Effects of Eutrophication on Concentrations and Speciation of Copper, Zinc, and Lead in West Falmouth Harbor

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Abstract

Humans have increased the delivery of heavy metals, many of which are toxic, to estuaries. The concentrations and bioavailability of heavy metals in estuarine sediments depends upon their chemical partitioning, which is partly determined by redox potential and sediment composition, such as concentrations of Fe and Mn compounds, sulfur, and carbon. Submerged vegetation may affect heavy metals in sediments by trapping fine particles with which they are associated. Because anoxic conditions and high carbon content favor relatively stable forms of heavy metals, eutrophication may increase their concentrations in sediments.

We measured the concentrations of total and labile Cu, Pb, and Zn in West Falmouth Harbor, an estuary on Cape Cod the inner portion of which is moderately eutrophied. We collected sediment cores from vegetated and unvegetated sites in the eutrophied inner harbor and the relatively pristine outer harbor. In addition to the heavy metals, we analyzed C, S, P, Mn and Fe contents. The Inner Harbor was more reducing than the Outer Harbor, and had significantly higher concentrations of C, S, P, and metals. Many of the depth profiles for the heavy metals and Fe and Mn resembled those of sulfur. In the Outer Harbor, concentrations of all components were notably higher in the vegetated than in the unvegetated site except for Cu and Zn, which were comparable between the two sites. Concentrations of all components were similar between the vegetated and unvegetated Inner Harbor sites. The ratio of labile to total metals showed no definite pattern with redox potential of the site or the presence or absence of vegetation. However, total concentrations of reduced metals were higher in the Inner Harbor.

Although the Inner and Outer Harbors appear to have baseline differences, especially in sediment mineralogy, the data suggest that conditions associated with eutrophication do increase heavy metal retention in West Falmouth Harbor’s sediments. Possible mechanisms include increased carbon inputs from algal blooms and slowed decomposition, increased sulfide formation due to anoxia, and physical stabilization of fine sediment. These mechanisms may affect heavy metal concentrations directly or via effects on Fe and Mn concentrations. The sediment-trapping and carbon-contributing effects of vegetation may explain increased retention of most components in the vegetated Outer Harbor site, but in the Inner Harbor its effect may be dwarfed by that of benthic algae. Because heavy metal concentrations were so low, any effect of vegetation on Cu and Zn in the Outer Harbor may have been confounded by other factors. Despite the lack of a pattern with labile:total metal ratios, higher concentrations of reduced metals in the Inner Harbor suggest that eutrophication increases a sediment’s reducing capacity. If coastal communities reverse eutrophication in an estuary and sediments are reoxidized, accumulated metals may be transformed into more bioavailable forms.

Key Words: Heavy metals, estuaries, sediments, contamination, eutrophication, vegetation, bioavailability, copper, zinc, lead.

Introduction

Estuaries receive anthropogenic heavy metals from several sources, including industrial effluent, atmospheric deposition, sewage sludge and wastewater treatment discharge, urban runoff, and boat hulls (Chappell 1998; US EPA 2002, Zago et al. 2001). These metals are often toxic to biota, and tend to accumulate in body tissue and become magnified in organisms of upper trophic levels. Many organisms, such as birds and commercially important fish, rely upon the high productivity of estuaries, and transport contaminants from these estuaries across ecosystem boundaries. It is critical, therefore, to understand the controls on the concentrations and bioavailability of heavy metals in estuaries.

Availability depends upon the chemical forms that metals take in sediments and waters. For instance, aqueous metals are generally more available than solid or sorbed metals, and some solid and sorbed phases, such as carbonates, are more mobile than others (e.g. oxides/hydroxides, sulfides, and organic-bound; Eggleton and Thomas 2004, Zago et al 2001, Zoumis et al. 2001). Factors such as redox potential, pH, and sediment disturbance disturbance determine the partitioning of metals among these phases. Heavy metals are often relatively immobile in anoxic sediments, due to precipitation as relatively stable sulfides, or complexation with metal sulfides or organic matter. However, when these sediments become oxic, metal complexes may be oxidized, and metals may speciate into less stable sorbed and solid phases (Eggleton and Thomas 2004, Zago et al 2001, Zoumis et al. 2001). For instance, Zoumis et al. (2001) found a shift in Cd and Zn from relatively stable sulfidic and organic forms to less stable carbonates with laboratory oxidation of sediments. The overall capacity for heavy metal retention in sediments is largely controlled by the concentrations of complexing agents, including iron and manganese, sulfur, and organic carbon.

Eutrophication of estuaries has strong implications for heavy metal dynamics. Under the anoxic conditions common in eutrophied estuaries, much of the metal may be sequestered in sediments. If desired reductions in nutrient and organic loads to these estuaries results in a return of oxic conditions to sediments, large stores of heavy metals may be released. However, macrophytes often establish in oxic estuarine bottoms, and may retain heavy metals by trapping associated sediments (through physical interception or a slowing of water velocity) or direct uptake. On the other hand, macrophyte patches may be relatively abundant in benthic fauna, which may release metals by bioturbation or ingest them directly; so although macrophytes may physically trap metals, they may not reduce their bioavailability unless they take them up in biomass.

In the following study, we examined the effects of redox conditions and the presence or absence of vegetation on the concentrations and speciation of heavy metals in the sediments of West Falmouth Harbor. This estuary on Cape Cod receives N-rich septic and Falmouth Wastewater Treatment Plant (FWTP) effluent plumes, and hosts numerous recreational boats (Giblin 2004). Although a denitrification unit will be online at the FWTP by the end of 2004, the Harbor's nutrient load should increase until about 2015, due to the 10-year lag time in plume movement. Currently the inner harbor, which has a water residence time of ~2.4 days, shows signs of intermediate eutrophication: the sediments are largely anoxic, and much of the eelgrass has disappeared. The outer harbor, which is well-flushed by tides from Buzzards Bay and has a water residence time of less than half a day, is relatively unaffected (Giblin 2004).

We focused on two heavy metals, copper and zinc. Copper is found in the paint on boat hulls, and zinc is a sacrificial anode in motors. We hypothesized that total concentrations of these two metals would be higher in anoxic than in oxic sediments, and in vegetated as opposed to unvegetated sediments. Thus, the expected ranking for total metal content by site was anoxic vegetated > anoxic unvegetated > oxic vegetated > oxic unvegetated. In addition, we predicted that a greater proportion of Cu and Zn would be in relatively available forms in oxic sediments.

We also measured concentrations of Fe, Mn, S, C, Pb, and P. Heavy metal concentrations in sediments are often positively correlated with those of the first four components, as indicated above. Thus, knowledge of the concentrations of these components provides a baseline against which to interpret heavy metal results. Lead profiles are useful in determining sediment history—they often show an increase followed by a decrease moving toward the surface, corresponding with onset of industrial pollution and the phasing out of leaded gasoline, respectively. An intact profile indicates a depositional setting, while an obscured one suggests the sediment has been eroded or reworked. We used profiles of phosphorus, which are known to decline with depth in saline waters, to further characterize the redox environments of the sediments.

Methods

SCUBA divers collected duplicate 6.5-cm sediment cores from a vegetated and an unvegetated station in each of the inner and outer areas of West Falmouth Harbor, yielding 8 total cores. We transported and handled the cores prior to analysis as described in Giblin et al. (1997). Using a platinum electrode (Bohn 1971; cited in Giblin et al. 1997), we measured redox potential (Eh) of even-numbered cores, also described in Giblin et al. (1997). Cores were sectioned in an N_2-filled glove bag at 1-cm intervals for the first 4 cm, 2-cm intervals down to 10 cm, and 4-cm intervals thereafter, to ~20-22 cm.

We used a 1 N HCl digestion to extract relatively unstable, bioavaliable metal fractions—mainly oxides, carbonates, and exchangeable fractions—and inorganic phosphorus. The metals from this digestion are referred to as "labile" or "extractable" below. Inevitably, a small amount of FeS is also extracted. Centrifuge tubes were filled with ~1-2 g of wet sediment and capped in the glove bag, and 20 mL of 1 N HCl was added to the tubes within several minutes or hours.

For the other analyses, we dried the remainder of each section. For total metal conent, we used a hot HCl/HNO_3 digestion and filtered and diluted the extracts according to the Forstner and Salomons. (1980) method (also described in Zago et al. (2001)), using 0.2-0.25 g sediment for each sample. Samples for total P were ashed, acidified with 1 N HCl, and shaken overnight as described in Harwood et al. (1969). We analyzed metals on a Perkin-Elmer 2380 atomic absorption spectrometer. Total and inorganic P extracts were prepared using the Murphy and Riley (1962) method, and analyzed on a Shimadzu UV-1610 spectrophotometer. We determined percent C for the sections 1, 2, 3, 5, and 8 (midpoint depths of 0.5, 1.5, 2.5, 5, and 12 cm) of Cores 1, 3, 5, and 7 with a Perkin-Elmer 2400 CHN elemental analyzer. Using a LECO SC-32 sulfur analyzer and coal standards, we measured total sulfur of each section of these four cores; of sections 1, 3, 5, 7, 9 , and 10 (midpoint depths of 0.5, 2.5, 5, 9, 16, and ~20 cm) of Cores 2, 6, and 8; and of sections 1-6 (extending to 10 cm) of Core 4.

Results

Baseline conditions

The four sites—Outer Harbor Vegetated and Unvegetated, and Inner Harbor Vegetated and Unvegetated—are referred to as OV, OU, IV, and IU, respectively. Coresponding cores are 1 and 2, 3 and 4, 5 and 6, and 7 and 8, respectively.

Redox potential (Eh) declines with depth at all sites (Figs 2-5). The profile for OU is erratic because it was difficult to push the probe through the sandy core, and as a result the readings fluctuated widely. At 3.5 cm, Eh in the Inner Harbor is 150-300 mV lower than that in the Outer Harbor. Within the first 4 cm, Eh at OV reaches a value ~50 mV lower than that of OU, and the final value reached by the OV core is markedly lower than that of OU. The difference between the vegetated and unvegetated sites is less for the Inner Harbor: although the average Eh in the first 4 cm of IV is much lower than that of IU, the two profiles level off to a similar value, close to the Eh (~-200 mV) at which sulfide formation is known to be high in sediments of saline waters.

We averaged the total and inorganic phosphorus concentrations over the top 4 cm of each core, and took the mean of the averages of each site's cores. Both total and inorganic phosphorus are several times higher in the top 4 cm in the Inner Harbor than in the Outer Harbor. OV has roughly 2x as much of both forms of P as OU, while the difference between IV and IU is much smaller (Fig 6, Table 1). Most of the phosphorus profiles decline overall with depth, similar to the Eh profiles (Figs 7-10). Inorganic P is positively correlated with labile Fe, with μmolar P: Fe ratios of about 1:10 in the Outer Harbor and about 1:22 in the Inner Harbor (Figs 11 and 12).

As with P, both carbon and sulfur in the top 4 cm are several times higher in the Inner Harbor than in the Outer Harbor (Figs 13 and 14, Table 1). OV has notably higher levels of C and S than OU, while the values for IV and IU are similar. Carbon declines overall with depth except in OV (Fig. 15). OV has a higher percentage of C than OU; in the Inner Harbor, although the average values for the top 4 cm are similar, IV has more C in the lower profile than IU. Sulfur increases overall with depth in Core 3 from OU (Figs 16 and 17), and one may tentatively describe the profiles for OV as increasing with depth, interrupted by the decrease around 16 cm. The profiles in the Inner Harbor generally decline and then increase with depth, except for a sharp decrease at 1.5 cm in Core 7.

Metals

Both total and extractable Fe and Mn in the top 4 cm follow the same pattern as P, C, and S in terms of differences between the Inner and Outer Harbors, and between OV and OU (Figs 18 and 19, Table 1). As an exception the difference between total Fe in the Inner Harbor site (IU>IV) may be larger than those between the two sites for P, C, and S. The total and extractable profiles for each metal usually resemble each other, and the Fe and Mn profiles resemble each other (Figs 20-27) and those of sulfur. For instance, in OV, all three profiles show the general pattern of sharp increase between 5 and 15 cm, followed by a decrease, while those of OU fluctuate less. In the inner harbor, the Fe and Mn profiles decline and then increase with increasing depth as does sulfur (with a second increase and decline between 7 and 10 cm for Mn and Fe). Strikingly, the “bulge” in the upper S profile for Core 7 is mirrored in the Fe and Mn profiles.

As with the other chemical components analyzed, total and extractable concentrations of Cu, Zn, and Pb in the top 4 cm of sediment are higher in the Inner Harbor (Figs 28 and 29, Table 1). Heavy metal concentrations in vegetated and unvegetated sites differ little overall, with some exceptions. Zn in the outer harbor is higher in the vegetated site, although this may be due to an anomalously high AAS value for one sample. In addition, extractable Pb is about 6x higher in OV than in OU. The relationship of the heavy metals to Fe and Mn, S, and C, can be seen more clearly in Figs 30-32. In many cases, total and extractable heavy metal profiles resemble each other (Figs 33-42) and those of Fe and Mn. A notable exception is Cu in the Outer Harbor. Both total and extractable concentrations are higher in OU than in OV, and increase with depth. In addition, both forms of Cu in IV, and mobile Cu in IU, decline with depth as do the other metals, but do not experience a corresponding increase. For all metals, total and extractable concentrations are positively correlated (Figs 43 and 44).

There is no clear pattern with harbor location or vegetation for the ratios of total to extractable metals (Figs 45 and 46). The ratios for Fe and Mn are on average lower in the Inner Harbor than in the Outer Harbor (0.63 and 0.62 vs. 0.50 and 0.59, respectively), but the difference is small and inconsistent among the four sites. The ratio for Cu is appreciably higher in OV than in the Inner Harbor, but the Zn ratios in these locations are essentially the same. (The ratios in OU are erratic (-176 for Cu and 7.4 for Zn) probably because the concentrations in the total extracts were too low for the AAS to detect reliably. In some sediment profiles the ratios decrease with depth, although many profiles have high scatter and no apparent pattern (Figs 47-54). The ratios throughout the profiles of iron, which is examined here as an indicator, have a negative relationship with sulfur content in the Outer Harbor, while the relationships in the Inner Harbor are mostly shallow, and three positive (Figs 55 and 56). In addition, the concentrations of reduced metals are several times higher in the Inner Harbor than in the Outer Harbor (Figs 57 and 58).

