THE FATE OF METALS INTRODUCED INTO A NEW ENGLAND SALT MARSH

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Abstract. As part of a study to investigate **the effect** of chronic eutrophication on salt marshes, a **sewage** sludge fertilizer has been applied to experimental plots in Great Sippewissett Marsh, MA., since 1974. **The** fertilizer contains substantial amounts of heavy **metals. Sediments** from fertilized plots contain **elevated** levels of Cu, Cd, Zn, Fe, Mn, Cr, and Pb. The above- and below-ground portions of the dominate grass, *Spartina alterniflora,* contain significantly higher levels ofCd, Cr, Cu, and Zn when compared to control plots. **The** mussel, *Modiolus demissus,* from fertilized plots contains elevated levels ofCu, Cd, and Cr. The fiddler crab, *Uca pugnax* contains more Cu and Cd than control animals. Low marsh sediments fertilized for 8 yr retained 15% Cd, 24% Fe, 27% Mn, 28% Zn, 45% Cr, 49% Cu, and 60% of the Pb in the fertilizer. Plots which had only received fertilizer for 1 yr retained a higher percentage of **the metals** which had been added. **The** differential solubilization of metals from the fertilizer appear to be one factor influencing metal retention on the plots although changes in sediment chemistry due to nutrient addition are also a factor.

1. Introduction

Salt marshes and estuaries often receive large metal inputs from wastewater discharge. For a number of metals, anthropogenic fluxes now exceed those from natural weathering processes (Galloway, 1979; Forstner and Wittmann, 1979; Helz, 1976; Bryan, 1980). The chemical and biological factors that regulate the fate and bioavailibility of metals in these environments are still poorly understood. Although wastewater contains a large number of components, including nutrients and organics, the effect of these other componets on metal behavior has largely been unexplored.

As part of a study to investigate the effects of chronic eutrophication of marshes, a fertilizer containing sewage sludge has been added to experimental plots in Great Sippewissett Marsh, MA, since 1974. The fertilizer contains substantial amounts of the heavy metals common in municipal wastewater, as well as organic and inorganic nutrients (Valiela *et al.,* **1975).**

To evaluate the ability of marsh sediments to sequester metals, the fate of the metals introduced with the fertilizer was examined. The metal content of the fertilizer was continuously monitored so that an accurate metal budget could be constructed. The amount of metal in **the sediment** from control and **experimental areas was measured**

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from 1976 until 1980, so that metal losses from the plots could be calculated. The dominant marsh grass, *Spartina alterniflora,* and several animals species were regularly sampled and their metal content was used as an indication of the bioavailability of metals in the plots. The effect of chronic vs. recent metal addition was studied by comparing marsh plots fertilized for 8 yr to plots which had been fertilized for 1 yr.

2. Methods

The original sets of experimental and control plots used in this experiment were established in Great Sippewissett Marsh, MA, in 1974. The plots are 20 m in diameter (area 314 m^2) and each is drained by a single creek. Two experimental plots (designated OXF) are treated with 75.5 g wk⁻¹ m⁻² of a commercial fertilizer which contains sewage sludge. Fertilizer is broadcast on the plots twice monthly from April to November. Two untreated plots (OC) serve as controls. The fertilization scheme and the experimental areas have been described previously (Valiela *et al.,* 1975).

In 1980 new sets of plots were established in a different area of the marsh. Two of the new plots (NXF plots) receive the same dosage of fertilizer as the OXF plots. Two untreated areas nearby serve as controls (NC). Samples were taken from these sites only during 1980.

Sediment samples for metal analysis were removed from the OXF and OC plots during 1975, 1976, 1978, 1979, 1980. At each sampling date 2 to 4 cores were removed from each plot. The top 2 cm depth of each core was used for metal analysis. Sediments were sampled one to three times a year: Cores were taken from each of the OXF and the NXF plots in the fall of 1980. These cores were divided into 0-2, 2-4, 4-6, 6-8, and 8-10 cm sections for metal analysis.

