

*Long-Term Retention and Loss of Heavy Metals
from Experimental Salt Marsh Plots*

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Abstract:

Following earlier studies of metal retention in Great Sippewissett Marsh I have tested the long-term retention of heavy metals by the marsh. Beginning in the early 1970s three different levels of fertilization, in the form of sewage sludge, have been added to experimental plots twice a month every year from April to November. The sludge contains elevated levels of Cd, Cr, Cu, Pb, Zn, Mn, and Fe and also contains nutrients. I took cores from the experimental plots and measured the concentration of these metals and total sulfur.

Three patterns of retention were found. Percent retention of Pb and Cd decreased with increasing fertilization. I hypothesize that they have precipitated out as metal-sulfides and that the decrease in sulfur concentration with fertilization increases the losses of these metals. Manganese and Fe are both retained more effectively with increased fertilization. I hypothesize that they form metal-oxides which can form to a greater depth in the more oxidizing environment of the fertilized plots. The percent retentions of Zn, Cu, and Cr are similar in all three levels of fertilization. This could be due to sorbtion to organic matter and metal-oxides.

Key Words: heavy metals, salt marshes, retention, lead, cadmium, copper, chromium, iron, manganese, zinc, sewage sludge

Intro:

Heavy metals pose large problems in ecosystems. They can adversely affect plants that take them up from the surrounding environment and animals that either take them up from the surrounding environment or ingest plants containing metals. Heavy metals also are a health risk to humans. Many forms of waste including sewage, wastewater, runoff, garbage, industrial waste, and others contain elevated levels of heavy metals. These can lead to contamination of groundwater, soil, estuaries, oceans, lakes, and many other areas. Starting in the 1970s, the high risk of contamination was recognized, resulting in new laws regulating the disposal of waste containing heavy metals (Scrudato and Pagano, 1991). It was hoped that a way to safely store

these forms of waste could be found. To be safely stored the metals would have to remain chemically or physically unavailable to the flora and fauna.

Estuaries, at the interface of a watershed and the ocean, are especially prone to contamination because of the large amount of runoff, groundwater infused with septic system effluent, and sewage that they receive. Thirty years ago, it was hoped that salt marshes could store metals in an unavailable form because marshes are often high in sulfides and metal-sulfides have low solubility (Giblin, 1986). To test this, an experiment was set up in the Great Sippewissett Marsh on the coast of Buzzards Bay on Cape Cod, Massachusetts. The experimental plots receive additions of sewage sludge contaminated with heavy metals including copper (Cu), chromium (Cr), zinc (Zn), lead (Pb), manganese (Mn), iron (Fe), and cadmium (Cd) (Giblin, 1980). The additions have continued through the present, although the level of metal contamination in the sludge has decreased a large amount (Greenbaum, 1999).

Added metals have several possible paths through the estuary. Metals can be lost from the sediment to the water and washed out to sea. Metals that remain in the sediment are bound in different ways. In anoxic conditions some metals, including Cd, Zn, Pb, and Cu form insoluble metal-sulfides (Giblin, 1983). In oxic conditions some metals such as Mn and Fe form hydroxide complexes which also have a low solubility and precipitate out (Gambrell, 1994). Other metals can adsorb to these metal-oxides and also be retained (Gambrell, 1994). However, it has been hypothesized that iron hydroxide metal complexes are a less stable form for metals to be stored. Variability in the oxic conditions, which can be altered by fluctuations in the water table with the tides can result in the complex solubilizing and the metals being released. It is also hypothesized that the repeated release and precipitation of metals results in a net loss from

the system (Greenbaum, 1999; Giblin). Finally, metals can sorb to organic matter within the sediments. However, this is not a long term sink since organic matter decomposes.

The retention and loss of metals in sediment is ultimately dependant on the redox potential, organic matter content, presence of sulfides, pH, and soil texture of the sediment (Gambrell, 1994). Metals can be released from metal-sulfides, iron hydroxide complexes, and organic matter by changes in the chemical properties of the sediments. Once released the metals are available to be take up by flora and fauna and can be washed out of the marsh.

Early results from this site indicated a large amount of loss from the plots, with less than 50% retention of Cu, Cr, Zn, Mn, Fe, and Cd and 60% retention of Pb (Giblin, 1983 in Greenbaum, 1999).

The goal of this study is to determine the current percent retentions of the metals and compare them to the percent retentions found in 1980. Greenbaum only compared the highest fertilized plots and the controls, which is useful in looking at the effect of contamination on retention, but comparing all three treatments will allow for a better understanding of the processes governing retention.

Site Description:

Great Sippewissett Marsh is a salt marsh located on the southern coast of Cape Cod, Massachusetts. In the early 1970's, experimental plots were established in the marsh to study the effects of added sewage sludge. Three treatment levels were created: low (LF), high (HF), and extra-high (XF) receiving 16.8 g fertilizer m⁻², 50.4 g fertilizer m⁻², and 151 g fertilizer m⁻² twice a month from April through November respectively. Fertilization of the HF and LF plots began in 1971 and the XF plots were created in 1974. The metal content of the sludge has varied over time, but the amount of sludge applied has remained consistent. Each treatment is replicated twice; there are two XF, HF, and LF plots. There are also two control plots which do not receive

sludge and two urea-phosphate (UP) plots which are supplemented with urea and phosphate equal to the nitrogen (N) and phosphorus (P) additions that the HF plots receive. Each plot is 20 m in diameter and is located on a stream that roughly bisects the treated area. (Fig 1)

Methods:

I collected two 20-31.5 cm long sediment cores 5.2 cm in diameter cores from six treatment plots; each treatment has two replicate plots. I collected one core from a CT plot and one from a UP plot. I located the cores in the upper marsh an equal distance from the creek running through each plot. This is to account for the strong differences in percent retention that Greenbaum (1999) found between the high and low marsh.