Discussion

The redox profiles show that the Inner Harbor sediments are much more reducing than those in the Outer Harbor, presumably because the Inner Harbor is more eutrophic. The benthic algal blooms in the Inner Harbor may account for its higher sediment carbon contents, which probably cause anoxia by creating biological oxygen demand. Assuming that the lower-profile sediments in the Inner Harbor were deposited several decades ago, IV and IU apparently had a baseline difference. The now-unvegetated site may have once contained thicker vegetation than the still-vegetated site. If sediment C levels in the Outer Harbor are representative of levels over the past few decades, there is apparently an *a priori* difference between the Inner and Outer Harbors. The Inner Harbor may be naturally more eutrophic, since it has a longer residence time, does not mix regularly with Buzzard's Bay, is closer to groundwater inputs, and has finer sediment, which may hold more clays and organic matter. In the Outer Harbor, detrital inputs from eelgrass roots and leaves undoubtedly account for the higher C content in the vegetated sediments. In addition, the vegetation may trap fine particles that are adept at adsorbing organic carbon.

The phosphorus profiles match the expectations for saline sediments: in the top layers, total and inorganic P are high because iron oxides and C are relatively abundant, but decline with depth as Fe oxides dissolve, releasing coprecipitated P, and C declines. The predictable behavior of P in our cores suggests that the sediment chemistry experiences the expected effects from the redox conditions. The Inner Harbor has more P despite being more reducing probably because more carbon is available to bind organic phosphorus and release inorganic P during decomposition. In addition, the fine particles in the sediment may contain adsorbed P or apatite, whereas the Outer Harbor sediments appear to be mostly quartz.

The correlation between inorganic P and Fe oxides also instills confidence in the data. The P:Fe ratios of both the Inner and Outer Harbor are above 1:28, the ratio at which Fe oxides generally become P-saturated in the laboratory. However, the ratio for the Inner Harbor may be high enough to indicate saturation. If Fe oxides are reduced and release their P, the remaining oxides may become saturated, leaving more P available to heterotrophs and producing a positive feedback to eutrophication.

The higher S values in the Inner Harbor correspond to the more reducing conditions, and the higher levels of C, which serves as a substrate for sulfate reduction. Core 3's profile for IU matches the expectations from the decline in Eh, while the cause of the dip in the IV profiles is unknown. An additional factor, such as a storm several years ago that resuspended sediment, may be responsible. The “hourglass figure” of the Inner Harbor profiles may indicate eutrophied sediments overlaying an older, more pristine profile in which S declined with proximity to the sediment surface (Giblin 2004; pers. comm.). In the Outer Harbor, although the top 2 cm are more oxidizing in the vegetated than the unvegetated sediment, the third and fourth sections of the vegetated sediment are more reducing. This may partially account for the higher S content in the top 4 cm of OV. In addition, OV apparently has more organic matter, which contains S as well as fueling sulfate reduction.

The higher Fe and Mn concentrations in the Inner Harbor are probably largely due to different baseline mineralogy of Inner and Outer Harbor sediments. Finer and less quartz-dominated sediments, such as those in the Inner Harbor, tend to have more Fe and Mn. However, eutrophication also appears to favor higher sediment Fe and Mn concentrations, most likely by increasing the amount of carbon to which these metals may bind. In addition, benthic algal mats may protect Fe- and Mn-containing fine sediment particles from resuspension.

Sulfur content also seems to strongly control Fe and Mn concentrations, as indicated by the strong correlation between the two in the top 4 cm of sediment, and the similarity of the profiles of these components. This relationship is also seen throughout the sediment profiles (Fig. 59 shows Fe as an example). We hypothesized that the preferential formation of sulfides over oxides was a mechanism by which anoxic sediments would be more enriched in heavy metals than oxic ones. However, this may not be the case for Fe and Mn, whose oxides are quite stable (albeit relatively bioavailable) (Giblin 1986).

The labile Fe and Mn profiles do not seem to show any strong spikes that do not correspond to the sulfur profiles (which would indicate oxides), except at 1.5 cm in Core 6, where the labile:total ratio also increases from the first centimeter. Furthermore, Fe and Mn are correlated with sulfur even in the top centimeter (Fig 60). This appears true even when the Outer Harbor is examined in isolation, to control for baseline differences in sediment mineralogy. However, when graphed in isolation, the Inner Harbor does not show this relationship (Fig 61). In terms of the relationship between Fe and Mn and S throughout the profiles, Fe and Mn content may in fact control S content: a greater proportion of sulfides produced in sediments with low Fe and Mn may escape as gas. In sum, if eutrophication increases Fe and Mn content in sediments, increased carbon content is the likely mechanism, as opposed to increased sulfide formation. Moreover, this is probably a coarse-scale control rather than a fine-scale control, since the Fe and Mn profiles do not mimic the C profiles. However, given the powerful correlation of these metals with S, the possibility the sulfide formation associated with anoxia does cause higher Fe and Mn retention should be investigated.

As for the relationship with vegetation in the Outer Harbor, the higher C (and perhaps S) contents of the vegetated site probably explain its higher Fe and Mn values. Additionally, the vegetation may trap and retain Fe- and Mn-containing fine particles. However, the Fe and Mn concentrations in the top 4 cm reinforce the impression from the previous data that vegetation has little effect on sediment composition in the Inner Harbor. The benthic algae in the Inner Harbor may function similarly to vascular plants in terms of C inputs and sediment stabilization, dwarfing any superimposed effect of vegetation.

The data for Cu, Zn, and Pb concentrations strongly support the hypothesis of higher levels in anoxic than in oxic sediments. Fe, Mn, and S may all exert fine-scale control, as indicated by similarity of their profiles to those of the heavy metals. If anoxia increases Fe and Mn concentrations as suggested above, this may be one mechanism by which eutrophication increases heavy metal concentrations, since metals bind to Fe and Mn compounds. Increased sulfide concentrations with oxygen depletion undoubtedly also account for higher heavy metal retention. For Cu and Zn in particular, sulfides are important controls on sediment concentrations (Eggleton and Thomas 2004). In a German estuary, Kersten and Kerner (1985, cited in Forstner 1987) found that Cr concentrations were higher in the sulfide-dominated reducing regions of sediment profiles, and that the prevalence of the more labile fractions associated with oxic conditions was inversely correlated to the total Cr concentrations. Thus, even though increased sulfide formation may not increase Fe and Mn retention, it is a valid mechanism for heavy metal retention. As with Fe and Mn, eutrophication may increase heavy metal concentrations in sediments by increasing C inputs. Although, as discussed for Fe and Mn, C content is only a coarse control on heavy metal content, it is surely an important one—it helps dictate the general range of the sediment's retention capacity. Additionally, algal mats associated with eutrophication may increase heavy metal concentrations by the same mechanisms proposed for Fe and Mn. These proposed controls on heavy metal concentrations in general appear to dominate for Pb: the similarity of the Pb profiles to those of Cu, Zn, and most of the other chemical constituents suggests that Pb concentrations in these sediments reflect retention capacity more than source strength.

It is not clear why vegetation in the Outer Harbor does not affect the Cu and Zn as it does Fe and Mn. Because the Cu and Zn concentrations were so low, factors such as tidal currents may be better able to confound the effects of vegetation. In addition, Cu and Zn are essential elements for plants, so vegetation may draw them down. In the Inner Harbor, where Cu and Zn are more abundant, drawdown would be small relative to loading. The effect of vegetation may register on higher heavy metal loads in clean harbors. Overall, vegetation did not appear to act synergistically with eutrophication in controlling sediment heavy metal contents, although it appears an important control on the baseline heavy metal concentrations to which the effects of eutrophication are compared. In this harbor, the sediment-trapping and C-contributing effects of vegetation appear to dominate over any opposite effects from bioturbators (see Introduction). The latter effect may dominate in other locations, however.

The lack of a clear effect of redox conditions on the proportions of labile to total metals contrasts with the literature reviewed in the Introduction and with Kersten and Kerner's findings. Although there is not enough oxygen in the Inner Harbor sediments to support an aerobic microbial community, there may be enough to bind a proportion of the trace metals present. The concentrations of even Fe and Mn are fairly low; Fe concentrations in the Inner Harbor are comparable to those found in other Cape Cod harbors by Chappell (1998), which she described as low. Despite inducing anoxia, eutrophication may increase metal oxide retention by increasing C content, which may adsorb oxides, or by promoting algal mats that stabilize fine particles.

If neither of these mechanisms occurs, the oxide fraction in reduced sediments may be a legacy from when the sediment was oxic. As such, it would indicate baseline differences in metal stocks between the Inner and Outer Harbors. Presumably, if eutrophication truly enhances heavy metal retention, the ratio of labile to total metals would decrease, since reduced substances would perform the extra retention (unless physical sediment stabilization by algal mats is important). The ratios for West Falmouth Harbor sediments might suggest that the differences in total metal stocks between the Inner and Outer Harbors are due almost exclusively to mineralogical differences. However, a different perspective emerges when one compares the concentrations of reduced metals between the Inner and Outer Harbor. The higher concentrations in Inner Harbor sediments may indicate a greater *capacity* to reduce metals, and thereby to retain them (Giblin 2004; pers. comm.).

In addition, as indicated in the Results, some traces of a positive relationship with the labile:total ratio and redox potential exist. The negative relationship with sulfur in the Outer Harbor supports the contention that reducing conditions favor a low ratio. The weak and mostly positive relationships in the inner harbor may result from the fact that the 1 N HCl digestion also extracts FeS and associated metals. Furthermore, the low end of the Inner Harbor's sulfur values may be more than is needed to bind the metals present, so that an increase in sulfur does not increase the denominator of the ratio. Giblin (2004; pers. comm.) also suggests that the effect of redox potential on metal speciation is realized more effectively in sediments that have a longer history of anoxia than those in West Falmouth Harbor. Perhaps not all the metal oxides present in the sediment at the onset of eutrophication have been reduced.

Although eutrophication in inner West Falmouth Harbor may have increased its heavy metal load, concentrations of Cu, Zn, and Pb are still much lower than those in some other Massachusetts estuaries (Table 2). They are far below those in Boston Harbor, which for many years received metal-laden sewage sludge (Zago et al. 2001), and Eel Pond, which used to have a marine railway and a gas pump (Chappell 1998). Even Inner West Falmouth Harbor's Cu, Zn, and Pb concentrations are lower than those of Waquoit Bay, which also receives essentially no industrial effluent. Boat traffic may be higher in Waquoit Bay, but incidentally, eutrophication occurred earlier there. It would be interesting to investigate whether the higher metal values in Waquoit Bay are due to different baseline conditions (e.g. sediment texure), or whether they are partly a legacy of eutrophication.

Conclusions

This study suggests that eutrophication does enhance heavy metal retention, by several possible mechanisms (Fig. 61). These include increased carbon levels from algal blooms and a reduction in decomposition rates under reducing conditions, increased sulfide formation as a result of anoxia, and physical stabilization of fine particles by algal mats. Increased amounts of sulfide and fine particles may directly increase heavy metal concentrations, or they may affect metal concentrations by increasing Fe and Mn retention, although this latter mechanism is uncertain. Baseline mineralogy differences between the Inner and Outer Harbor may account for much of the difference in heavy metal stocks, but the positive correlation of the heavy metals to C and S contents, which are known to increase with eutrophication, suggests that it is legitimate to ascribe some of the difference to eutrophication. As discussed, the Inner Harbor probably is in a naturally higher trophic state than the Outer Harbor, but this does not weaken the conclusion. The results indicate how heavy metal concentrations in sediments from an estuarine area in a relatively high trophic state differ from those in an area with a lower trophic state, and suggest what might happen if humans promote an estuary to a higher trophic status.

As suggested in the Introduction, increased heavy metal loads with eutrophication may pose a hazard if eutrophication is reversed and oxidizing conditions return. Even if a “pulse” of metals released into solution with reoxidation does not occur, total metal stocks will have been elevated. If the relatively high stores of reduced metals accumulated during the anoxic period are oxidized, the sediments will have a higher load of labile metals than they started out with. To confirm the support we found for our hypotheses, it would be useful to account more fully for differences in baseline factors. For instance, although qualitative observation suggests that boat traffic, and hence metal load, were comparable at all four sites, this was not quantified. In addition, this study should ideally take place in an estuary with oxic and anoxic sediments of similar baseline mineralogy. In an estuary with higher heavy metal loads, the effects of vegetation on metal concentrations and of anoxia on speciation may emerge more clearly.

Eutrophication of West Falmouth Harbor may not pose a heavy metal toxicity hazard, since loading rates are so low. However, if eutrophication is protracted, heavy metals may accumulate to potentially toxic levels. The hazard is probably much greater, though, for estuaries with higher loading rates. If eutrophication can springload estuary sediments to pose a heavy metal danger, managers should be prepared to address this as they seek to restore estuaries. This possible effect of eutrophication as heavy metals may also strengthen arguments made to the public about the importance of protecting estuaries from nutrient and organic matter pollution.

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Tables and Figures

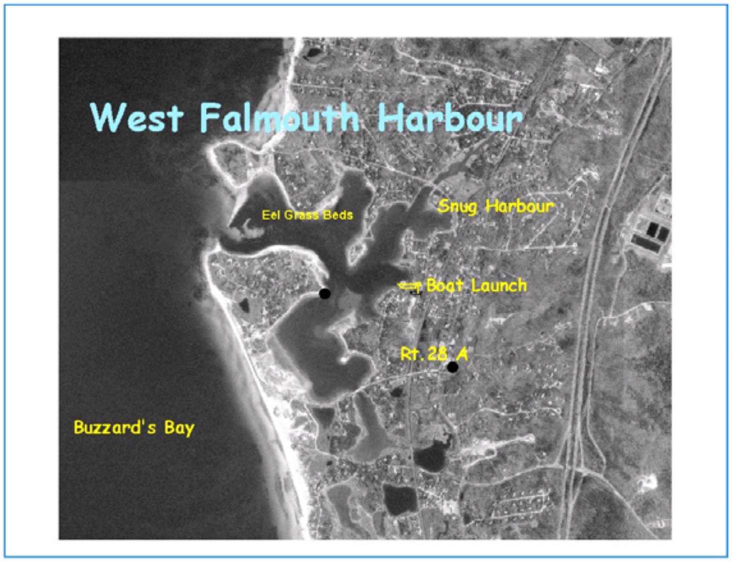


Fig. 1. Study location.