The metal content of the fertilizer was measured several times a year from 1974 until 1980. Several fertilizer batches were pooled and four separate metal determinations were made each year.

Samples of marsh grass, *Spartina alterniflora,* were collected from the OC and OXF plots two to six times a year from 1977 until 1980. The above ground portions of the plant were analysed after each collection. The below ground portions of the plant were analyzed once or twice a year. Only live roots and rhizomes were analyzed for metal content. A root or rhizome was defined as live if it was still white and attached to the aboveground portion of the plant. Grasses from the NXF plot were sampled during the fall of 1980.

Specimens of the ribbed mussel, *Modiolus demissus,* were collected for metal analysis during the spring and fall of each year. Fiddler crabs, *Uca pugnax* were collected once a year, usually during the summer. The fiddler crabs were not present in the fertilized plots during 1979.

Samples of mud were taken from the creeks that drain the plots. Samples were taken from all plots during the fall of 1980. Samples were always taken near the center of the plots and consisted of the top few mm of mud scraped from the surface.

Metal analysis of the fertilizer, grasses, and animals were performed by atomic

absorption analysis after digestion in hot nitric acid. Hydrogen peroxide was added to the cooled digest to destroy any residual organic matter. Because the sediments contain substantial amounts of pyrite (Howarth, 1979), sediment samples were digested in aqua regia.

The concentration of labile metals in sediments from the fertilized plots was measured on cores taken in December 1980, after fertilization had ceased. Labile metals were defined as metals which would be released from the sediment by 0.1 N HC1 (Tucker and Kurtz, 1955; Cross *et al.,* 1970). Four cores were taken from each plot and split in half. To measure labile metals, 30 ml/gdw of 0.1 N HC1 was added to each 1/2 core in a small flask. The flasks were shaken for 4 h, the extracts filtered through a glass fiber filter, and the concentration of metals in the extract was determined. The remaining $1/2$ of the cores were analysed for total metals as previously described. The percentage of labile metals was also measured in Milorganite, the sludge fertilizer applied to the plots during 1979 and 1980.

3. Results

3.1. METAL CONTENT OF THE FERTILIZER

The metal content of the fertilizer varied considerably over the course of the study. The sludge based fertilizer applied from 1974 through 1976 contained 720 lbs/ton of Chicago sewage sludge which contributed to the heavy metals added to the sediment with the fertilizer (Figures 1 to 7). The fertilizer applied in 1977 and 1978 contained very little sewage sludge and the concentration of all metals, except Mn was much lower than in the previous fertilizer. During 1979 and 1980 the sludge based fertilizer Milorganite was applied. The fertilizer contained more heavy metals than the fertilizers used previously.

3.2. METAL CONCENTRATIONS IN THE OXF PLOTS

The addition of sludge based fertilizers to experimental marsh plots has raised the metal content of the top 2 cm of the sediment significantly (t test $p < 0.01$) over the control plots (Figures 1 to 7). The Cr, Fe, and Pb concentration of the top 2 cm of the sediment has continued to increase with increased metal loading (Figures 2, 6 and 7). In spite of the high metal content of the fertilizer used in 1979 and 1980 the concentration of Cd, Zn, Cu, and Mn has increased only slightly or decreased from the concentrations measured in 1977 (Figures 1, 3, 4 and 5).

The aboveground portions of *Spartina alterniflora* from the OXF plots contain elevated levels of Cd, Zn, Cu, and Cr (Figures 1, 2, 3, and 4). There is no significant difference in the levels of Pb, Mn and Fe in the aboveground portions of grasses from the OXF or OC plots (Figures 5, 6, and 7). The roots and rhizomes of grasses from the OXF plots also contained elevated levels of Cd, Zn, Cu, and Cr (Figures 1, 2, 3, and 4). Plant roots from the fertilized plots also contained elevated levels of Pb and Fe (Figures 6 and 7). The roots of grasses from both control and OXF plots were higher in metals than the rhizomes. Except for Cu and Pb, the metal content of rhizomes from **all** the plots was

Fig. 1. The Cd added to the OXF plots and the metal concentration in sediments from the OXF and control plots (top), the amount of metal found in Spartina alterniflora tops, and roots and rhizomes (middle), and the metal concentration in animals (bottom).

