Chapter 2

METAL POLLUTION IN SAN FRANCISCO BAY SALT MARSH PLANTS

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The San Francisco Bay is an estuarine system. As such, its salt marshes play an essential role in the upkeep of the ecosystem by contributing to the food chain, processing pollutants, and providing habitat for many species of wildlife. Bay marshes have been severely degraded since settlement of the area by Europeans; they have declined both in quantity and in quality.

Among the many causes of salt marsh degradation, pollution by natural and synthetic substances may have particularly subtle short- and long-term effects. Heavy metals, although present in the natural environment, may become concentrated enough to act as hazardous pollutants on the salt marsh ecosystem. Since heavy metals are very persistent in nature, their effects may also persist, thus posing a threat to the long-term integrity of the salt marshes.

This paper will attempt to define the immediate effects of four heavy metals--cadmium, copper, lead and zinc--on salt marsh plants and the less immediate ramifications of such effects. Results of a study conducted to determine concentrations of the four heavy metals in typical Bay Area salt marsh plant species will be presented and used to gauge the magnitude of possible ecological disturbance due to presence of these metals.

Past Work

Most studies of interactions between plants and heavy metal pollution have concentrated on terrestrial species and ecosystems. These studies have examined mechanisms for uptake, conditions affecting uptake, physiological and chemical effects of metals on plants, and ecological effects of metal pollution (Lepp, 1981a). Each of these factors has been examined with regard to cadmium (Page *et al.*, 1981), copper (Lepp, 1981b), lead (Koeppe, 1981), and zinc (Collins, 1981).

Salt marsh food chain relationships are fairly well understood. Although most work in this area has concentrated on eastern and southern marshes, some investigators have studied the particular ecology of Bay Area salt marshes (Harvey *et al.*, 1977; Jones and Stokes, 1979).

Metal contamination of the waters and sediments of San Francisco Bay has been well documented. The geographic distribution, sources, and behavior of many metals has been investigated (McCulloch *et al.*, 1971; Peterson *et al.*, 1972). One study also examined a particular case of severe metal contamination at Point Isabel in South Richmond (McClenaghan, 1980).

Interest in metal contamination in the biota has centered around shellfish. Many studies of uptake, effects, seasonal variation and spatial variation of metals in shellfish have been conducted around the Bay. A number of investigators have also related their findings to presence of these metals in waters and sediments (Ninayahuar, 1982; Thomas, 1982; McClenaghan, 1980; Luoma and Cain, 1979; Girvin et al., 1975). Evidence for metal contamination in salt marsh plants in the Bay Area salt marshes is lacking, but some studies in other parts of the country have examined quantitative processing of metals in salt marshes (Banus et al., 1975).

Methods

Two San Francisco Bay marshes were chosen for comparison. The salt marsh at Tomales Bay (Marin County) is probably quite pristine, with little metal pollution, whereas the salt marsh on the Emeryville Crescent (Alameda County) is exposed to a considerable amount of pollution from freeway exhaust, nearby industry, and San Francisco Bay water. Two characteristic marsh plant species were selected for testing. Pickleweed (*Salicornia virginica*) was chosen because at both marshes it comprises the greatest biomass, and could be considered the dominant species; if pickleweed were significantly affected by metal pollution we could expect the whole marsh to suffer. Salt grass (*Distichlis spicata*) was selected because it grows at the highest part of the intertidal zone, tolerates the highest salinities, and may have unusual chemistry. Cadmium and lead were chosen for testing because both are toxic to organisms and tend to be present in high concentrations in urban environments. Copper and zinc were chosen because, although they are nutrients in small amounts, they can be harmful when concentrated, as they tend to be in urban environments.

Pickleweed and salt grass were collected from each marsh within a three day period in February; only above-ground portions were collected. The samples were dried for 24 hours at 65°C and weighed to determine dry weight. The dry plant material was then digested in hot 70% nitric acid for about seven days. At the end of this period, 25 ml of hydrogen peroxide were added in 5 ml doses to complete digestion. Additions of acid and peroxide were stopped when a clear solution resulted. At this time a fine white substance remained at the bottom of each beaker. A known volume of each solution was tested with a Perkin-Elmer 360 Atomic Absorption Spectrophotometer to determine concentration of each metal. I am grateful to Mr. Tommie Morrison for his generous assistance with the testing process.