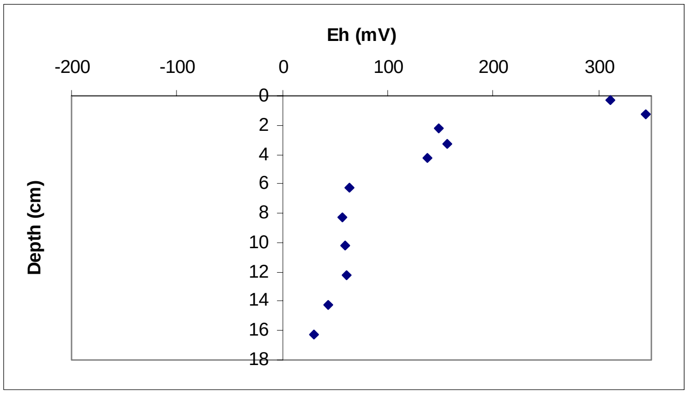


Fig. 2. Redox potential (Eh) of vegetated Outer West Falmouth Harbor sediments.

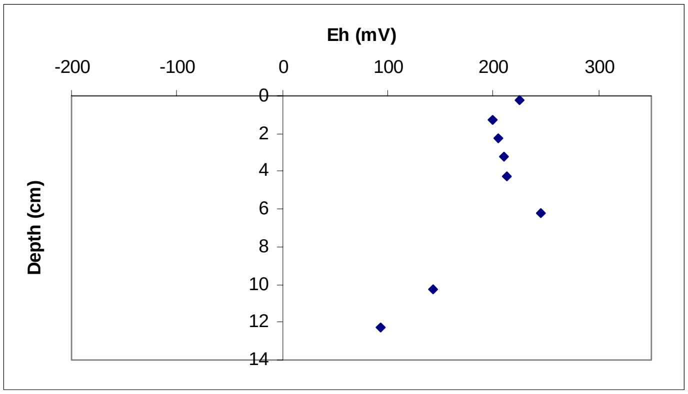


Fig. 3. Redox potential (Eh) of unvegetated Outer West Falmouth Harbor sediments.

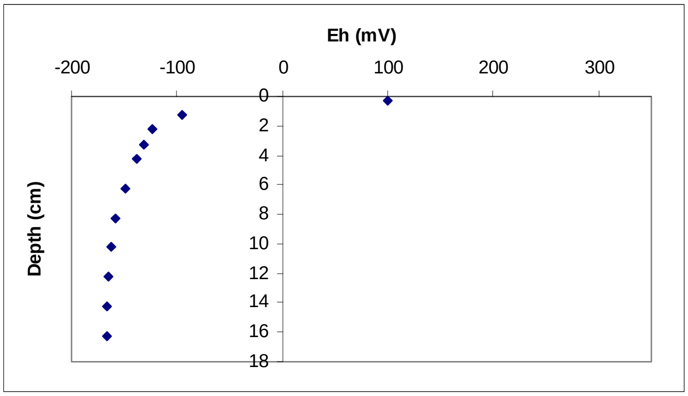


Fig. 4. Redox potential (Eh) of vegetated Inner West Falmouth Harbor sediments.

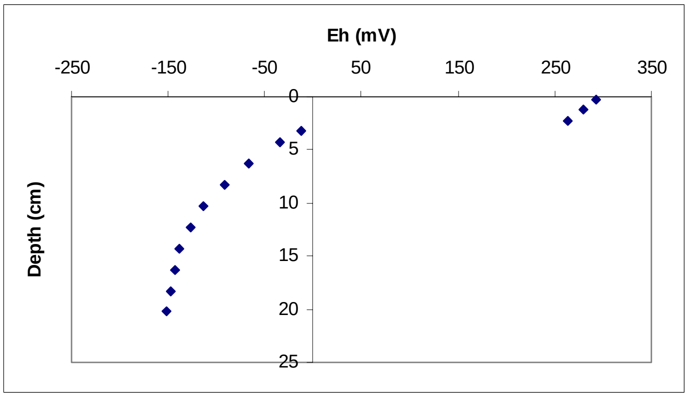


Fig. 5. Redox potential (Eh) of unvegetated Inner West Falmouth Harbor sediments.

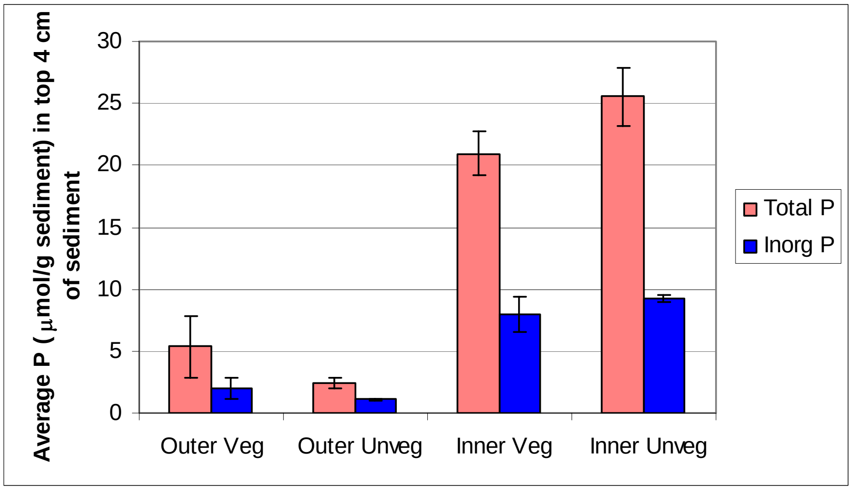


Fig. 6. Phosphorus averaged over 4 cm of West Falmouth Harbor sediments.

Table 1. Summary of soil constituents averaged over top 4 cm of West Falmouth Harbor sediments.

Site	C (% sediment by weight	S (% sediment by weight)	Total P (mmol/g)	Inorg P (mmol/g)	Total Fe (mg/g)	Labile Fe (mg/g)	Total Mn (mg/g)	Labile Mn (mg/g)
Outer Veg	1.02	0.15	5.34	1.96	2.93	1.65	1.72	0.91
Outer Unveg	0.20	0.09	2.42	1.07	0.95	0.66	0.72	0.52
Inner Veg	4.01	0.79	20.96	7.97	11.07	6.41	5.22	3.36
Inner Unveg	3.73	0.87	25.54	9.24	14.47	5.93	5.94	3.17

Site	Total Cu (mg/g)	Labile Cu (mg/g)	Total Zn (mg/g)	Labile Zn (mg/g)	Labile Pb (mg/g)
Outer Veg	0.005	0.004	0.043	0.013	0.91
Outer Unveg	0.006	0.010	0.012	0.016	0.52
Inner Veg	0.028	0.018	0.073	0.054	3.36
Inner Unveg	0.033	0.019	0.084	0.063	3.17

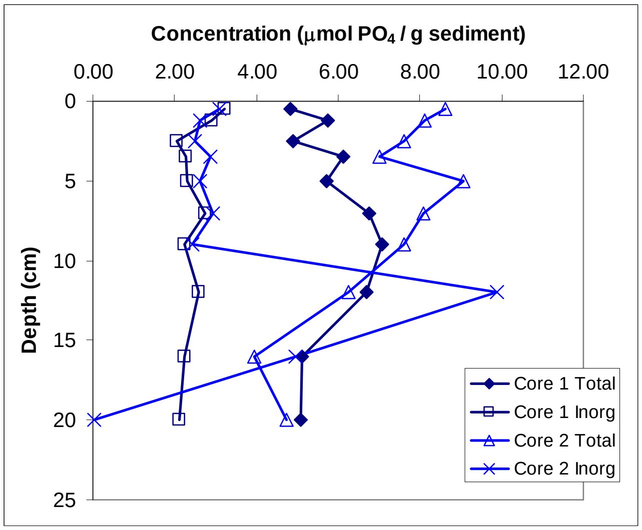


Fig. 7. Phosphorus in vegetated Outer West Falmouth Harbor sediments.

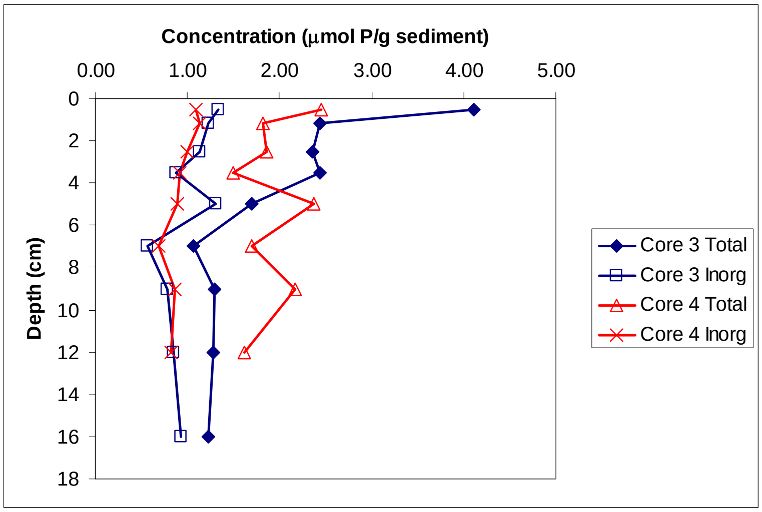


Fig. 8. Phosphorus in unvegetated Outer West Falmouth Harbor sediments.

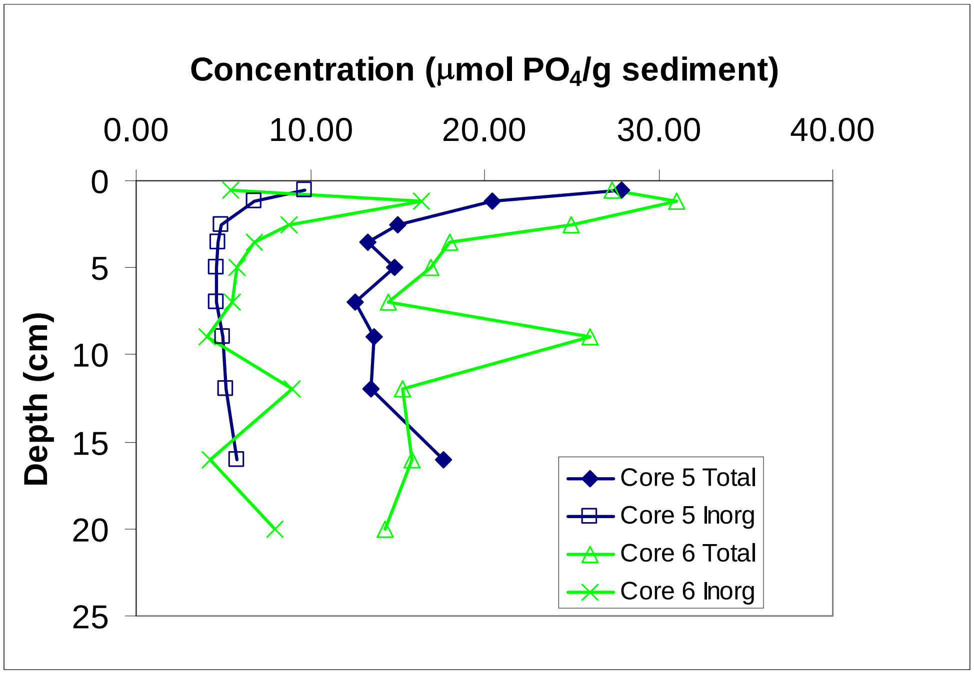


Fig. 9. Phosphorus in vegetated Inner West Falmouth Harbor sediments.

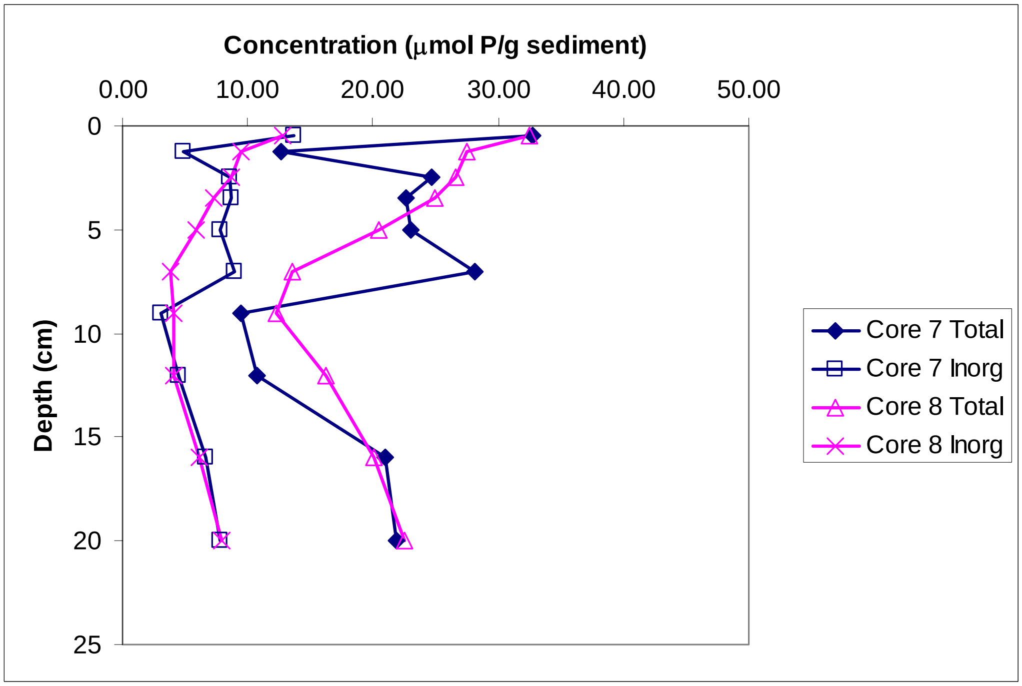


Fig. 10. Phosphorus in unvegetated Inner West Falmouth Harbor sediments.