I divided each core into nine to twelve subsections depending on the length of the core. I cut the top 14 cm into seven 2 cm thick sections and the bottom into 4 cm sections with the final section being of variable thickness depending on the length of the core. Each subsection was oven dried at 60 °C for at least 4 days and weighed to determine the bulk density.

I analyzed all of the subsections from one core of each plot for metal content and sulfur (S) content, giving two true replicates of each treatment. The replicate cores of both HF plots and one LF plot were also analyzed for metal and partially analyzed for S. I ground a subsample of each subsection using a Wig-L-Bug amalgamator model 6 prior to analysis.

I used acid digestion to oxidize the sediments, extracting the metals for analysis. After homogenizing a subsection by mixing and grinding I added 5 mL of 12 M nitric acid (HNO₃) to approximately 0.5 g of sample; 0.7 g of sediment was digested from each of the UP and CT samples. I heated the samples for 1-2 hrs at 65-80 °C in a water bath. After the samples cooled to room temperature I added 5 mL of 12 M trace metal grade hydrochloric acid (HCl) and reheated the samples to 65-80 °C in a water bath for an addition 1-2 hrs and allowed the samples to cool. I diluted the sample to a total volume of approximately 30 mL with deionized water

after cooling and filtered them using coarse fast Fisherbrand Q8 filter paper into 100 mL volumetric flasks. Each extraction was further diluted with deionized water to 100 mL. I stored 20 mL of sample in glass scintillation vials.

Using a Perkin Elmer 2380 Atomic Absorption Spectrophotometer I determined the metal concentrations of the extracts. I analyzed for Cu, Cr, Zn, Pb, Mn, Fe, and Cd following the protocol of the Atomic Absorption Spectrophotometer.

I used a LECO SC32 Sulfur Determinator to measure the total S in the ground sediment of one complete core per plot and also of the replicate cores from the HF plots and one of the LF plots.

In order to do a mass balanced inputs and retention calculations to determine the amount of metals lost and percents retained I used yearly average metal contents provided by Miloganite after 1980. The 1980-89 yearly averages were not available for Fe nor were the 1980-92 yearly averages of Mn. In these cases I used an average of the known Fe and Mn values. Prior to 1980 the metal content of the fertilizer applied was tested; when available I used those values (Giblin, 1983; Giblin, 1986). Only Zn, Pb, and Cd concentrations in the sludge added to the HF and LF plots in 1971-72 were available. We used trends in contamination and averages to estimate the concentration of all metals in 1973 and of Cr, Cu, Fe, and Mn for 1971-72. Using bulk densities determined from dry weights and the known volume of each core subsection and the metal content of each subsection I calculated the total metal content of each core and scaled up to the current metal content of the plots.

Results:

The depth of the reducing environment is deeper in the fertilized plots than CT (Fig 2). Percent S increases beginning at 8 cm in the CT plot and much deeper, 24 cm, in the UP plot (Fig 2). The XF plots show strong reducing environment, indicated by high S content, at 20 cm

below the surface (Fig 2). The average of the HF plots has two S peaks, one close to the surface and one below 20 cm (Fig 2). The individual HF plots have quite different S profiles (Fig 3). There is much more S and a continuous increase in the percent S in HF9 (Fig 3). In the other HF plot, HF2, percent S begins to increase at 16 cm (Fig 3).

The profiles of each metal are based on the average metal content for each treatment with standard error. The profiles of Pb, Cu, and Cr all show maximum concentrations of the metal deeper in the sediment with increased fertilization; the XF peak is located at a lower depth than the HF which is lower than the LF (Fig 4, 5, and 6). Zinc is retained at the surface in all treatments but the profiles also reveal a maximum concentration of Zn deeper in the sediment (Fig 7). The maximum concentration occurs deeper with higher rates of fertilization (Fig 7). Manganese is located primarily at the surface (Fig 8). The XF plots do show deeper accumulation of Mn than the other plots, but even they have little Mn below 8 cm. Iron is also most abundant at the surface, although it is present to a greater depth than Mn before tapering off (Fig 9). There is very little Cd in any of the plots (Fig 10). The highest amount of Cd is in the XF plots at 16-20 cm, however there is a large amount of variability between the two replicate plots.

The CT plots were used to determine the amount of each metal present in the marsh independent of the experiment. Therefore, the total amount of each metal found in the CT core was subtracted from the total of each treatment to determine the amount due to fertilization. The total amount of metal is calculated to a depth of 30 cm for all treatments. The total amount of each metal increases with increased fertilization for each metal (Fig 10). The XF plots do not have a significantly different amount of Cd than the HF or LF plots, but they are significantly different from each other (Fig 10a). The XF and HF plots do not have significantly different

amounts of Cr but they do have significantly more Cr than the LF plots (Fig 10b). The total amounts of Pb, Cu, Zn, Mn, and Fe are all significantly different by treatment (Fig 10c, d, e, f, g).