Error could have resulted at several steps in the process. Especially relevant for this study were the inaccuracies in measurement of volume of the sample solutions. In addition, it is possible that the lead standards were improperly prepared, since none of the samples gave a positive reading when tested for lead. Also, a machine error of 10% is possible (Morrison, 1984, pers. comm.).

Results

Concentrations of each of the four metals in the samples are shown in Table 1. Both cadmium and copper are present in greater amounts in the Emeryville Crescent plants. As noted, there is apparently no lead in any of the plants; zinc concentrations vary, and no pattern emerges.

	Cadmium	Copper	Lead	Zinc
Tomales Bay Pickleweed	0.167	6.87	0	30.52
Tomales Bay Salt Grass	0.143	5.34	0	15.06
Emeryville Crescent Pickleweed	0.424	7.41	0	12.71
Emeryville Crescent Salt Grass	0.480	6.79	0	16.17

TABLE 1. Concentrations of heavy metals in salt marsh plants, ppm dry weight.

Cadmium concentrations are lower in the Tomales Bay plants, which contain 0.617 ppm for the pickleweed and 0.143 ppm for the salt grass, than in the Emeryville Crescent plants, which contain 0.424 ppm in the pickleweed and 0.480 ppm in the salt grass.

The pattern for copper differs, however. The pickleweed from both locations contains slightly more copper than the salt grass, with the Emeryville Crescent plants again showing higher total copper concentrations. The Emeryville Crescent pickleweed contains 7.41 ppm copper; the salt grass from that location contains 6.79 ppm. From Tomales Bay, the pickleweed contains 6.87 ppm, and the salt grass contains 5.34 ppm.

No pattern emerges for zinc concentrations. The Tomales Bay pickleweed contains 30.52 ppm zinc, and the corresponding salt grass contains 15.06 ppm. The Emeryville Crescent pickleweed contains 12.71 ppm zinc, and the salt grass from that marsh contains 16.17 ppm.

Salt Marsh Function and Ecology

To assist in understanding the ramifications of metal pollution in salt marshes of the Bay Area, it will be helpful to examine the ecology of the salt marsh, as well as the specific effects of the four metals on plants. The main causes for concern over metals in the salt marsh ecosystem lie in two possibilities: that food chain magnification of the metals could endanger higher-order consumers (such as humans, birds, or sport-fishing species) (Figure 1), and that metal pollution could harm the plant community of the salt marsh to the point at which the salt marsh could no longer function, and thus no longer help support the food chain for which it is the main primary producer (Figure 2).

Test results (Table 1) show that both cadmium and copper concentration are higher in the plants from Emeryville Crescent, suggesting that metal pollution is more severe in San Francisco Bay than

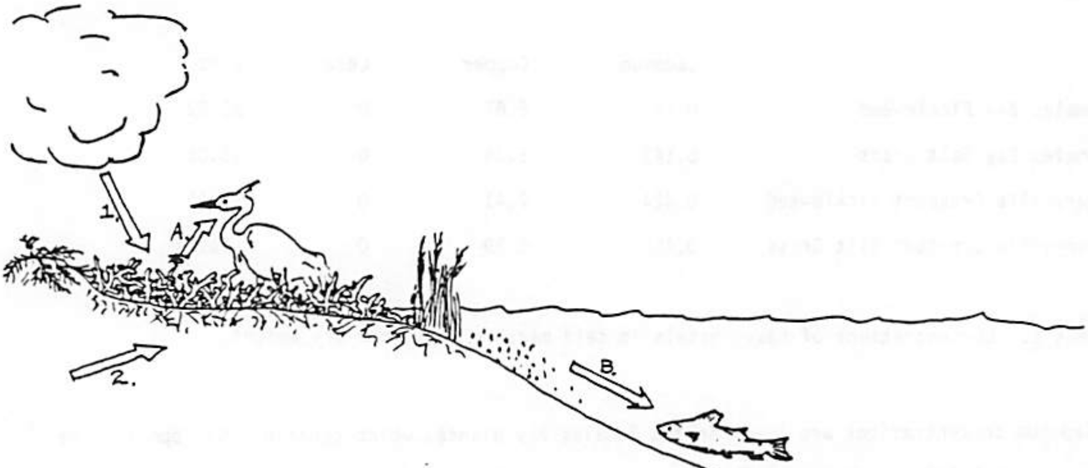

Figure 1. Simplified Salt Marsh Ecosystem, Showing Pathways of Heavy Metals Through Food Chain. 1 = Aerial Input; 2 = Soil Contamination; A = Herbivory Route; B = Detritus Route.

in the relatively pristine conditions at Tomales Bay. Apparently salt marsh plants take up more zinc than other metals. Further experimentation could determine whether and how plants are affected by metals, whether iron and other metals in the soils are protecting plants from more toxic metals through competitive binding, and how the specific conditions of the Bay marshes affect the behavior of relevant metals in terms of salt marsh plants and their ecological function.