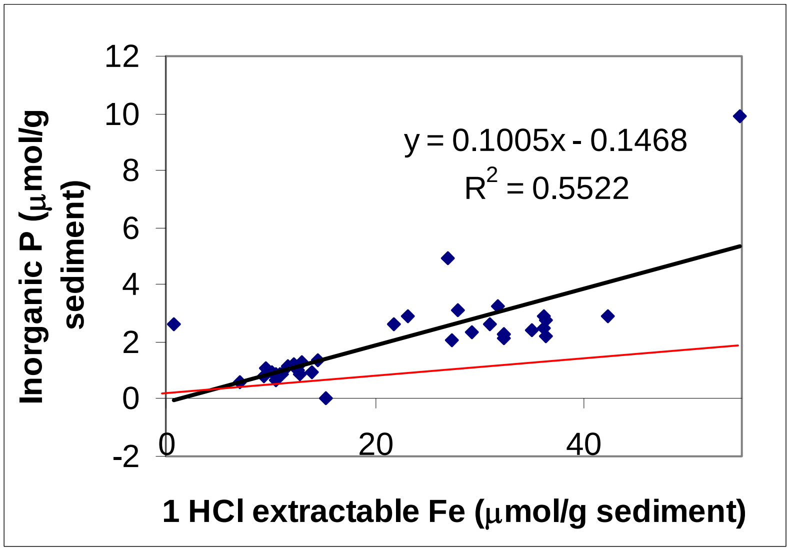


Fig. 11. Ratio of inorganic P to extractable Fe in Outer West Falmouth Harbor sediments. Red line indicates P:Fe ratio of 1:28.

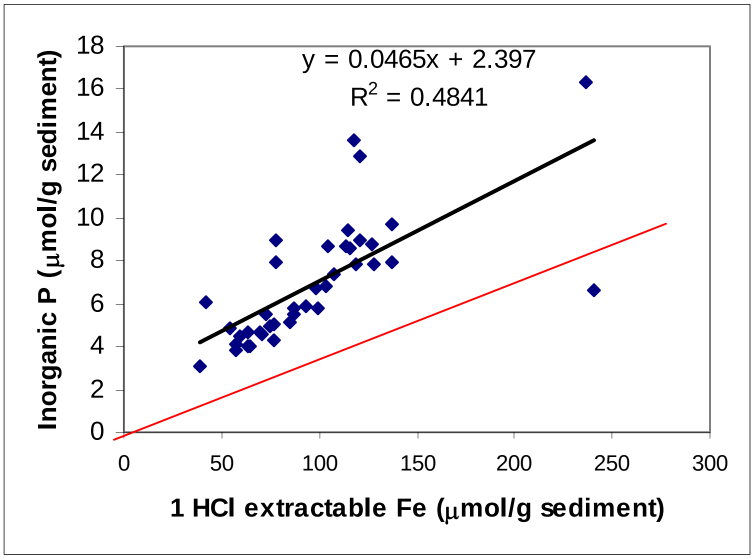


Fig. 12. Ratio of inorganic P to extractable Fe in Inner West Falmouth Harbor sediments. Red line indicates P:Fe ratio of 1:28.

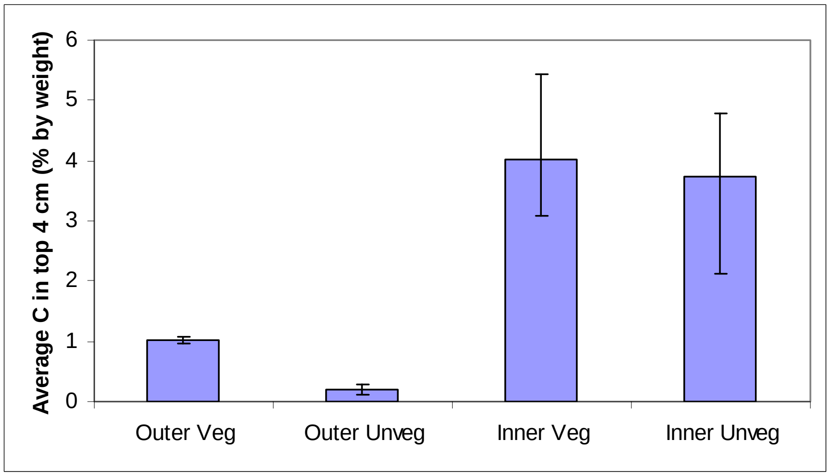


Fig. 13. Carbon averaged over top 4 cm of West Falmouth Harbor sediments.

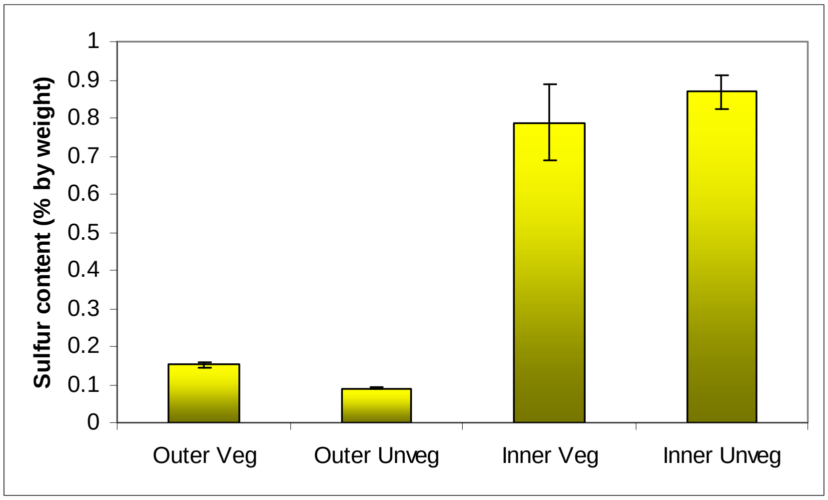


Fig. 14. Sulfur in top 4 cm of West Falmouth Harbor sediments.

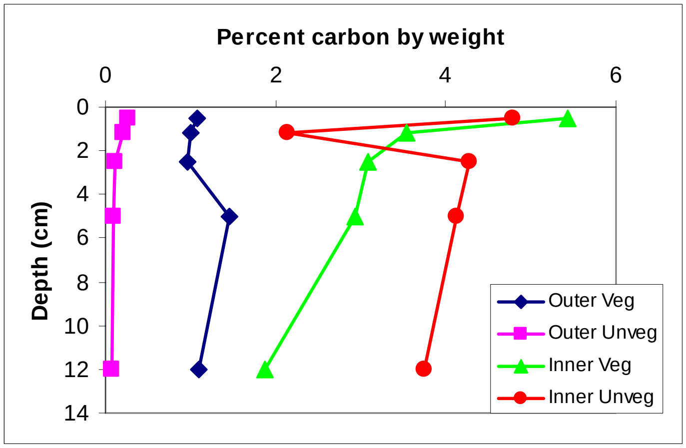


Fig. 15. Carbon content of West Falmouth Harbor sediments.

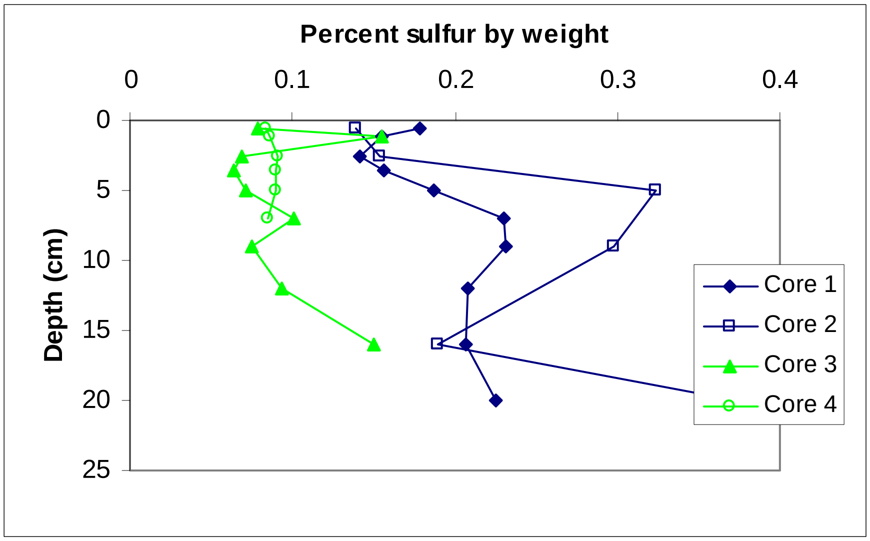


Fig. 16. Sulfur content of Outer West Falmouth Harbor sediments.

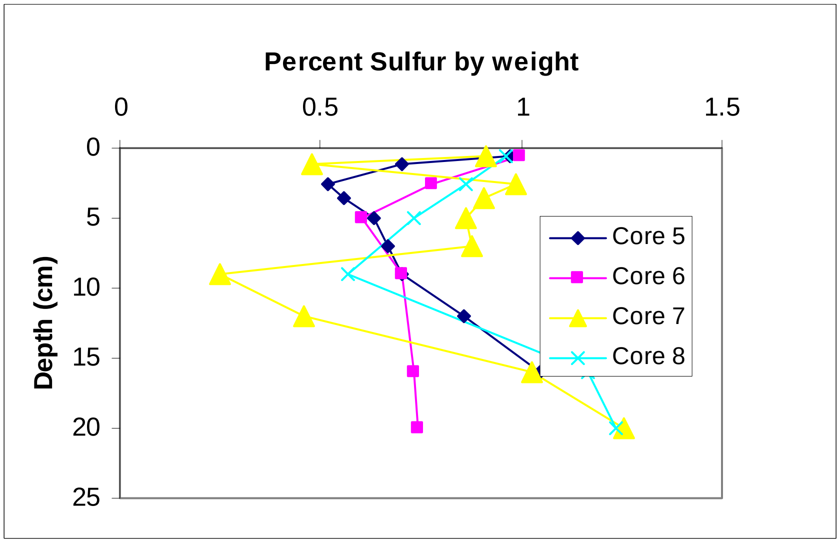


Fig. 17. Sulfur content of Inner West Falmouth Harbor sediments.

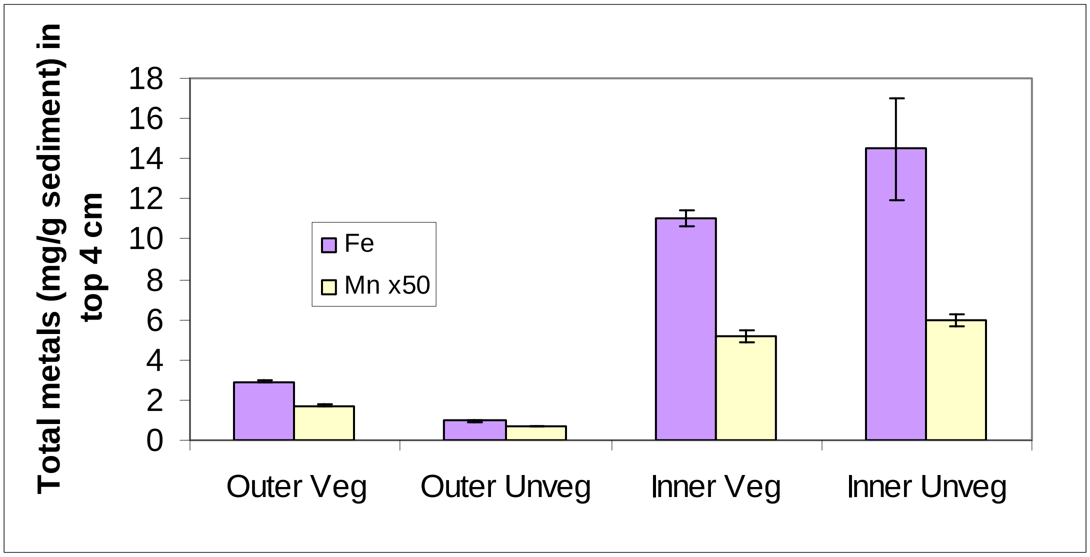


Fig. 18. Total Fe and Mn averaged over top 4 cm of West Falmouth Harbor sediments. Mn concentrations were multiplied by 50 to allow them to be graphed on the same scale as Fe.

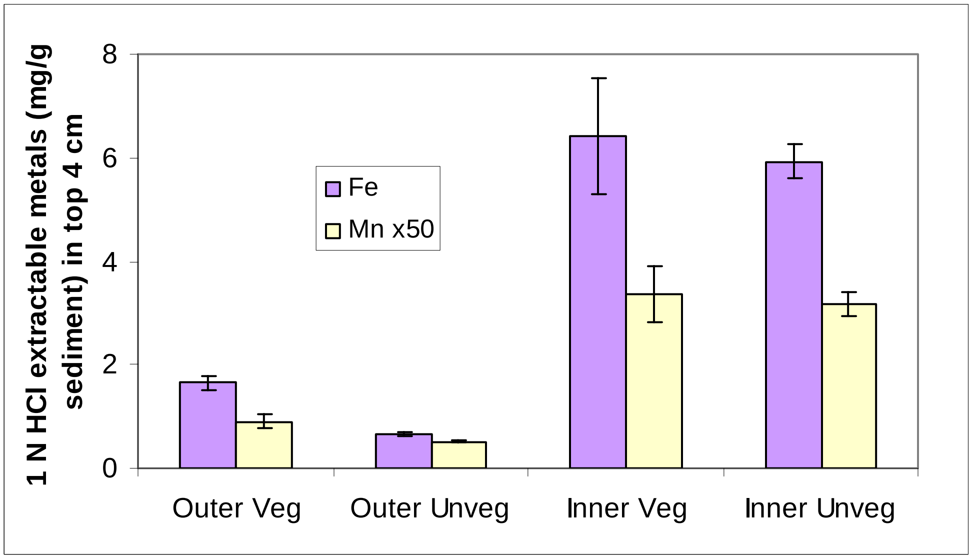


Fig. 19. Easily extractable Fe and Mn averaged over top 4 cm of West Falmouth Harbor sediments. Mn concentrations were multiplied by 50 to allow them to be graphed on the same scale as Fe.