The percent retention is based on the amounts added and the average total of each treatment. All of the percent retentions are calculated from 30 cm long cores; metal content below 30 cm was not used. Lead and Cd all have decreasing percent retention with increasing amounts of fertilizer. Manganese and Fe both have increased percent retention with increased fertilization. Chromium Cu, and Zn all have similar retentions in all three treatments although percent retention of Zn increases in the XF and HF plots relative to the LF. (Table 1).

Discussion:

The depth at which metals are retained in the sediment is dependant on the chemistry of the sediment as well as the physical characteristics of the sediment. This includes the redox conditions, depth of the water-table, pH, sulfide content, and organic matter content (Gambrell, 1994). As a function of these conditions, as well as the chemical characteristics of the individual metal, metals are found in different forms. The most available forms are soluble and include free ions, soluble inorganic complexes, and soluble organic complexes. Metals can bind the exchangeable ions sites of minerals. Metals precipitate out of solution as inorganic compounds, metal sulfides, and metal oxides. Metals also adsorb to metal-oxides and organic matter. The least available form is within the lattice structure of a mineral. (Gambrell, 1994)

The conditions of a marsh are continuously changing. Tidal patterns flood and drain the marsh daily altering the redox potential of the sediment. When the tides are high little oxygen (O₂) can diffuse into the sediment, but at low tide after the water has drained out air fills the pore space oxidizing the sediment. The redox potential of the sediment is also affected by plant growth. Plants remove water from their surroundings through their roots and release it to the

atmosphere through evapotranspiration (Giblin, 1983). Additionally, in highly saturated soils such as marsh sediments plants move O₂ to their roots through aerenchyma, oxidizing the sediment around them (Lacerda *et al.*, 1997).

The major difference between the treatments is the depth in the sediment at which the conditions become reducing. I used total sulfur profiles to locate the depth of reducing conditions; sulfur loss occurs in oxidizing environments so an increase in percent sulfur can indicate that the environment is not oxidizing. I found that total sulfur peaked deepest in the XF plots and closest to the surface in the LF plots (Fig 2). Giblin (1988) also found that an increase in S occurred deeper with fertilization when comparing the XF and CT plots. This may be due to increased plant biomass with added nutrients (Valiela, 1975) which increases the oxidation of the sediment (Howes *et al.*, 1981).

Total inventories of each metal reveal that for all seven metals the amount of metal increases with fertilization (Fig 10); however, percent retentions reveal that the patterns of loss are not the same for all metals (Table 1). Chemistry of the metal and sediment result in different forms of metal including metal-sulfides, metal-oxides, and metal sorbed to organic matter. The depth profiles of each metal by treatment indicate peaks in metal concentration. These peaks are located at different depths varying both with treatment and by metal (Fig 4, 5, 6, 7, 8, 9, 10). The profiles show patterns consistent with different metals being retained in all three forms and in some instances a combination of retention mechanisms. This lends further support to the idea that retention is dependant on the chemistry of the metal, conditions of the sediment, and rate of inputs.

Lead is known to form lead-sulfide complexes in anoxic conditions (Thomson *et al.*, 1975 in Giblin *et al.*, 1986). These are relatively stable so long as conditions do not become

oxidizing, in which case the sulfide is oxidized releasing the Pb as a soluble ion (Gambrell, 1994). It appears that the major control of Pb mobility is the formation of lead-sulfides, as seen in other locations (Billon *et al.*, 1991). Profiles of Pb concentration reveal that the XF plots have the deepest peak and LF plots retain Pb closest to the surface (Fig 4). This corresponds with the S profile patterns (Fig 2). The Pb peaks occur at the beginning of increases in S concentration. The average HF profile does not match as nicely, however the individual plots' Pb and S profiles match quite well. This may be due to the strong differences in S profiles of the two HF plots (Fig 3). Lead is retained throughout the HF9 core which also has steadily increasing S content (Fig 11 and 3). The peak of Pb in HF2 is less closely mirrored by the S profile, but the accumulation of Pb does occur at the beginning of the increase in percent S, as it does in the XF and LF plots (Fig 11 and 3). The deeper peak of S in the HF2 at 20 cm does not have a corresponding peak of Pb. It is possible that the Pb peak in HF2 does not coincide with the larger peak of S because the metal has not had time to travel through the sediment to a depth of 20 cm or that it is trapped higher in the sediment in the form of lead-sulfides at the shallower S peak. This supports the idea that S is the major control on Pb retention. Additionally, percent retention of Pb increases with decreasing application of fertilizer (Table 1). Since adding fertilizer increases plant biomass, increasing evapotranspiration, resulting in a deeper oxic zone (Howes *et al.*, 1981) we would expect less retention with more fertilization if Pb is being retained as PbS.

Copper also forms meal-sulfides but can additionally form oxides and adsorb to hydrous-oxides (Gambrell, 1994). Copper is being immobilized in the sediment as both copper-sulfides and copper-oxides. The presence of copper-oxides is suggested by the consistently high concentrations of Cu in all three treatments at the surface (Fig 5). But clearly there is more

going on. A peak of Cu occurs below the oxic zone in each treatment (Fig 5). The peak Cu content occurs deepest in the XF and least deep in the LF and correspond with the depths of S peaks, suggesting that Cu is being trapped as copper sulfides when it encounters S (Fig 5 and 2). Copper shows the same pattern of percent retention as Pb, decreasing retention with increasing fertilization, although to a lesser degree, again supporting the theory that copper-sulfides are forming (Table 1).