The salt marsh makes three essential contributions to the ecosystem of which it is a part. First, it is a highly productive community, with net primary production estimated to be about 2500 $g/m^2/yr.$, compared to 125-200 $g/m^2/yr.$ for open ocean, and 2500-7500 $g/m^2/yr.$ for tropical swamp, the most productive type of community (Ricklefs, 1976, p. 617). Some of the salt marsh production is consumed by herbivorous insects; the remainder moves through the food chain as detritus and is consumed by decomposers such as deposit and filter feeders (Figure 1). Through these two interconnected cycles, salt marsh primary production provides energy to terminal predators such as predatory fish, birds, and humans, before it returns to the detritus cycle (Harvey et al., 1977).

The second important function of the salt marsh is to filter pollutants which would eventually enter the Bay through freshwater inflow. Since by nature a salt marsh is at sea level, freshwater

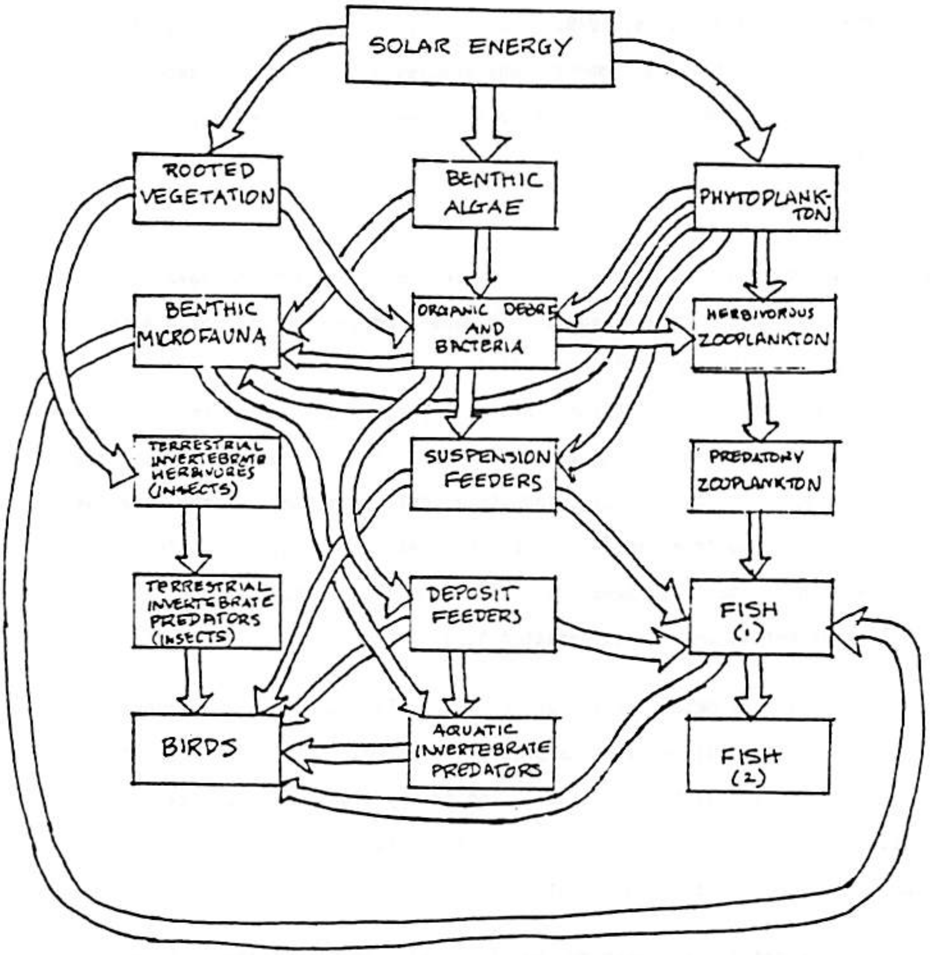

Figure 2. Aquatic Ecosystem Based on a Flow of Net Primary Energy.
Source: Adapted from Harvey et al., 1977, Figure 6.