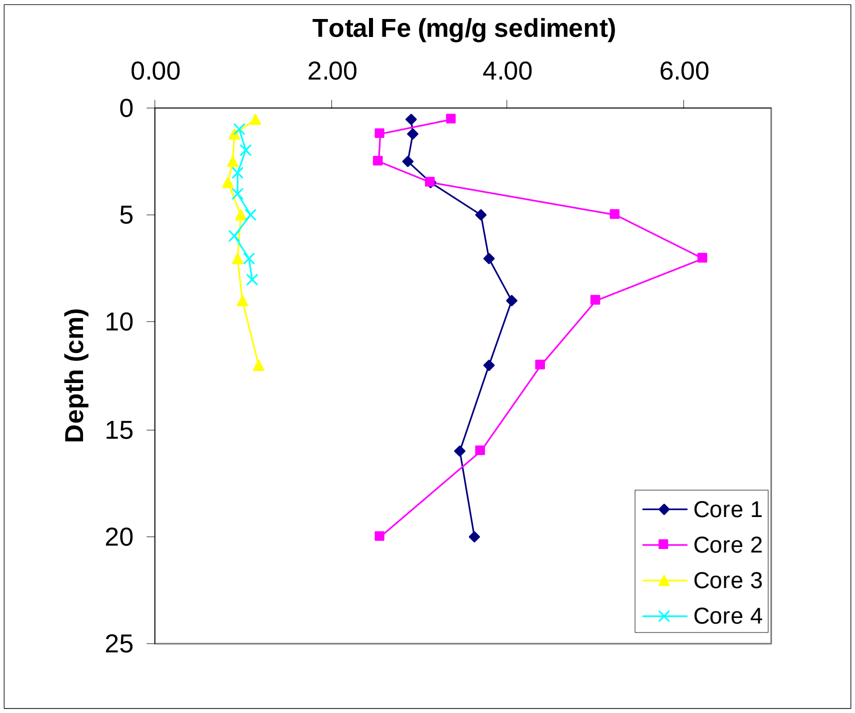


Fig. 20. Total Fe in Outer West Falmouth Harbor sediments.

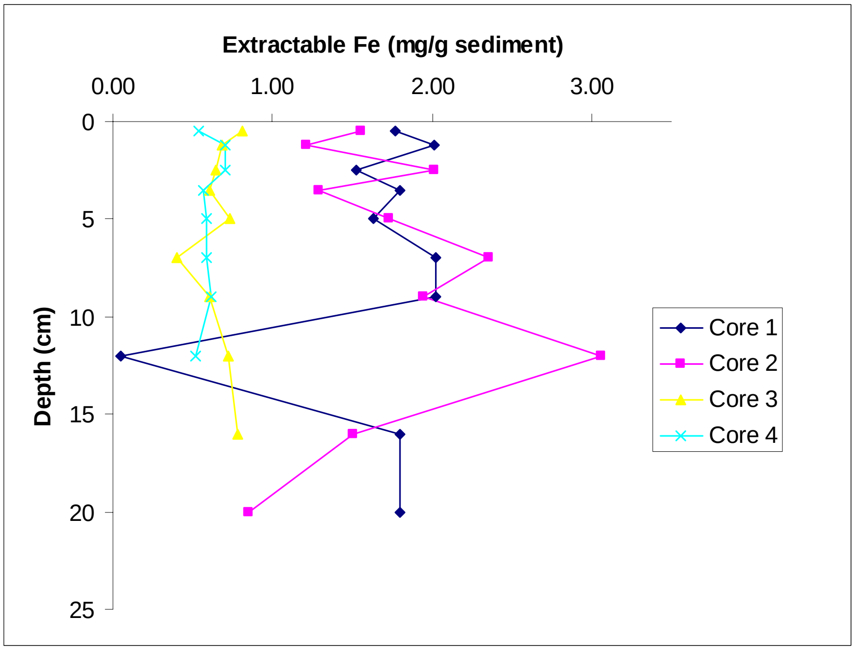


Fig. 21. Easily extractable Fe in Outer West Falmouth Harbor sediments.

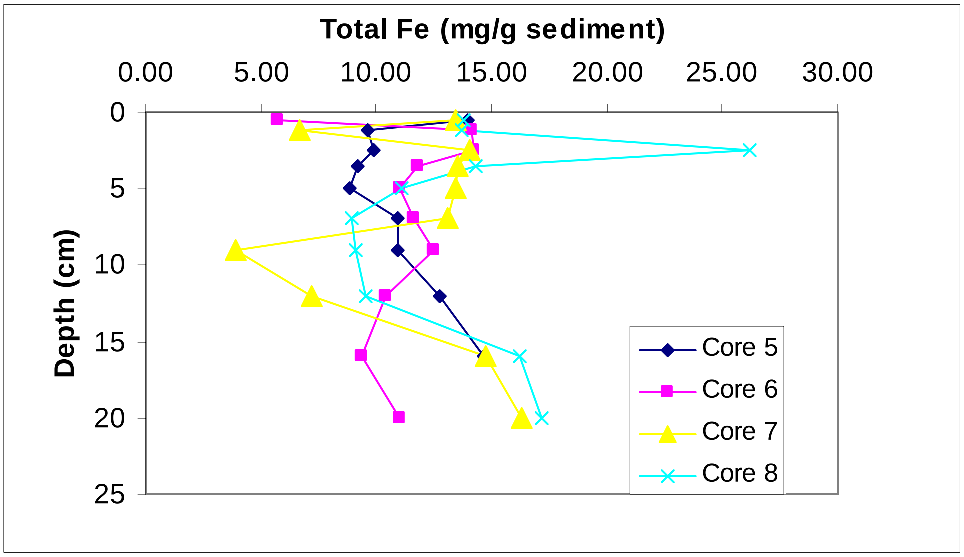


Fig. 22. Total Fe in Inner West Falmouth Harbor sediments.

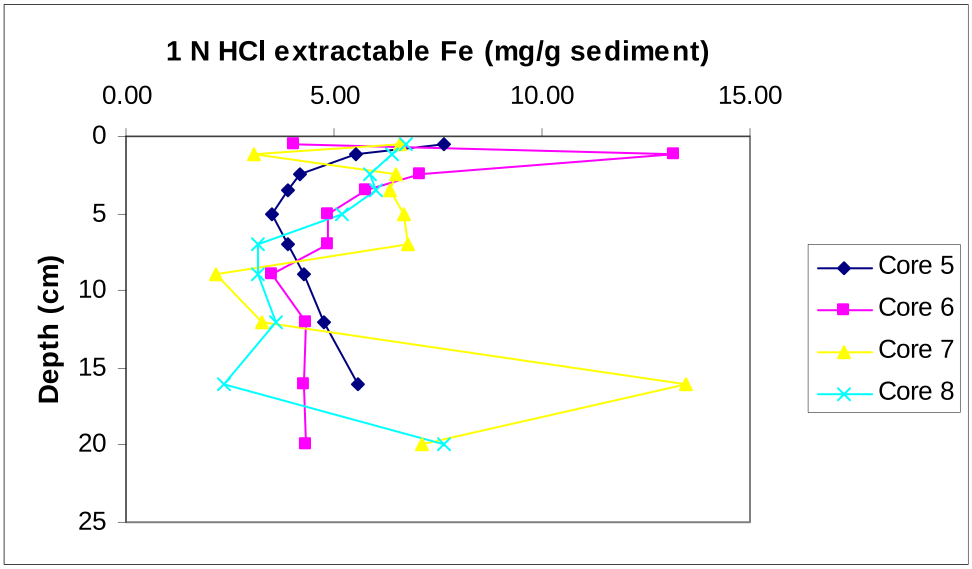


Fig. 23. Easily extractable Fe in Inner West Falmouth Harbor sediments.

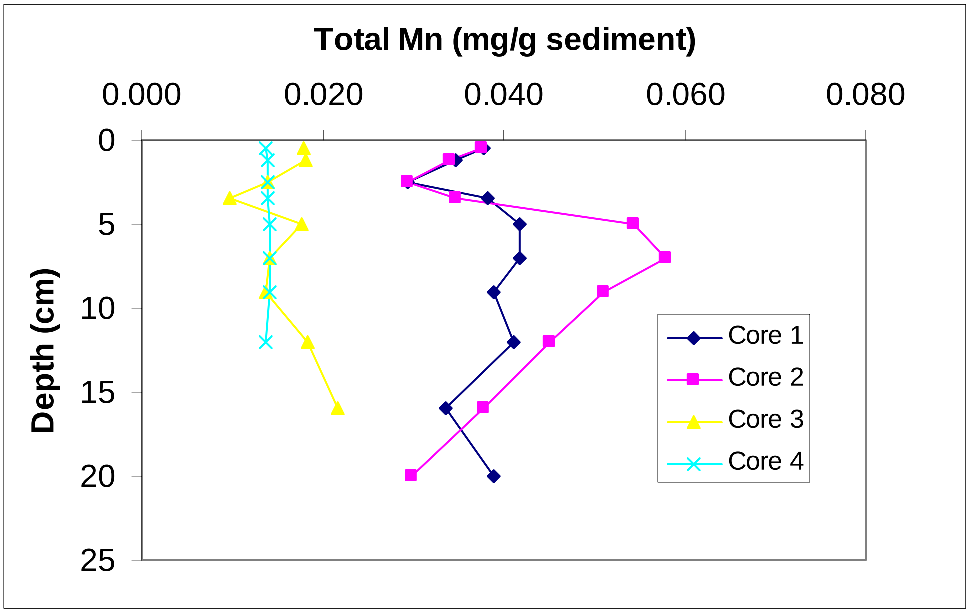


Fig. 24. Total Mn in Outer West Falmouth Harbor sediments.

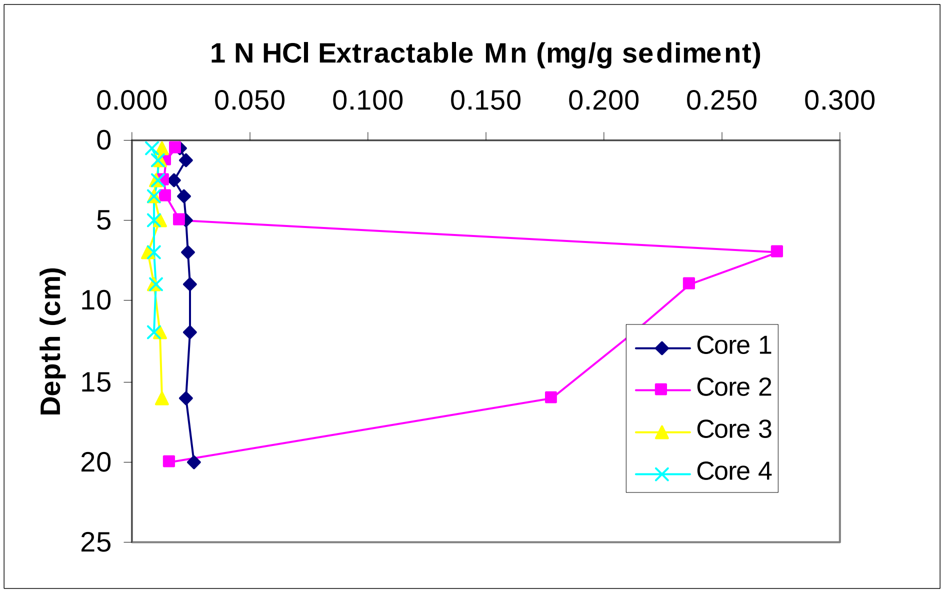


Fig. 25. Easily extractable Mn in Outer West Falmouth Harbor sediments.

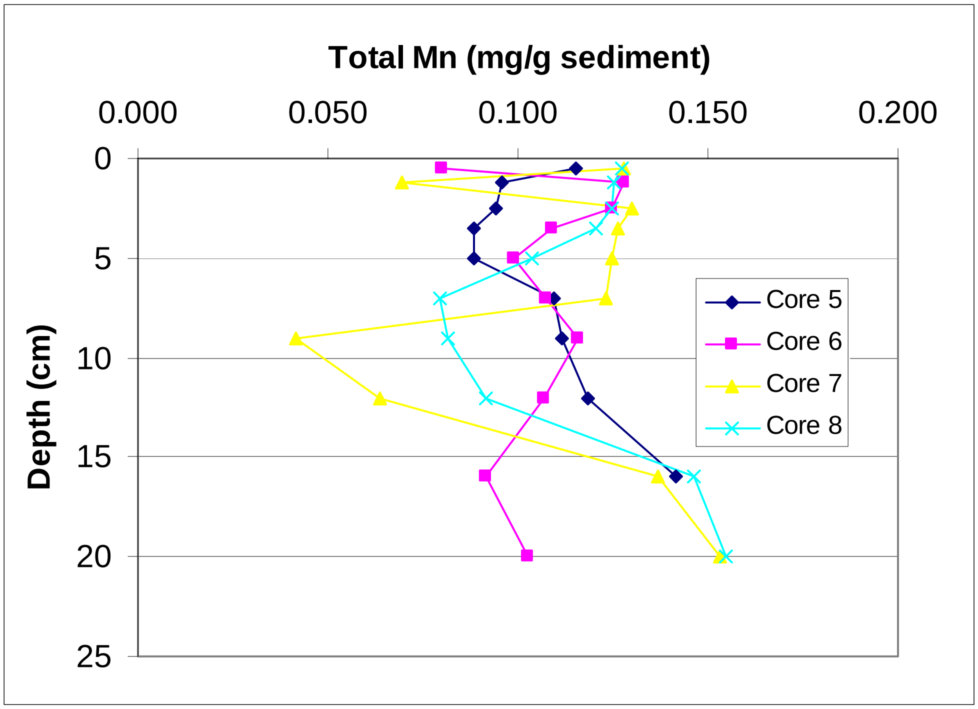


Fig. 26. Total Mn in Inner West Falmouth Harbor sediments.