Zinc retention appears to be strongly related to percent S. The profiles of Zn and S in the HF plots are strikingly similar; the Zn profiles follow the two different S profiles of the replicate plots (Figs 12 and 3). The LF and XF profiles both have Zn peaks that coincide with S peaks (Figs 7 and 2). However, Zn percent retention is higher in the XF plots than the LF (Table 1). The highest Zn percent retention is in the HF plots, but this may be driven by the one replicate with the high percent S.

Chromium also seems to be bound in metal-sulfides. The Cr profiles show the XF peak deeper in the sediment than the HF or LF peaks (Fig 6). The low amounts of Cr at the surface suggests that Cr is not forming or bound to oxides. However, percent retention is fairly consistent across the different treatments with the highest in HF (Table 1).

Manganese appears to be bound in manganese-oxides. Manganese does form oxides which can also bind other metals (Gambrell, 1994). Given that the oxic zone reaches deeper in the fertilized plots, (Howes *et al.*, 1981) it is possible that manganese-oxides form to depths greater than the usually observed 1-2 cm. There is by far the greatest amount of Mn in the XF plots and it is present to a much greater depth than the other plots (Fig 8). The pattern of percent retention, increasing with fertilization, also suggests that Mn is primarily bound in manganese-oxides (Table 1).

Iron also seems to be bound in oxides. The profiles of Fe all show the highest concentration in the surface sediments, extending to a maximum of 8 cm in the XF plots and tapering off at shallower depths in the HF and LF plots (Fig 9).

The Fe and Mn oxides may also be responsible for occluding other metals at the surface which could explain the elevated concentrations of metals normally assumed to form metal-sulfides over metal-oxides such as Cu, Pb, and Zn (Gambrell, 1994).

Cadmium's profiles reveal that little Cd is present at any depth in the sediment, the most being $40 \mu\text{g Cd g soil}^{-1}$ in one of the XF plots at 20 cm (Fig 10). The average concentration at 20 cm in the XF plots is $22 \mu\text{g Cd g soil}^{-1}$. The LF and XF plots both have Cd peaks that correspond with their S peaks (Figs 10 and 2). The HF plots have two peaks, at 8 and 24 cm which corresponds with the two S peaks of the HF plots (Fig 10 and 2).. It is possible that the Cd is being held at both places as cadmium-sulfides. Perhaps the Cd that is not bound by in the initially reducing environment travels until it is trapped by the more highly reducing environment larger amount of S at 20 cm. The percent retention of Cd decreases with fertilization with corroborates hypothesis of the sulfide retention since there is more opportunity for Cd loss in the more highly fertilized plots (Table 1).

The percent retentions vary widely for the different metals. Retention above 100% was seen for Pb in LF and HF plots and for Cr in HF plots (Table 1). This probably means that there was more metal added than is accounted for. This is possible give that metal content of the fertilizer can vary widely over the course of a year but an annual average, rather than direct testing of the fertilizer applied, has been used since 1980. The highest percent loss was of Mn in all three treatments and the highest retention was of Pb in the HF and LF and of Cu in the XF plots (Table 1).

I sampled only the high marsh, for consistency. However, Greenbaum (1999) found much lower percent retention in the low marsh than the high of the XF plots. If this pattern is true in all three treatments, I must assume that my estimates of percent retention are over estimates. Further sampling within each plot, including multiple distances from the creek, would give a more accurate assessment of the percent retention of each metal by the experimental plots.

Conclusion:

Although early studies suggested that salt marshes were a potential sink for heavy metals, retaining metals in forms unavailable to organisms, long-term study reveals that salt marshes are imperfect sinks. The higher percent losses seen by Greenbaum (1999) in the low marsh suggest that the marsh is less effective at retaining heavy metals than this study concludes.

All three mechanisms (sorption to organic matter and precipitation of metal sulfides and metal oxides) appear to contribute to the retention of heavy metals in the experimental plots. However, the marsh is an imperfect sink with losses of all metals (Table 1). It is therefore important to keep heavy metals out of marshes. The combination addition of heavy metals with extra nutrients had a surprising effect of altering the redox potential of the sediment and therefore the retention rates. Since contamination of metals often occurs from wastewater effluent with high nutrient levels this effect must be kept in mind when considering how to dispose of wastewater.