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Fig. 2. The Cr added to the OXF plots and the metal concentration in sediments from the OXF and control plots (top), the amount of metal found in Spartina alterniflora tops, and roots and rhizomes (middle), and the metal concentration in animals (bottom).

Fig. 3. The Zn added to the OXF plots and the metal concentration in sediments from the OXF and control plots (top), the amount of metal found in Spartina alterniflora tops, and roots and rhizomes (middle), and the metal concentration in animals (bottom).

Fig. 4. The Cu added to the OXF plots and the metal concentration in sediments from the OXF and control plots (top), the amount of metal found in Spartina alterniflora tops, and roots and rhizomes (middle), and the metal concentration in animals (bottom).

Fig. 5. The Mn added to the OXF plots and the metal concentration in sediments from the OXF and control plots (top), the amount of metal found in Spartina alterniflora tops, and roots and rhizomes (middle), and the metal concentration in animals (bottom).

Fig. 6. The Fe added to the OXF plots and the metal concentration in sediments from the OXF and control plots (top), the amount of metal found in *Spartina alterniflora* tops, and roots and rhizomes (middle), and the metal concentration in animals (bottom).

Fig. 7. The Pb added to the OXF plots and the metal concentration in sediments from the OXF and control plots (top), the amount of metal found in Spartina alterniflora tops, and roots and rhizomes (middle), and the metal concentration in animals (bottom).

similar to the aboveground portion of the plant. The Cu content of rhizomes was significantly higher and the Pb content of rhizomes was significantly lower than the aboveground portions. There was no clear relationship between the metal concentrations of the grasses and that being added with the fertilizer or present in the surface sediments (Figures 1 to 7).

In 1976 the levels ofCd, Cr, and Cu in the ribbed mussel, *Modiolus demissus* from the OXF plots were significantly higher than mussels from the control plots. The fiddler crab, *Uca pugnax,* contained elevated levels of Cu and Cd in 1976. In 1977 and 1978 the amount of metal in the fertilizer was quite low. During these two years the metal levels of animals from the OXF plots dropped and by 1978 there was no significant difference in the concentration of any of the metals in animals from control and fertilized plots. The fertilizer used in 1979 and 1980 had much higher levels of metals than fertilizers used previously. During these years the concentration of Cu, Cd and Cr in mussels was again significantly higher than control mussels. The levels of Cu and Cd in *Uca* were also significantly higher than controls.

TABLE I

The amount of metal found in sediment (ppm), creek mud (ppm), and the mussel, *Modiolus demissus* (ppm), taken from control (OC & NC average), OXF and NXF plots. (An * in the column margin indicates two samples not significantly different $(p < 0.05)$ while '**' indicates all three samples are not significantly different).

Metal	Plot	Sediment $0-2$ cm	Creek mud top cm	M. demissus
Cu	C	10	18	13.8
	NXF	176	28	$17.1*$
	OXF	285	71	23.1
Fe	\mathcal{C}	12320	13591	126
	NXF	28269	2966	124 **
	OXF	31 200 *	4413 *	133
Pb	C	33	48	0.8
	NXF	281	$63 *$	2.4 **
	OXF	446	$121*$	2.1
Cd	C	1.4	3.9	4.1
	NXF	36.7	7.9	$7.4*$
	OXF	13.7	$8.2*$	17.5
Mn	C	52	71	5.8
	NXF	125	79 **	$4.3***$
	OXF	$118*$	50	6.4
Zn	\mathcal{C}	46	86	53.2
	NXF	358	$103*$	56.0
	OXF	$450*$	$149*$	$67.4**$
$_{\rm Cr}$	$\mathbf C$	3	3	0.8
	NXF	2750	244	2.3
	OXF	3465	727	$3.1*$