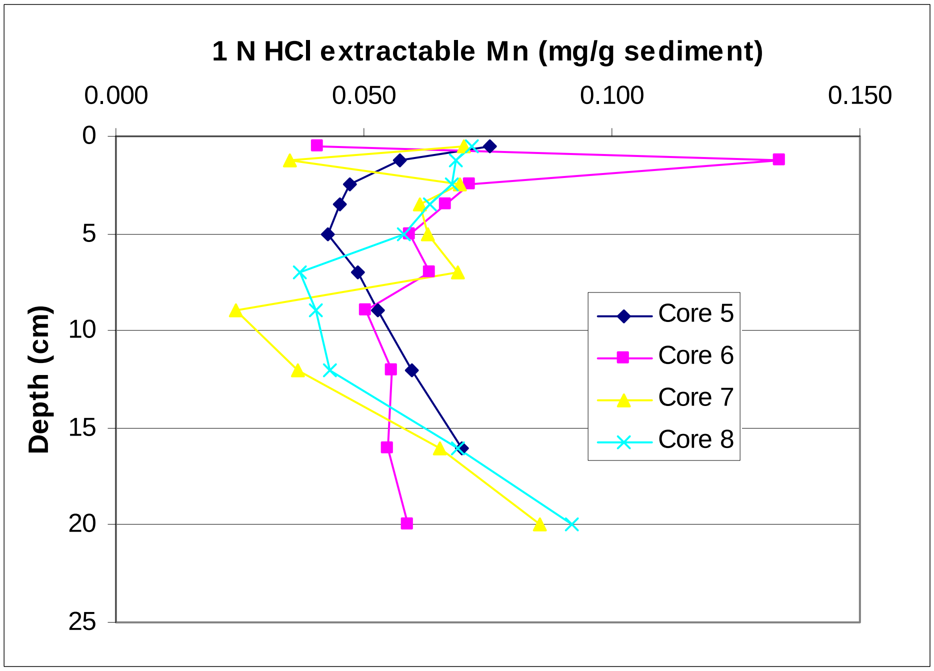


Fig. 27. Easily extractable Mn in Inner West Falmouth Harbor sediments.

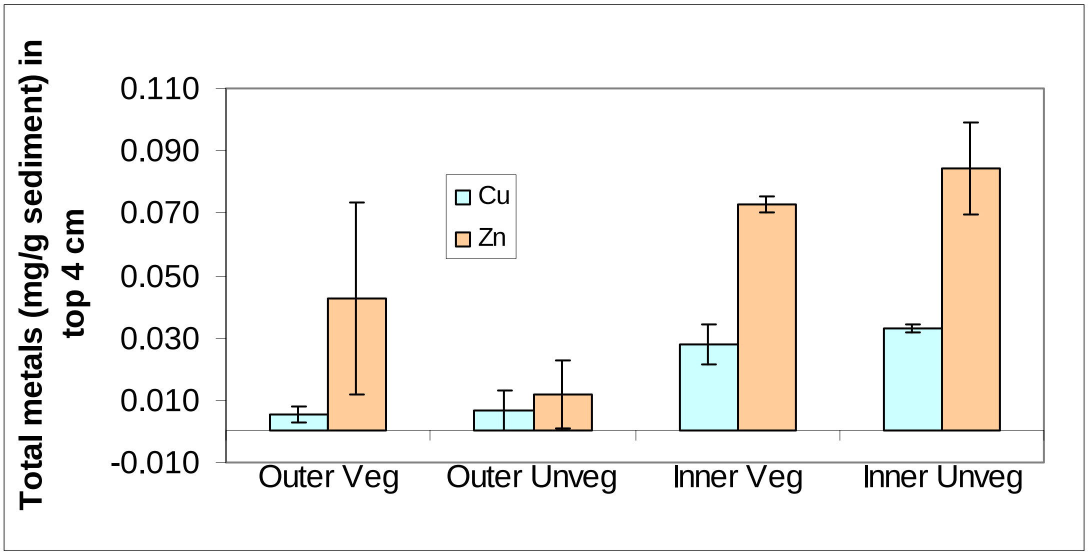


Fig. 28. Total Cu and Zn averaged over top 4 cm of West Falmouth Harbor sediments.

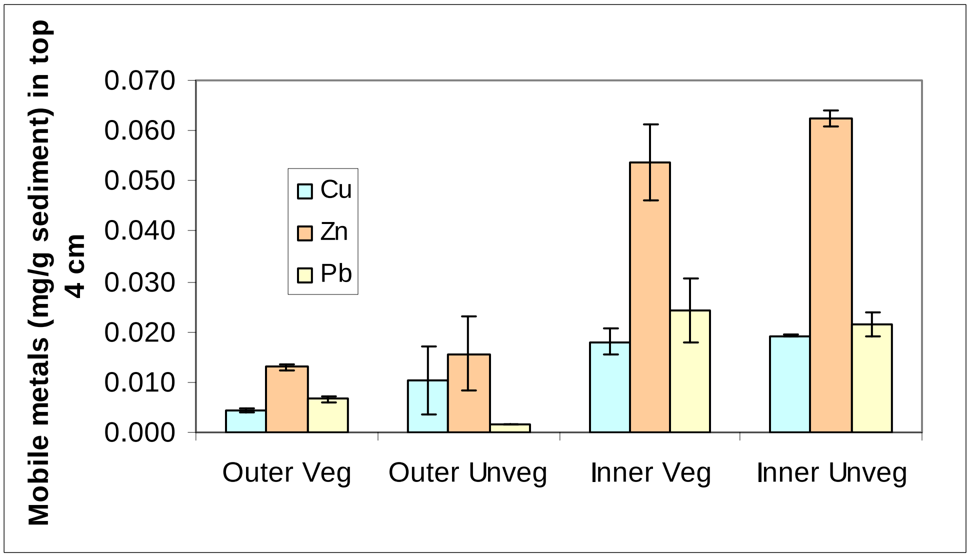


Fig. 29. Easily extractable Cu and Zn averaged over top 4 cm of West Falmouth Harbor sediments.

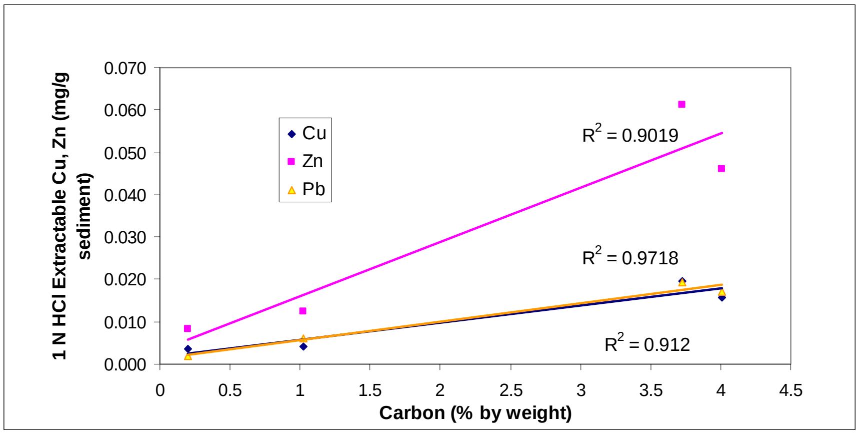


Fig. 30. Relationship of extractable heavy metals averaged over top 4 cm of West Falmouth Harbor sediments to average carbon contents.

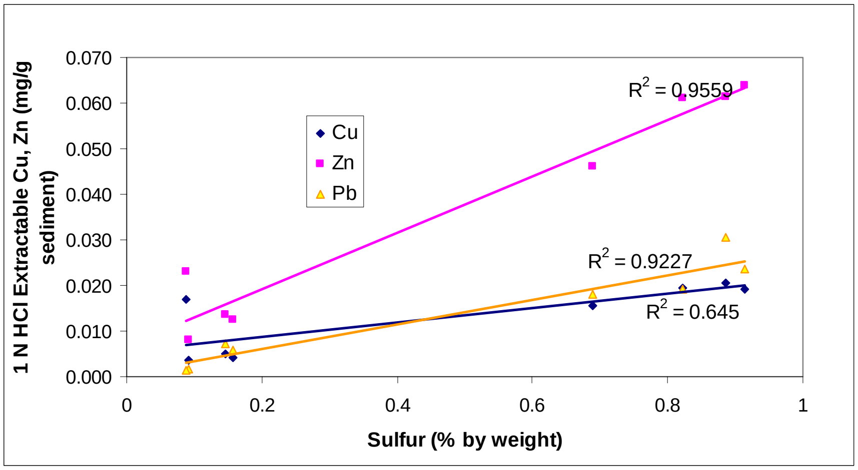


Fig. 31. Relationship of extractable heavy metals averaged over top 4 cm of West Falmouth Harbor sediments to average sulfur contents.

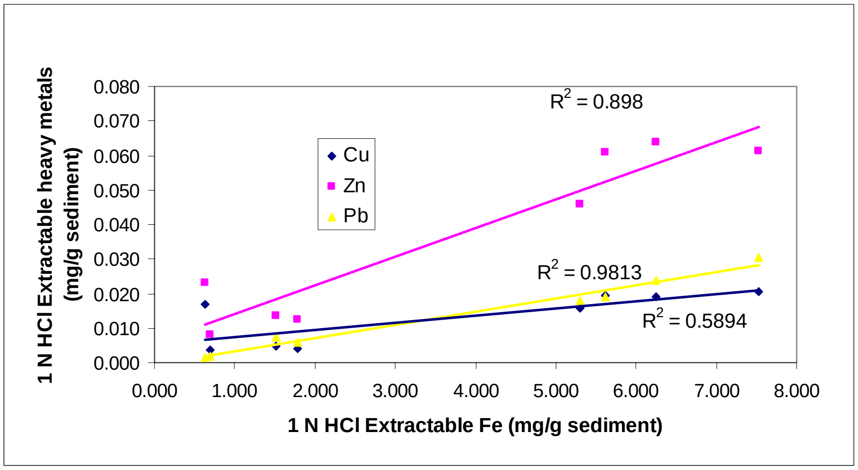


Fig. 32. Relationship of extractable heavy metals averaged over top 4 cm of West Falmouth Harbor sediments to average extractable Fe contents.

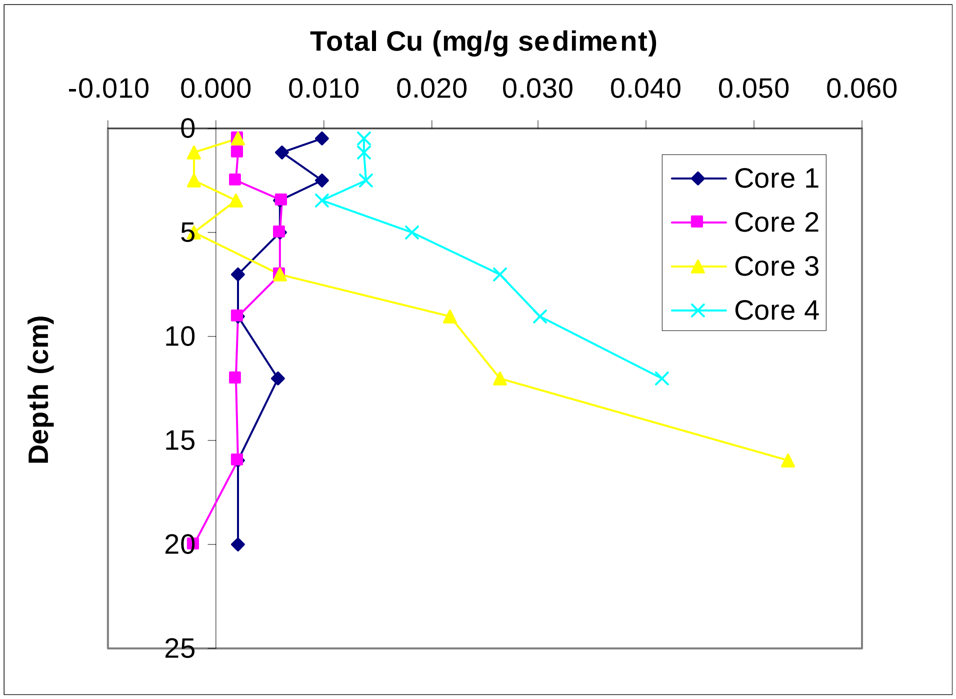


Fig. 33. Total Cu in Outer West Falmouth Harbor sediments.

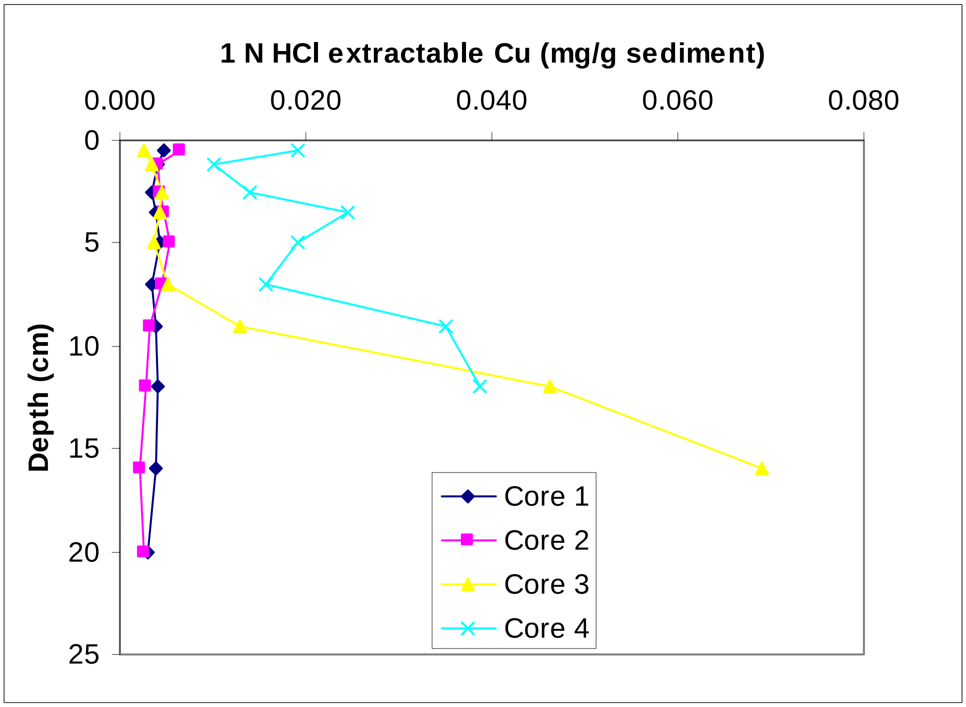


Fig. 34. Easily extractable Cu in Outer West Falmouth Harbor sediments.