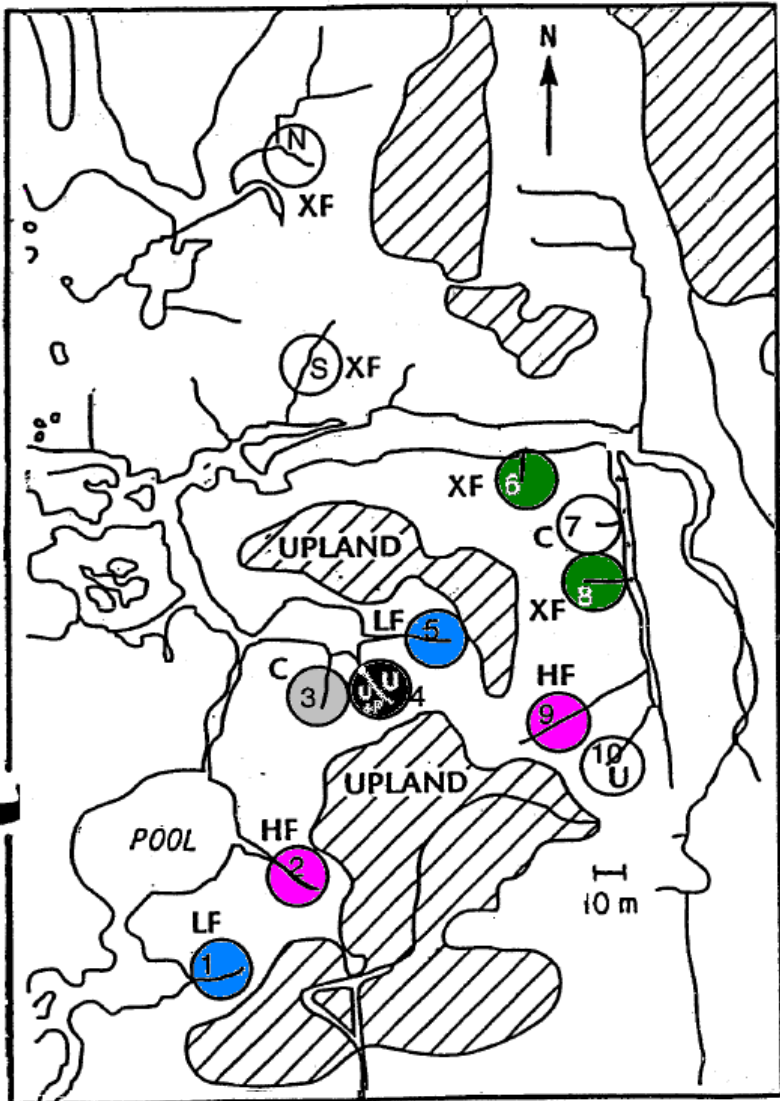
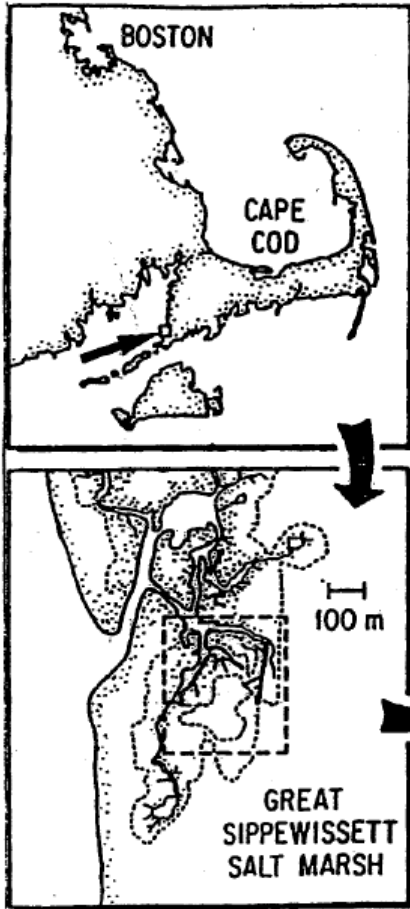
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Map A and B
 Location of Great Sippewissett Marsh on Cape Cod and on the Coast of Buzzards Bay



Map C
 Experimental Layout of the Fertilised Plots in Great Sippewissett Marsh. The Symbols Denote the Fertilisation Type and Plot Number as Explained in Table 3.5.1.

Source: Giblin, A. E. Personal Correspondence

Figure 1. Map of experimental plots in Great Sippewissett Marsh. The plots sampled for this study are colored: CT – grey, UP – black, XF – green, HF – pink, and LF – blue.

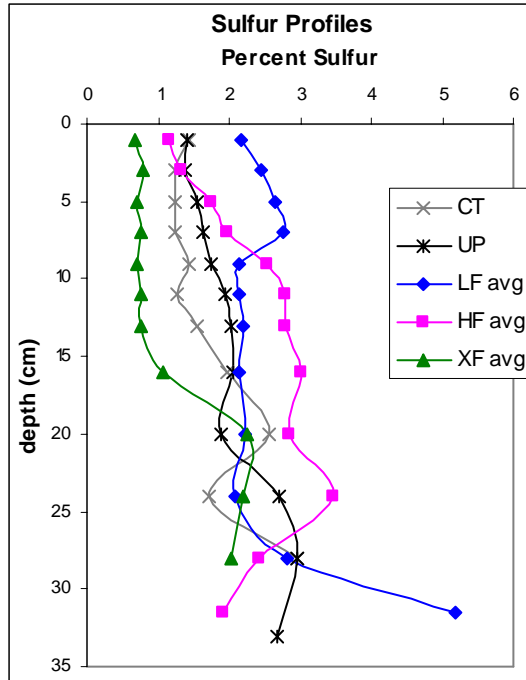


Figure 2. Average percent sulfur profiles.

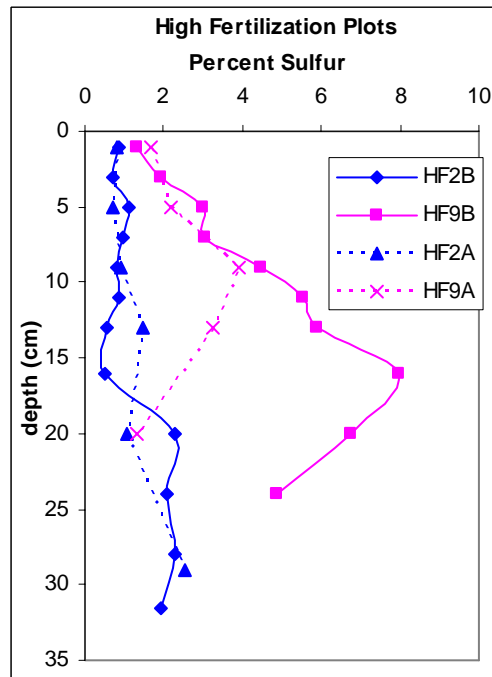


Figure 3. Percent sulfur profiles of individual HF cores. Each plot has two replicate cores.