3.3. COMPARISON WITH NXF PLOTS

Plots which only received fertilizer during 1980 also have a higher metal content than control plots (Table I). Except for Cd and Mn, the metal concentration on a ppm basis is greater in the OXF sediment than the NXF sediments although the differences are not always significant (Table I). However, because the OXF sediments are considerably denser than the NXF plots the total metal inventory of all metals except Cd in the OXF plots is much greater than the metal concentrations indicate. Sediments from the creeks which drain the fertilized plots are also elevated in some metals (Table I). In the OXF creeks, the levels of Cu, Pb, Cd, Zn, and Cr are higher than control creeks $(p < 0.05)$. **The levels of Cr, Cd and Cu in the NXF creeks are intermediate and only Cr, Cu and Cd are significantly higher than the controls. The ribbed mussel from the OXF plots also has higher levels of Cu, Cr, and Cd than the mussels from control creeks. Mussels from the NXF creeks contain intermediate levels of Cu, Cd, and Cr but only the Cr content is significantly higher than control mussels.**

Grasses from the NXF plots contained elevated levels of Cd and Cr compared to

TABLE **II**

The amount of metal found in grasses (ppm) taken from control (OC and NC **average), OXF and NXF plots.** (An '*' **in the column margin indicates two samples** not significantly different $(p < 0.05)$ while '**' indicates all three samples are not

grasses from control plots (Table II). The Cd and Cr content of roots from these plots were also significantly higher than control grasses. The Zn and Cu content was intermediate between the control and OXF plots. The $Zn \& Cu$ content of NXF grasses was also intermediate to control and OXF grasses but only the copper content was significantly higher than controls.

3.4. SEDIMENT INVENTORY

The amount of metal from the fertilizer retained by the experimental plots was calculated by subtracting the metal content of control plots from the metal content of the fertilized sediments. The percentage of the metals added with the fertilizer retained at each depth in the sediment was then calculated for the NXF and OXF plots (Table III). A greater percentage of all of the metals contained in the fertilizer has been lost from the OXF plots than has been lost from the NXF plots (Table III). Not all of the metal which was in the fertilizer is found in the top 2 cm of the marsh sediment (Table III). A greater percentage of the metals from the fertilizer is found in the OXF plots than in the newly fertilized plots. At depth the iron content of the fertilized plots, and the Mn content of the OXF plots is lower than control sediments (Table III).

TABLE III

Total inventory of the metals in the fertilized plots as a percentage of what was added in the fertilizer

3.5. LABILE METALS

The percentage of labile metal in the sediment was related to the percentage of metal which was retained in the top 2 cm of the sediment (Figure 8). More than 75% of the total Mn, Zn, and Cd in the sediment of fertilized plots was labile (Table IV). About 65% of the copper and less than 20% of the chromium was labile in both OXF and

Fig. 8. The percentage of metal retained by the sediment vs. the percentage of labile metal in the top 2 cm of the sediment.

NXF sediments. The percentage of labile Fe and Pb was quite different in the two fertilization treatments. In the new XF plots only 22% of the iron was labile while 70% of the Pb was labile. In sediments from the OXF plots the situation was reversed, 61% of the iron was labile but only about 27% of the Pb was extracted into 0.1 N HCl. The percentage of labile metals in the sediments is quite similar to the percentage of labile metals in the fertilizer (Table IV) except for Pb, Fe, and Cr.