inflow moves slowly, permitting suspended materials to settle out into marsh substrates. The dense vegetation traps incoming materials, making them subject to chemical and biological action. Salt marsh plants act as a carbon monoxide sink, and filter nitrates and phosphates from incoming waters (Harvey et al., 1977). Additionally, salt marsh plants help keep biochemical oxygen demand in balance when seasonal changes in other estuarine functions cause fluctuations (Sweetser, 1980; Harvey et al., 1977, pp. 69-74).

Third, the salt marsh functions as essential habitat for many species, some of which are rare or endangered. These include the Salt Marsh Harvest Mouse, the Clapper Rail, the Black Rail, and two subspecies of song sparrow (Jones and Stokes, 1979; Olson, 1982). Endangerment or rarity seems to be correlated with very specific habitat requirements; any species with obligatory dependence on a habitat such as the salt marsh, which has dwindled by 85% in the last hundred years, is running out of resources far faster than it can adapt to changes.

Metals in Plants

Plants have always encountered metals as part of their environment, and tend to have mechanisms for dealing with them. Of the four metals considered in this paper, copper and zinc have nutrient value to plants, whereas lead and cadmium do not (Lepp, 1981a).

Metals may enter plants from aerial contamination, through the soil, or through the food chain (Figure 1). Sources of aerial contamination include automobile exhaust and industrial emissions; soil contamination can result from mining by-products, industrial pollution, metal-laden detritus, or rain. Agricultural chemicals or industrial activities upstream may also contaminate freshwater inflows into the salt marsh with heavy metals. Sewage outfalls generally contain higher than normal concentrations of all four metals under consideration here.

Uptake of heavy metals - Plant uptake of metals varies by metal, by plant species, and according to other metal ions present. Other conditions, such as precipitation (dilution of soil solution), organic content of soil (providing external binding sites), and pH may also affect uptake by plants (Lepp, 1981a). Since factors may affect each other, it may be impossible to determine true causes of uptake or lack of uptake of a metal in a given situation.

Effects of heavy metals - Once the metals have entered the plant, effects will again be determined by a combination of factors which may behave synergistically or antagonistically. The pH, other metals present, or particular plant species may alter a plant's reaction to a metal. General effects of metals include chlorosis, impaired enzyme activity, or impaired reproductive processes. Metals can harm the health of individual plants; if they harm the health of most of the individuals in the community, function and survival of the community may be impaired, thus threatening the integrity of the ecosystem. Understanding the effects of metal pollution on individual plants can aid in understanding the danger of heavy metal pollution for the community. Known effects and uptake considerations of the four metals under consideration will be briefly reviewed here.

Lead - At very high test concentrations, lead has been shown to decrease photosynthesis and reduce root and shoot growth (Koeppe, 1981). Lead may inhibit uptake of phosphates, which are necessary to plants. At normal roadside concentrations, however, few significant effects can be definitely attributed to lead. Aearosol lead can accumulate on leaf surfaces but does not appear to enter plants or to interfere with leaf function at usual roadside concentrations. Soil lead may enter the plant through the roots but will collect in extracellular spaces in the roots as lead phosphate, rendering it virtually harmless (Koeppe, 1981). Recent evidence suggests that in estuarine systems, iron levels are negatively correlated with lead uptake by organisms, i.e., presence of iron in the soil will inhibit lead uptake (Luoma, 1984). Low pH and low organic content of soil both increase bioavailability of lead to plants. Test results (Table 1) show that no lead is present in the above-ground portions of the salt marsh plants. Barring experimental error, it seems likely that any lead taken up by these plants is stored in the roots, and does not significantly harm the plant. In addition, if significant amounts of iron are present in salt marsh soils, lead uptake may be inhibited. It is also possible that lead never accumulates on leaf surfaces due to the rinsing action of the tides.

Cadmium - Cadmium toxicity produces chlorosis and reduces production. Toxic effects occur at very different cadmium levels from plant to plant (Page et al., 1981), and cadmium levels in salt marsh plants, especially those at Emeryville Crescent (Table 1), could be harmful if these species are susceptible.