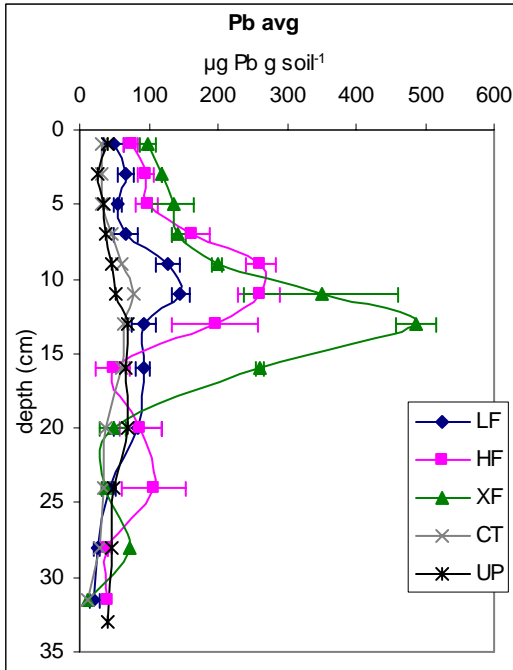


Figure 4. Averaged lead profiles by treatment with standard error bars.

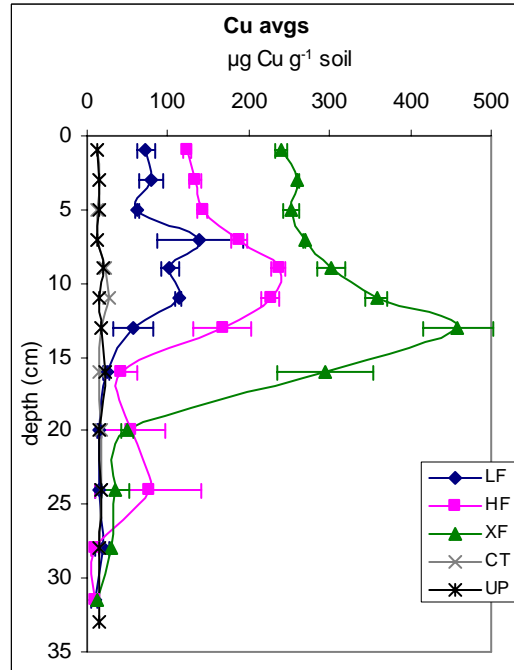


Figure 5. Averaged copper profiles by treatment with standard error bars.

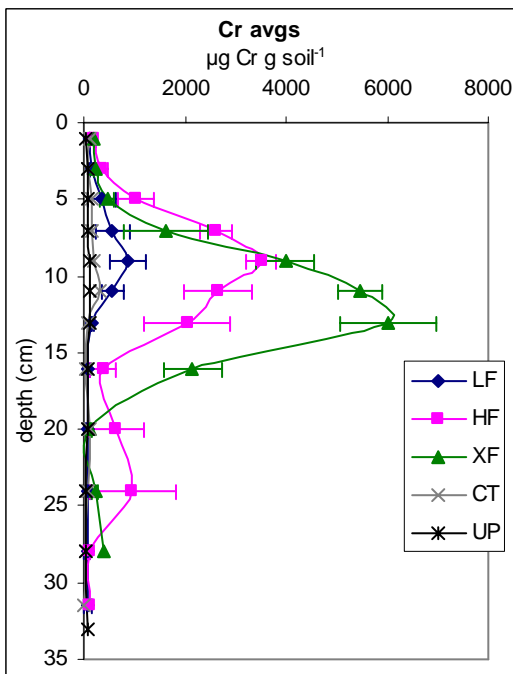


Figure 6. Average chromium profile with standard error bars.

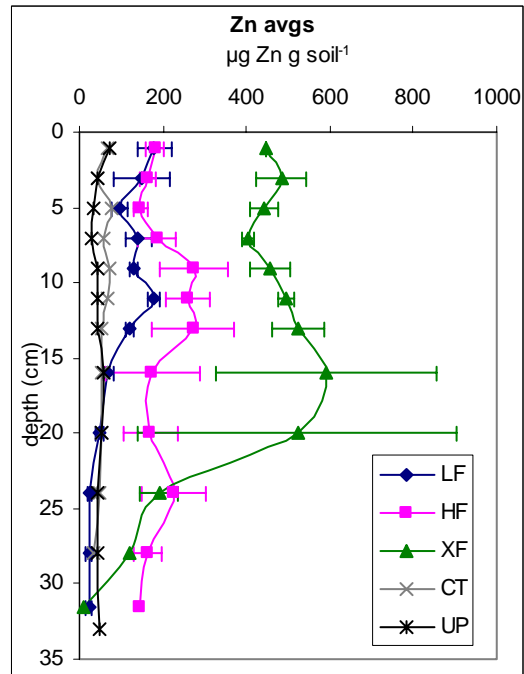


Figure 7. Average zinc profile with standard error bars.

