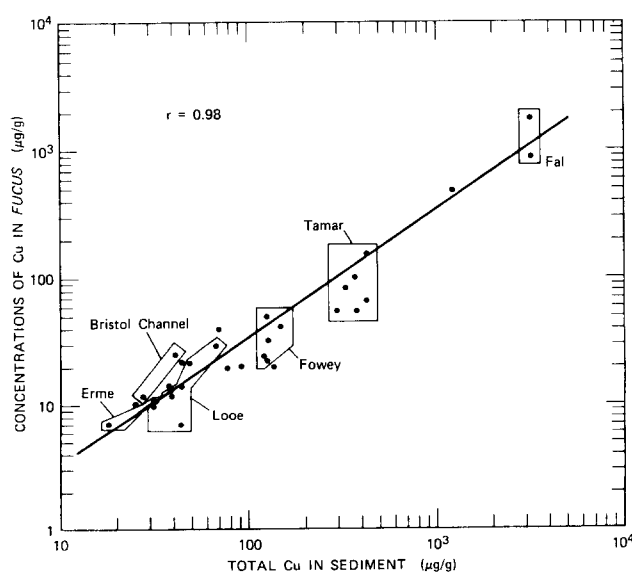


Fig. 1 Correlation of Cu in *Fucus vesiculosus* with total concentrations of Cu in sediments. Estuaries where more than one station was sampled are enclosed in boxes.

TABLE 1

A comparison of the correlation between metal concentrations in *Fucus* and total metal in sediments, with the selectivity coefficient (Ragan *et al.*, 1979) describing the strength of metal complexation with polyphenols from *Fucus*. Thirty-two stations were included in all correlations ($n = 32$).

Metal	Correlation with total metal in sediment (R)		Selectivity coefficient for chelation with <i>Fucus</i> polyphenols*
	Total	HCl †	
Cu	0.98 ‡	0.90 ‡	106
As	0.84 ‡	0.72 ‡	N.M.
Pb	0.67 ‡	0.50 ‡	81.3
Zn	0.42 §	0.29	5.5
Ag	0.30	0.48	N.M.
Fe	0.26	—	N.M.
Co	0.10	0.28	3.6
Hg	0.02	0.11	N.M.
Cd	0.004	0.07	2.7
Mn	0.001	0.11	1.0

*Ragan *et al.* (1979).

† 'Corrected' for particle contamination.

‡ $p < 0.001$.

§ $p < 0.01$.

N.M., not measured.

tions for Ag, Cd, Co, Fe, Hg and Mn were below the level of significance (Table 1).

Because correlations with sediments differed among metals, it is unlikely that the correlations resulted from particulate contamination on the algae. However, to eliminate this possibility, it was assumed that all Fe in the seaweed was adsorbed as particles of Fe oxide, and that the ratio

$$Fe_F/Fe_S = M_P/M_S,$$

where $Fe_F = Fe$ in *Fucus*,

$Fe_S = Fe$ in sediment,

$M_P =$ metal on particles contaminating *Fucus*,

$M_S =$ metal in sediment.

Thus, metal values in *Fucus* could be 'corrected' for particle contamination by

$$M^*_F = (Fe_F/Fe_S \cdot M_S),$$

where M^*_F represents the 'corrected' value. Correcting in this manner for possible sediment adsorption made little difference in the correlation coefficients and did not affect the differences in correlation among metals.

Concentrations of metals in *Fucus*, corrected for sediment adsorption, were also regressed against the concentration of metal extracted by 1 N HCl from sediments (Table 1). Concentrations of Ag in *Fucus* correlated substantially more strongly with 1 N HCl-extractable Ag than with total Ag. An HCl extract also measures the bioavailability of Ag to bivalves and polychaetes substantially better than do measurements of total Ag concentrations (Luoma & Bryan, 1982). Correlations between sediment and seaweed were slightly weaker for Cu, As, Pb and Zn when the HCl extract was employed.

The strength of the correlations between metal concentration in *Fucus* and sediments followed an order similar to the strength with which at least some metals complex to polyphenolic proteins in *Fucus* (as measured by Ragan *et al.*, 1979; Table 1). Cu and Pb, the metals with the highest selectivity coefficients for binding, showed the strongest correlation of tissue and sediment concentrations. Metals with weak selectivity coefficients for the algal proteins showed weak correlations between sediment and algae.

Discussion

Correlations between metal concentrations in algal tissues and concentrations in sediments could result if metals were scavenged by algal tissues in contact with surface sediments. *Fucus* contacts suspended sediments continuously, and contacts bed sediments at low tide, when it lies on the sediment surface; thus providing opportunity for scavenging. The significant correlation of algal tissues and sediments only among metals which bind most strongly to *Fucus* tissues is consistent with sediment scavenging as a source of metal uptake. Scavenging should occur only for metals whose strength of binding to algal tissues exceeds their strength of binding to particles. The more strongly each of these metals is complexed by macroalgae, the smaller the proportion of the body burden of that metal that might originate from solution.

Correlations between metal concentrations in algae and in sediment could also occur if concentrations of biologically available metal in solution were controlled by total concentrations of metals in sediment. Seeliger & Edwards (1977) observed that Cu and Pb in several benthic algal species from Raritan Bay correlated with concentrations in solution and fixed to suspended materials. However, the distribution of metals between sediment and water varies widely among different physicochemical forms of sediment-bound metals (Luoma & Jenne, 1977). Luoma & Bryan (1981) showed that Cu and Pb were partitioned among several forms in sediments of the estuaries of south-west England. Thus, even if sediments controlled solute concentrations of As, Cu, Pb and Zn in these estuaries, those controls should not be a function of total metal in sediments.