4. Discussion

Salt marsh sediments are anoxic below 1 cm (Teal and Kanwisher, 1961) and contain high levels of sulfides (Howarth *et al.*, 1982). Since metal ions such as Pb, Cu, Zn, and Cd form insoluble and relatively stable sulfides (Thomson *et al.,* 1975) it was expected that marsh sediments would act as a sink for some metals (Banus *et al.,* 1975; Valiela *et al.,* 1976; Siccama and Porter, 1972). Recent studies have shown that although high metal concentrations are often found in coastal sediments (Dinker and Nolting, 1977; Greig *et al.,* 1977; Greig and McGrath, 1977), Cd, Zn, and Mn are extensively remobilized and a large percentage of these metals which enter estuaries and marshes are lost to deeper water (Windom, 1975; Holmes *et al.,* 1974; Helz *et al.,* 1975; Holliday and Lisa, 1976; Sundby *et al.,* 1981). Substantial fluxes of copper through some estuaries have also been reported (Windom, 1975; Holliday and Liss, 1976). Most studies concerning the fate of Fe, Pb, and Cr in marshes and estuaries have concluded that they are extensively removed and well retained by the sediment (Sholkovitz, 1976; Windom, 1975; Church *et al.,* 1981; Siccama and Porter, 1972), although exceptions have been found (Helz *et al.,* 1975).

The sediment data from Great Sippewissett (Table III) show that the majority of the Cd, Zn, Mn, and Fe, and almost half of the Pb, Cu, and Cr added with the fertilizer are lost from the experimental plots. The uptake of the metals by the grasses and animals

on the plots, and the differential losses of the metals show that metals are being chemically remobilized, and not simply being lost from the plots as particulates. Studies of Hg on the experimental plots have shown that particulate metals are not being lost in the short *Spartina* zone of the experimental plots where this study was done (Breteler *etal.,* 1981).

Plots fertilized for 1 yr retain a greater percentage of the metals in the fertilizer than plots which have been fertilized for eight years (Table III). This may partially be due to the solubility of the fertilizer (Table IV). The percentage of labile metals in the XF plots is quite similar to the percentage in the fertilizer. It may take time to break down the organic components in the fertilizer sufficiently to release the metals held within the particulates. The density of the OXF plots has increased with time (Breteler and Giblin, 1978) further supporting the hypothesis that part of the fertilizer is quite refractory and remains as particulates in the sediment.

4.1. CAUSES OF METAL REMOBILIZATION

A major factor influencing metal mobility is the redox condition within the sediment (Lu and Chen, 1977). The N present in the fertilizer stimulates grass production in the experimental plots (Valiela *et al.,* 1975), which increases the oxidation of the sediment (Howes *etal.,* 1981). The plots which have been fertilized for 8 yr have much lower sulfide concentrations in the pore water than control plots (Giblin, 1982). Sulfide concentrations in the pore water from the new XF plots are also lower than the surrounding area but not nearly as low as the OXF plots. The increased sediment oxidation has greatly reduced the importance of metal sulfide formation and increased metal solubility in the pore waters (Giblin 1982). At marsh pH's, Pb, Zn and Cd may form soluble complexes (Long and Angino, 1977; Hahne and Kroontje, 1973). Banus *et al.* (1975) found higher percentages of Pb, Zn, and Cd were retained in plots fertilized for 2 yr with lower dosages of fertilizer than is being applied in the XF plots. Plots receiving less N are also more reduced than the OXF plots (Howes, 1981), The differences in metal retention between Banus' and this study may be caused by the differences in redox conditions in the experimental plots.

Iron is quite soluble at low Eh and pH conditions (Hem, 1972) but in marsh sediments iron is normally rapidly precipitated with sulfides as $FeS₂$ (Howarth, 1979). Pyrite is undersaturated in interstitial water from the fertilized plots for most of the year (Giblin, 1982) and Fe is probably lost from the experimental plots by diffusion and tidal flushing. The Fe concentration from 2 to 6 cm depth in cores from the fertilized plots is much lower than cores from control plots, which contain large amounts of pyrite Fe. This indicates that sedimentary Fe, as well as the Fe in the fertilizer, is being remobilized. Manganese is also quite soluble under acid reducing conditions (Gotah and Patrick, 1972; Collins and Boul, 1970; Hem, 1972). Losses of Fe and Mn from the experimental plots may be controlled by precipitation as metal oxides near the sediment water interface. Iron oxide minerals are more abundent in the top several cm of the OXF plots than in control plots (Giblin, 1982).