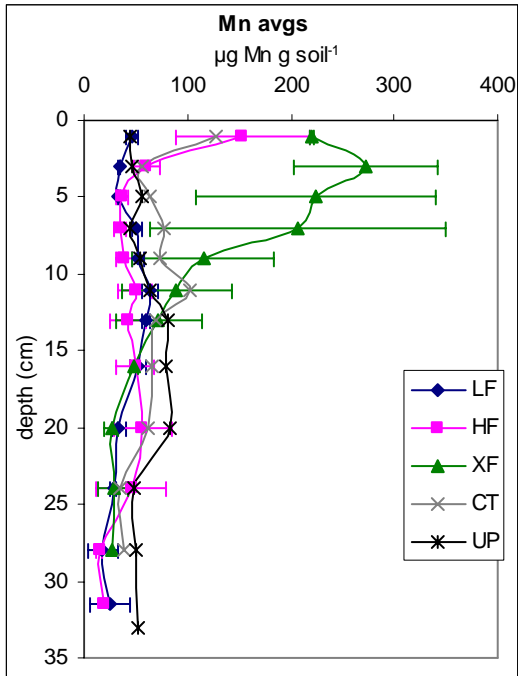


Figure 8. Average manganese profile with standard error bars.

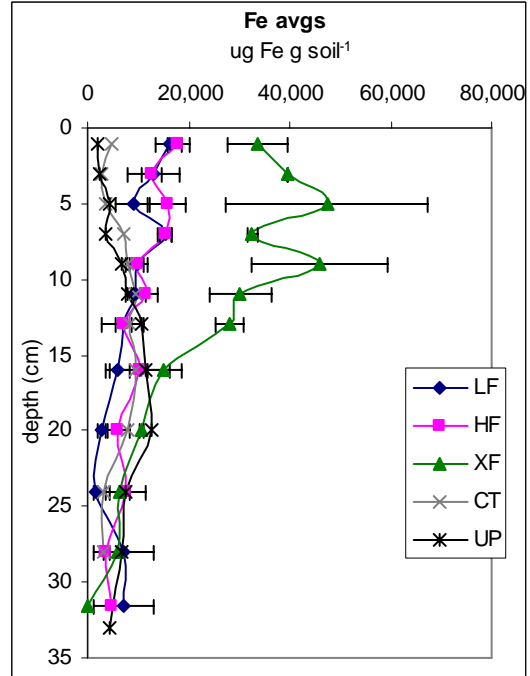


Figure 9. Average iron profile with standard error bars.

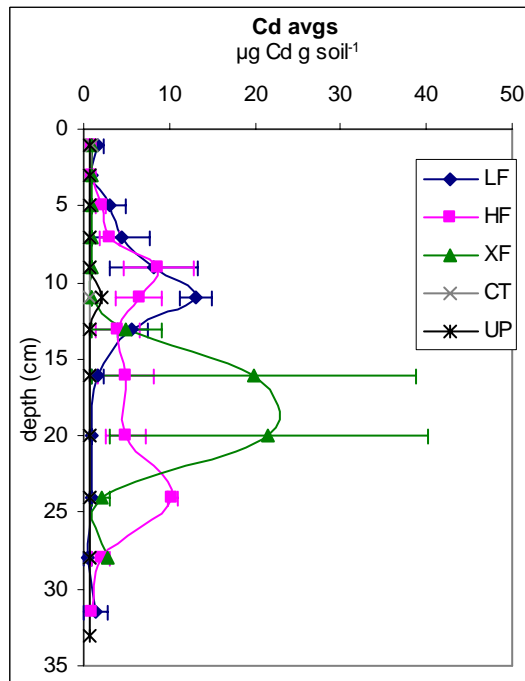


Figure 10. Average cadmium profile with standard error bars.