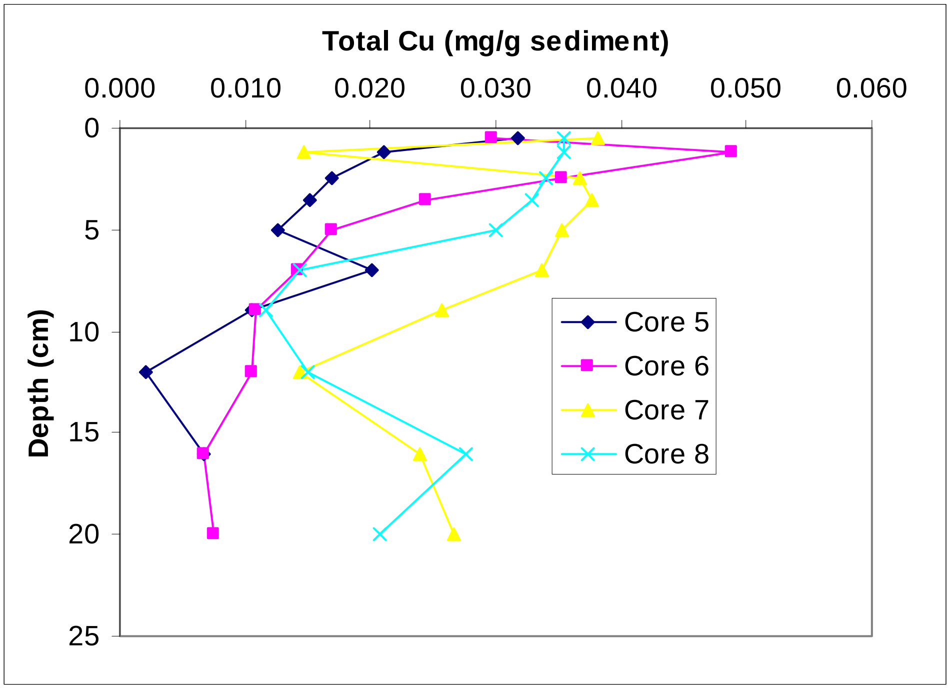


Fig. 35. Total Cu in Inner West Falmouth Harbor sediments.

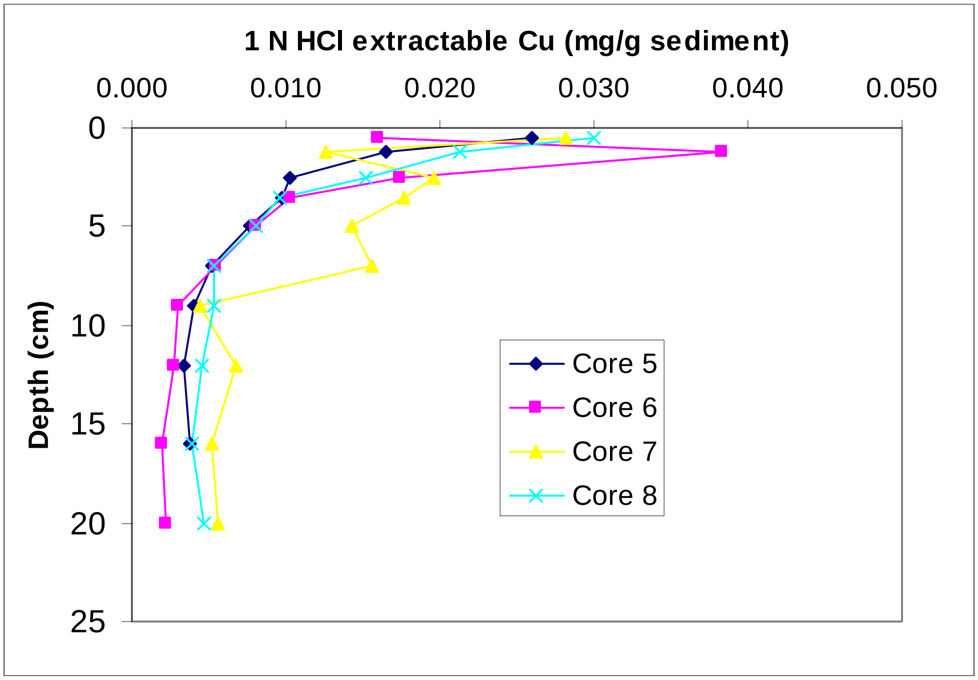


Fig. 36. Easily extractable Cu in Inner West Falmouth Harbor sediments.

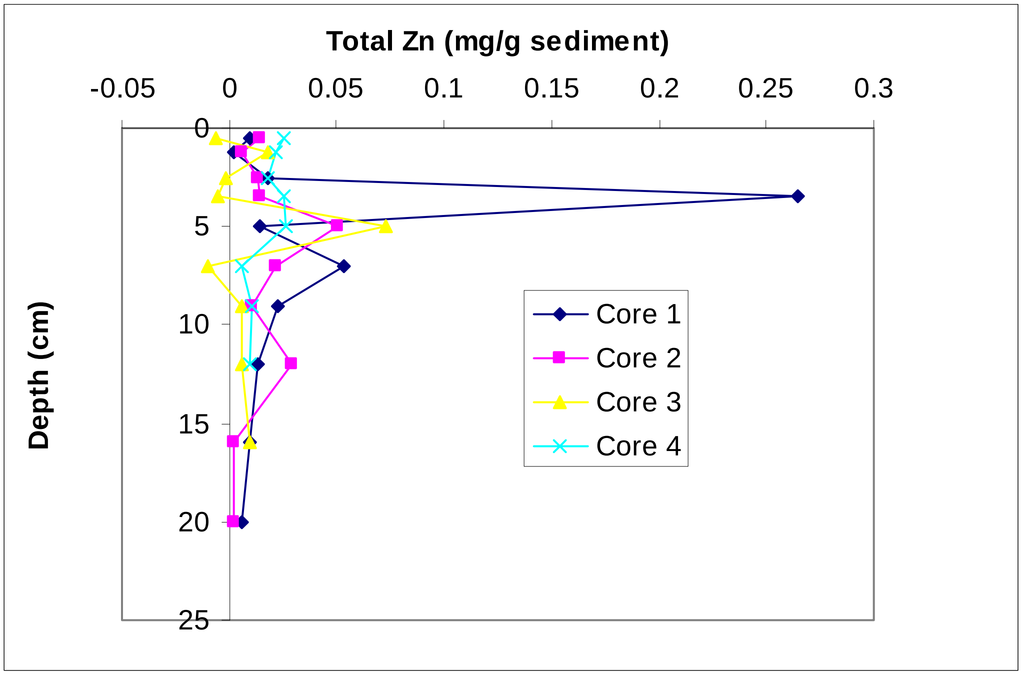


Fig. 37. Total Zn in Outer West Falmouth Harbor sediments.

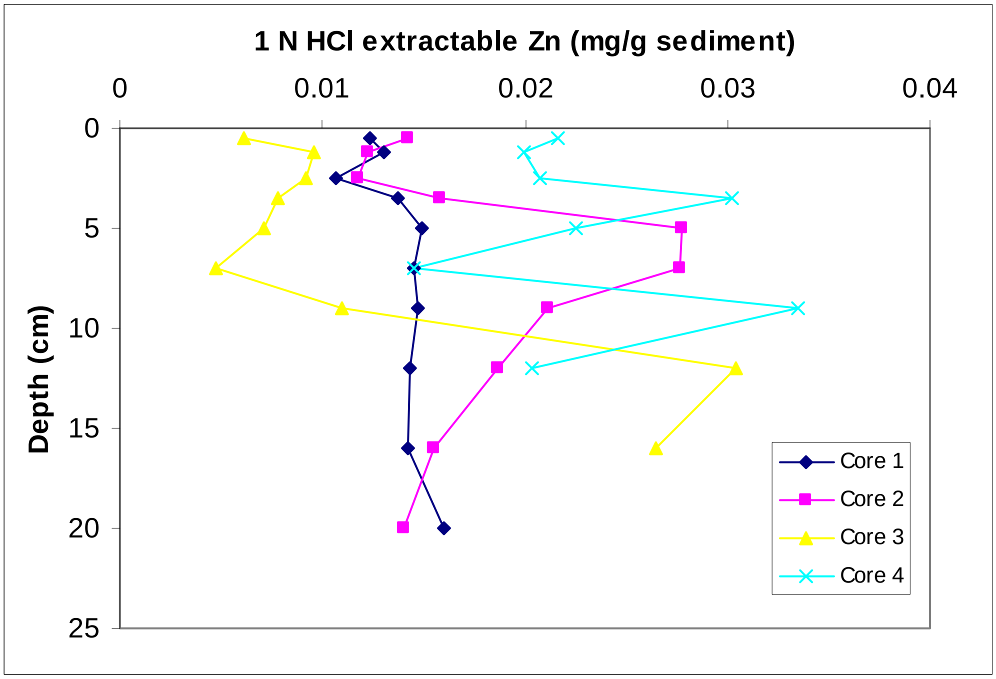


Fig. 38. Easily extractable Zn in Outer West Falmouth Harbor sediments.

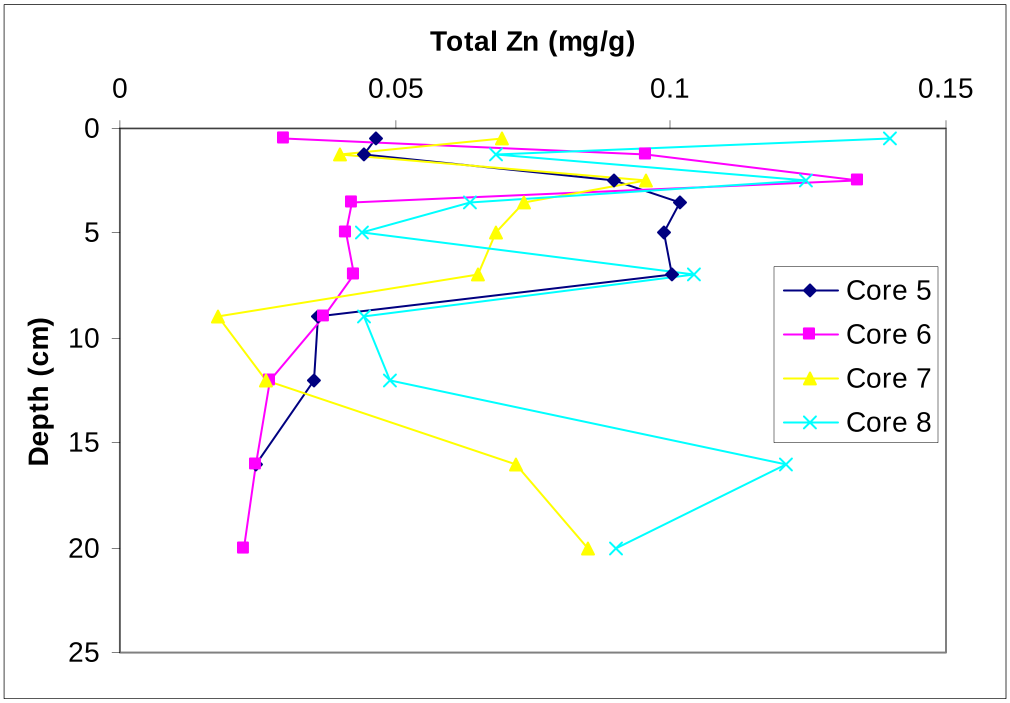


Fig. 39. Total Zn in Inner West Falmouth Harbor sediments.

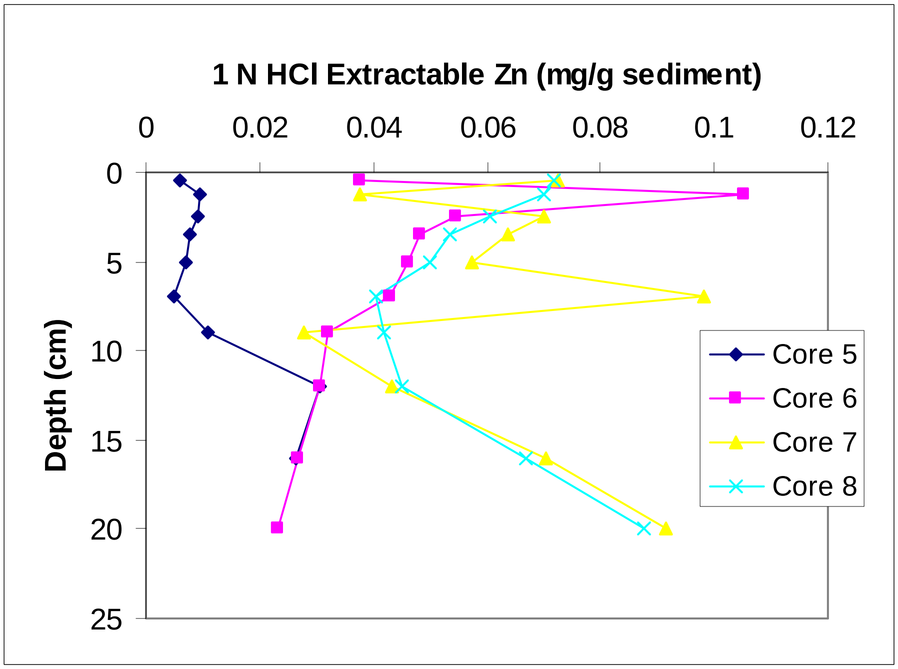


Fig. 40. Easily extractable Zn in Inner West Falmouth Harbor sediments.