Organic complexes also contribute to the solubilization of metals (Rashid, 1971, Hallberg *et al.,* 1980, Rashid and Leonard, 1973). A substantial amount of the Cu and Fe in the pore water is complexed with organics (Giblin 1982). Although we have not measured the fraction of Cr or Pb associated with organic material, stability constants indicate that it could be potentially quite important.

Cadmium was the most extensively remobilized metal in the marsh. Studies from other estuaries where there is wastewater discharge show remobilization of Cd from the sediment (Helz *et al.,* 1975; Holmes *et al.,* 1974). The remobilization of all metals from sewage sludge in the experimental marsh plots is greater than has been reported for marine sewage disposal. Sediment data from the Los Angeles County sewage outfall indicate that although most of the metals in wastewater are solubilized before deposition, little or no remobilization of metals takes place from the anoxic sediment after deposition (Morel *et al.,* 1975).

4.2. METAL PROFILES IN THE SEDIMENT

The highest concentration of metals is found closest to the surface of the sediment. Undoubtly some of this metal is contained in undissolved fertilizer. However, the low metal penetration into the sediment is unexpected since pore water from the top 8 cm of the sediment from the OXF plots is frequently undersaturated for metal minerals. Exchange and surface chemical controls will also effect metal mobility in sediments (James and MacNaughton, 1977) and it is possible that adsorption of metals onto iron oxides and hydroxides is limiting their penetration into the sediment. Oxidized iron minerals have been shown to be good adsorbers of heavy metals (Benjamin and Leckie, 1981) and oxidized iron minerals are abundent in the surface of the OXF plots (Luther *et al.,* 1982). This hypothesis has not been tested and deserves further study.

4.3. METALS IN THE BIOTA

The metal concentration of the aboveground portions of the grass did not remain constant throughout the growing season. For almost all metals the patters were similar from year to year, although the pattern isn't obvious in 1980 because only two samples were taken. The causes for the changes in metal content as the grasses grow, senesce

and decay seem to be related to changes in sediment redox and physiological changes in the grasses as previously discussed (Giblin *et al.,* 1980).

The lead content of above ground fertilized and control grasses was never significantly different from each other but decreased each year samples were taken (Figure 7). Lead levels in the rhizomes of these plants were always below our detection limits (0.05 ppm), so it seems probable that most of the Pb in the aboveground part of the plants comes from airborne contamination. Plants can accumulate Pb by taking in airborne particles through the stoma (Buchauer, 1973; Zimdahl, 1976). The steady decline in the lead content of the grasses from 1976 to 1980 may be related to the decrease in the use of leaded gasoline. Recent work has shown that most analyses of biological tissues are seriously contaminated and true lead concentrations in the marine food chain lie in the range of 1 to 500 ng (Burnett and Patterson, 1979). These levels are below our detection limits so our conclusion that lead levels in plants and animals of the experimental plots are not elevated compared to controls must be viewed as tenative. Most of the Pb we measured in whole *Uca* is probably in the carapace and muscle levels may be much lower.

The addition of metals to the marsh by sludge fertilization raised the Cu, Cd, Cr, and Zn content of the grasses. The uptake of metals by the grasses did not have a significant impact on the metal losses from the sediments. Less than 5% of any metal which was added is taken up by the above-ground portions of the grass. The metals also do not have a measurable effect on grass production. The production of grass in enhanced equally by fertilization with metal-containing sludges, or with fertilizer containing the equivalent amount of nutrients without metals (Giblin *et al.,* 1980).

Animals in the experimental plots also contained greater concentrations of some metals than animals living in control plots. The effect of sludge fertilization on the populations of these animals was not examined in this study. Sludge fertilizer contains other components, such as pesticides, which confounds the effects of metals on the animals (Krebs and Valiela, 1978). The high concentration of Cd found in mussels from the plots indicates that Cd concentrations in commercial shellfish from sludge fertilized areas should be monitored.

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