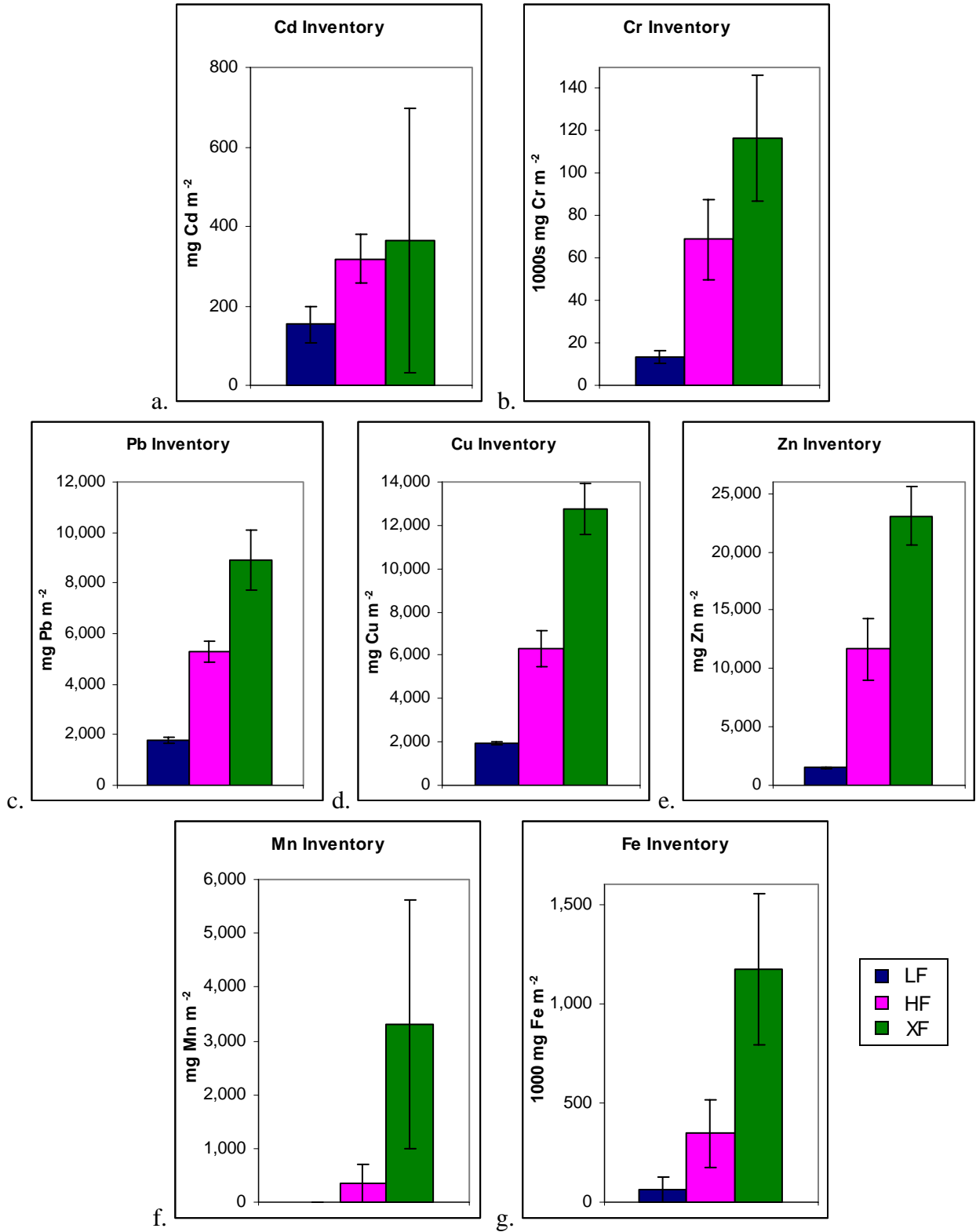


Figure 10. Total inventories of each metal in 30 cm cores. The amount of metal is calculated from two replicate plots and does not include the amount of metal present in the control plots. Standard error bars are shown.

Table 1. Percent retention of each metal calculated using the amount of metal in a 30 cm core. The amounts found in the control plot are assumed to be the metal content present independent of the experiment and as such are subtracted from the treatments' amounts.

	Pb	Cu	Zn	Cr	Cd	Mn	Fe
XF	62 ± 8	65 ± 6	45 ± 5	67 ± 17	18 ± 16	19 ± 13	44 ± 14
HF	102 ± 12	89 ± 15	55 ± 21	110 ± 31	36 ± 14	4 ± 6	28 ± 23
LF	112 ± 7	90 ± 4	26 ± 1	69 ± 16	67 ± 20	0 ± 0	21 ± 21

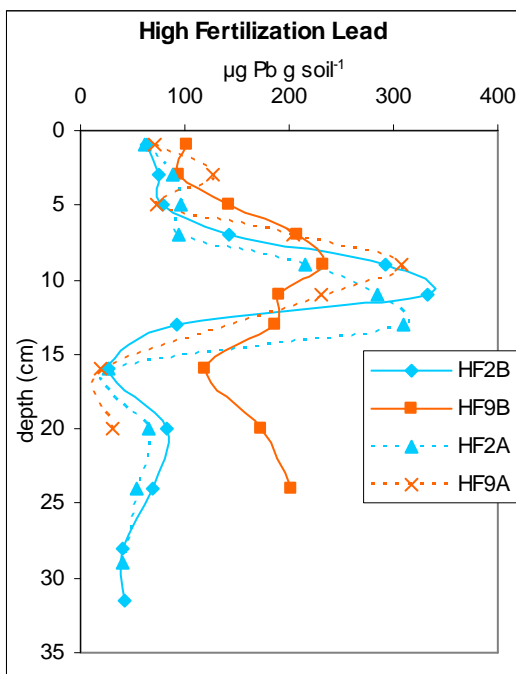


Figure 11. Lead profile of each HF core.

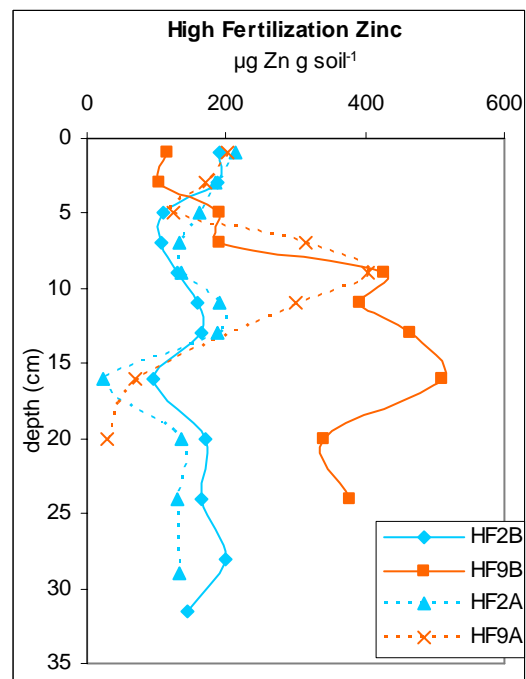


Figure 12. Zinc profile of each HF core.