The correlations of some sediment-bound metals with concentrations in *Fucus* raise questions about the proper interpretation of metal concentrations in algal tissues, especially over wide concentration gradients. If further investigation indicates that sediments do contribute a significant proportion of the body burden of As, Cu, Pb, Ag and Zn in benthic algae, then such algae may not be useful directly as indicators of solute concentrations of these metals. However, the difference between observed concentrations in algae and concentrations predicted from the correlation of algae and sediment might be an alternative method of measuring at least relative differences in biologically available concentrations of solute Cu, As, Pb and Zn in different environments. Using these statistical differences, many of the benefits of using algae as indicator organisms could be retained.

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Marine Pollution Bulletin, Vol. 13, No. 11, pp. 396–398, 1982
Printed in Great Britain

0025-326X/82/110396-03 \$03.00/0
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BASELINE

Levels of Heavy Metal Pollutants in Two Species of Marine Nematodes

Numerous studies have been conducted on levels of heavy metals in a wide range of marine organisms around the British coastline (Preston *et al.*, 1972; Wright, 1976). However, very few investigations have been concerned with the accumulation of metals by members of the meiobenthos, which occupy an important position in the ecology of intertidal estuarine sediment (Gerlach, 1971), and none have considered heavy metal levels in free-living marine nematodes.

Two closely related species were selected for study. *Enoplus brevis* (Bastian) is a euryhaline species (Brenning, 1973) inhabiting intertidal estuarine sediments. *Enoplus communis* (Bastian) can be found living commensally in the byssus threads of seed mussels (*Mytilus edulis*) (King, 1978) or in holdfasts of kelp (*Laminaria hyperborea*)

(Moore, 1971). Both species are abundant on the north-east coast of Britain and are of a suitable size for this type of study, averaging 5–7mm in length.

The incidence of copper, zinc, lead, cadmium and mercury was studied in specimens taken from three sites on the north-east coast (Fig. 1).

Method

Specimens of *E. brevis* and *E. communis* were collected from the three sites which exhibit varying levels of pollution by heavy metals.

Budle Bay is about 50km from any known sources of pollution and was used as the unpolluted site. The River Blyth estuary is known to be significantly polluted by heavy metals (Lobel, 1981) and to contain large populations of nematodes (Capstick, 1952). The River Tees estuary has been long known to be extensively polluted (Alexander *et al.*, 1935; Porter, 1973).

Specimens of *E. brevis* were obtained by collecting the upper 2 cm of intertidal sediment in a plastic container. In the laboratory this sediment was sieved through nylon mesh using clean, filtered seawater and the nematodes picked off the mesh with the aid of a hand lens and mounted needle. Seed mussels were collected at low tide and returned to the laboratory where *E. communis* were removed using a similar method.

According to Flegel & Martin (1977), contamination of biological samples by ingested sediment may be sufficient to interfere with heavy metal analyses. Since both species imbibe sedimentary material it was necessary to eliminate this source of error by removing the gut contents by the method of D. Wright (pers comm.) who used mild ultrasonication after narcotizing the animals using 2% propylene phenoxitol in seawater (Ellenby & Smith, 1964). Individuals were dried in a vacuum desiccator at room temperature to constant weight and then weighed using an electronic balance. Aristar nitric acid was used in sealed vials at 200°C to digest individual animals and analysis for copper, zinc, lead and cadmium was carried out using a Varian Techtron 1200 atomic absorption spectrophotometer fitted with a carbon rod atomizer.

The procedure used for mercury analysis was adapted from that of Hatch & Ott (1968) and involved the use of gold wire as an adsorbing agent (Reimers *et al.*, 1973).

Results

The results of the analyses of copper, zinc, lead, cadmium and mercury in the nematodes from the three sites are shown in Tables 1 and 2. Lobel (1981) and Lobel

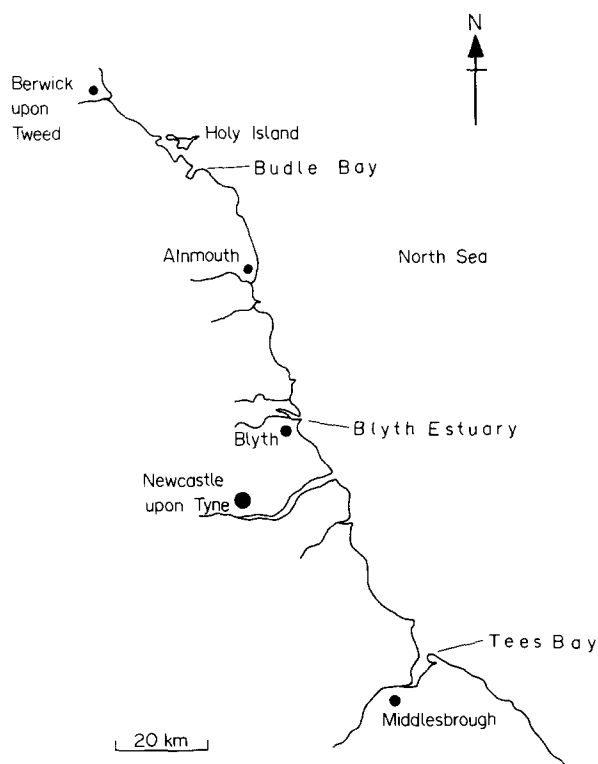


Fig. 1 A sketch map of the north-east coast of Britain showing the sites of study.