Since cadmium is a rare element, plants have few mechanisms for dealing with it in their environment. Plants take up more cadmium under acidic conditions and when soil cation exchange capacity is low, as with lead (Page et al., 1981). However, plants do take up cadmium even when only small amounts are available, showing a two- to twenty-fold increase over soil levels. Cadmium measurements in Bay sediments reveal levels no higher than 2.5 ppm (Bradford and Luoma, 1979). Since results of the tests for this report showed that none of the salt marsh plants contained more than one-fifth this level, it seems likely that Bay Area salt marsh plants are not significantly concentrating cadmium, and are protected by the organic soils in which they grow.

Copper - Since copper is a plant nutrient, plants can suffer both from copper deficiency and from copper excess (Lepp, 1981b). Deficiency may result in reduced photosynthesis and chlorosis, and may inhibit enzymes associated with floral initiation, thus threatening both plant survivability and reproducibility. Copper excess can stunt growth, cause chlorosis, and inhibit root development. Further, it can inhibit enzyme activity in the soil itself, to the plant's detriment.

Bioavailable copper tends to be in the form of organo-copper complexes. Uptake is probably passive, and as with other metals, is affected by environmental conditions, especially nitrogen status of the soil. Where copper levels are particularly high, some species are known to accumulate amounts of the metal, and appear to become copper-tolerant rapidly (Lepp,1981b). Researchers have observed that in the clam Macoma balthica, 15% of certain populations can survive saturation of their seawater with copper. It is hypothesized that some genetic mechanism is activated by high copper levels (Luoma, 1984). Perhaps a similar mechanism in plants explains the swift appearance of copper-tolerant ecotypes.

Test results (Table 1) indicate that there is probably more copper present at Emeryville Crescent than at the control site, but concentrations in this range are probably not toxic, especially if prolonged exposure has induced copper tolerance.

Zinc - Zinc, like copper, is a vital plant nutrient, so that both excess and deficiency can harm plants (Collins, 1981). Zince is associated with the activities of over 80 plant enzymes, as well as with plant RNA and DNA. Therefore, deficiency could inhibit growth, development, and differentiation of plants and plant cells. Symptoms of both deficiency and excess include chlorosis and stunted growth; in the field, dangerously high levels of zinc are rare.

Uptake is affected by temperature, pH, other soil metals and minerals, and organic content of the soil. Unlike cadmium, lead, and copper, zinc is taken up more readily at a slightly alkaline pH, and in more organic soil. Since Bay salt marsh soils are acid and organic, uptake is probably not excessive or deficient.

Local evidence for zinc contamination is complex. In the southern part of the Bay, where most pollutants are prevalent, zinc concentration seems to be relatively low (Bradford and Luoma, 1979). Shellfish researchers have, accordingly, found little cause for alarm over zinc levels in the clam Macoma in the southern Bay (Luoma and Cain, 1979). However, along the Emeryville and Oakland shoreline, and some other Bay shoreline locations, zinc concentrations in clams and sediments are consistently higher (Bradford and Luoma, 1979; McClenaghan, 1980). The plants tested for this study contained more zinc than other metals (Table 1), but no pattern emerges that is consistent with known zinc concentrations in sediments. The range of zinc concentrations found in the plants probably do not harm the plants themselves, but may add significant amounts of zinc to the food chain. This magnification may in turn endanger organisms which feed high on the food chain.

Conclusions

Bay Area salt marshes play an essential role in supporting the local food chain by providing habitat, food energy, and pollutant filtering. Heavy metals could pose a problem for the ecosystem if they affected the health or reproduction of the salt marsh plants, or if they became incorporated into the food chain through salt marsh plants. In the present study, no metal levels were found to be of immediate danger, but the possibility remains that subtle interactions of the factors influencing the uptake and effects of these potentially hazardous metals could harm the plants and/or the ecosystem of which they are a part. Metal levels in plants at Emeryville Crescent are generally higher than the levels at Tomales Bay, suggesting that the higher levels of pollution at Emeryville have become incorporated into the plants. However, none of the metal levels were found to be obviously dangerous for the plants themselves. Negative effects are probably sublethal or related to food-chain magnification. Further experiments are needed to pin down such effects and interactions. A thorough understanding of the dangers of pollutants such as heavy metals is necessary to preserve the integrity of ecosystems so that we may continue to enjoy the benefits they confer on us.

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