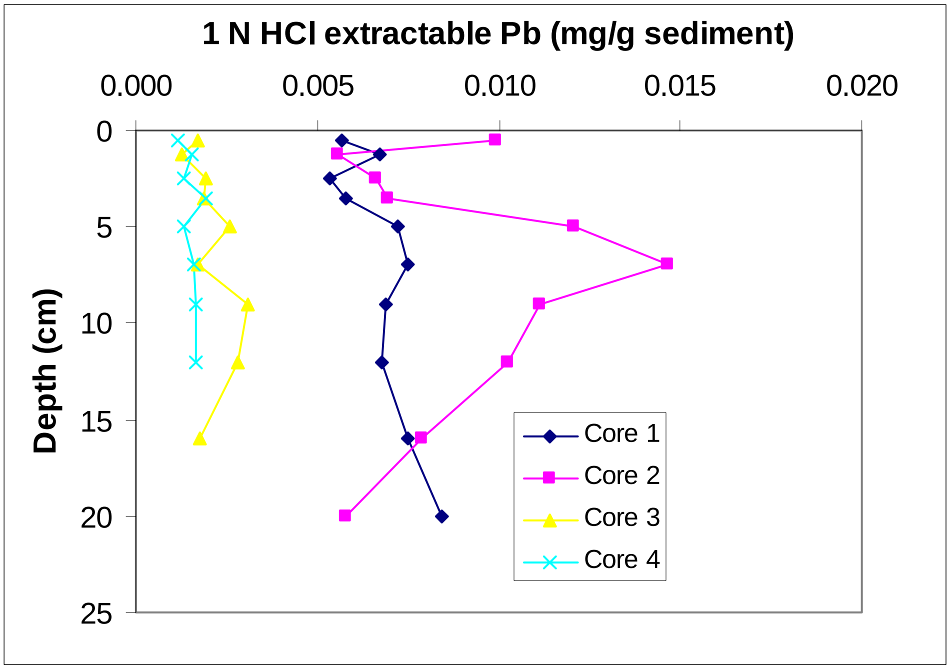


Fig. 41. Easily extractable Pb in Outer West Falmouth Harbor sediments.

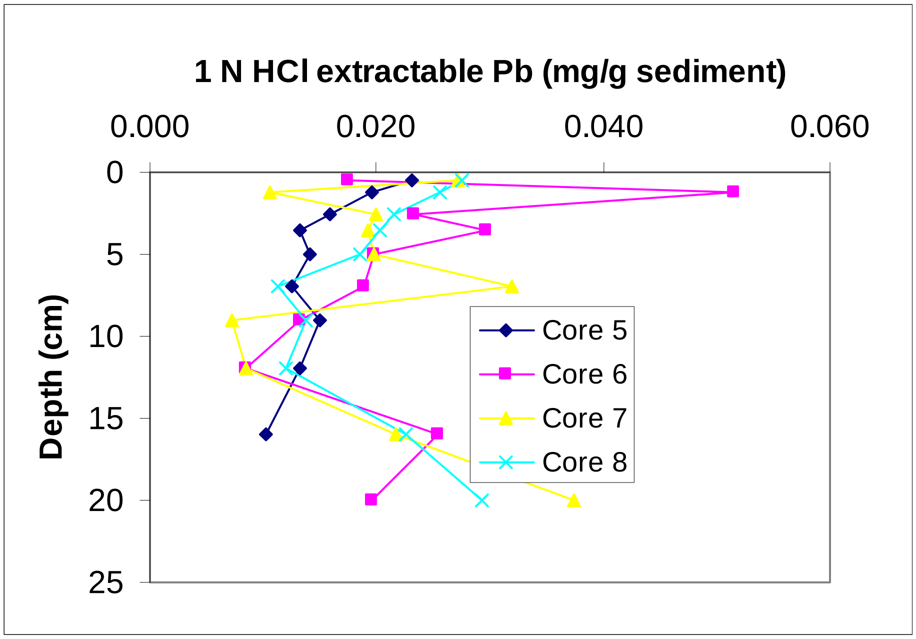


Fig. 42. Easily extractable Pb in Inner West Falmouth Harbor sediments.

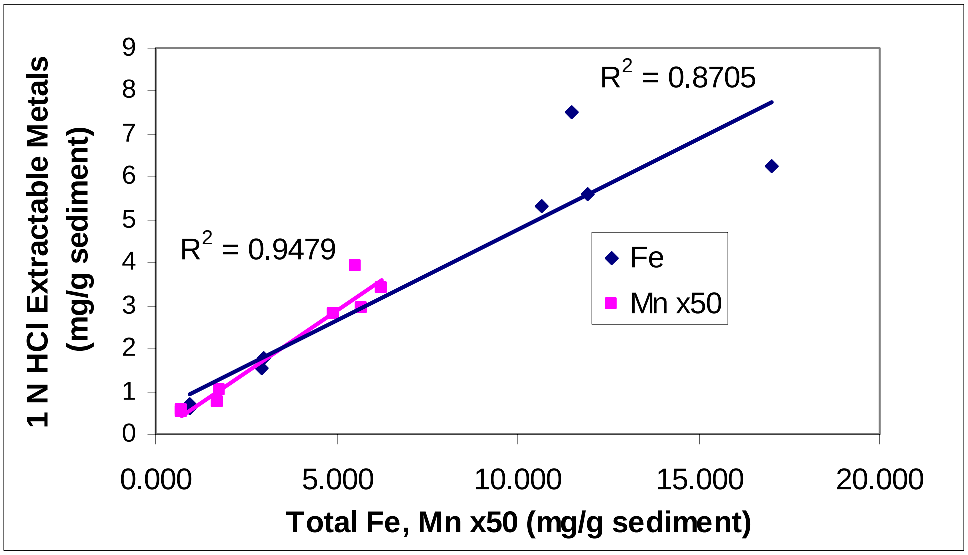


Fig. 43. Relationship of easily extractable to total Fe and Mn in West Falmouth Harbor sediments (averaged over top 4 cm).

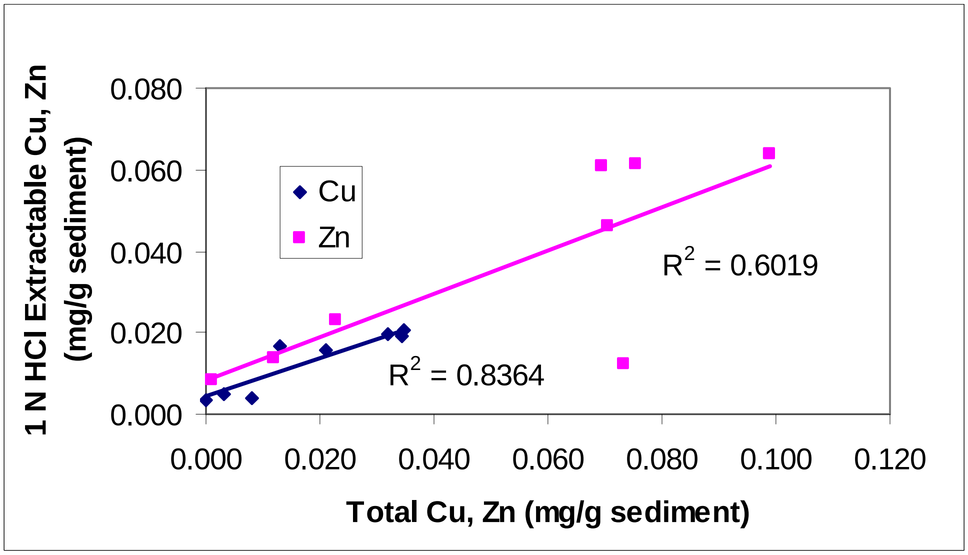


Fig. 44. Relationship of easily extractable to total Cu and Zn in West Falmouth Harbor sediments (averaged over top 4 cm).

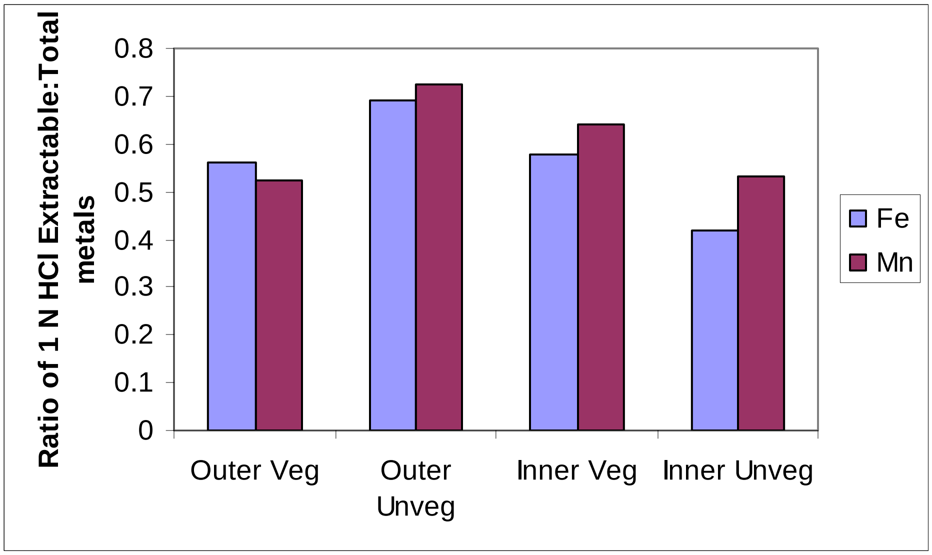


Fig. 45. Ratio of extractable to total Fe and Mn in West Falmouth Harbor sediments. The average over the top four cm was taken for each metal fraction in each core. The ratio of these averages was determined for each core, and the averages of replicate cores averaged for each site.

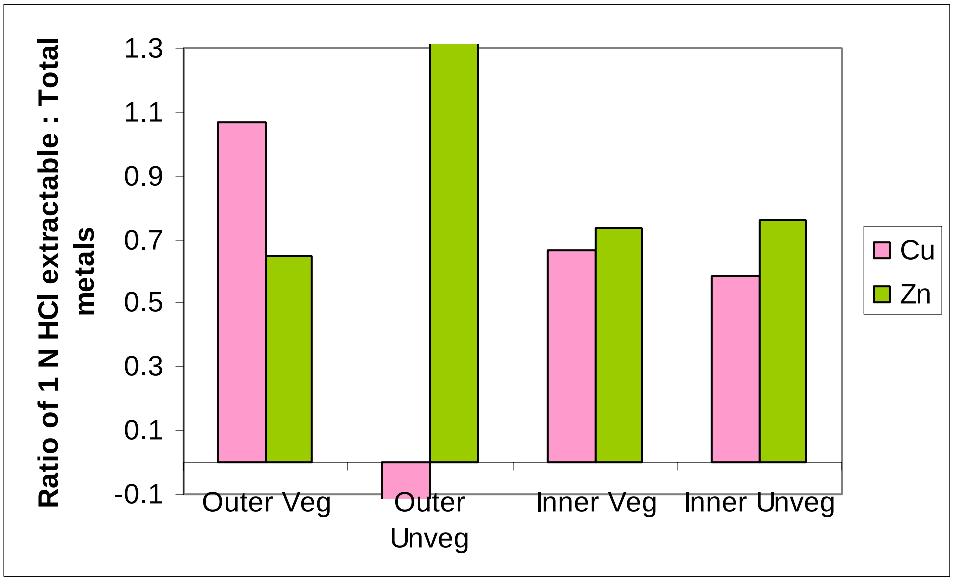


Fig. 46. Ratio of extractable to total Cu and Zn in top 4 cm of West Falmouth Harbor sediments.

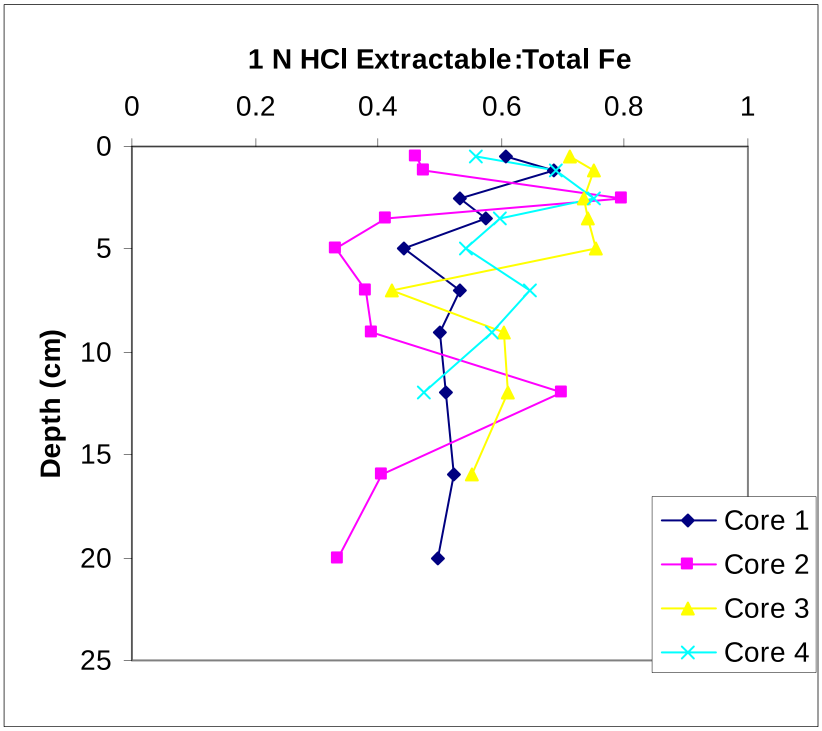


Fig. 47. Ratio of easily extractable to total Fe in Outer West Falmouth Harbor sediments.

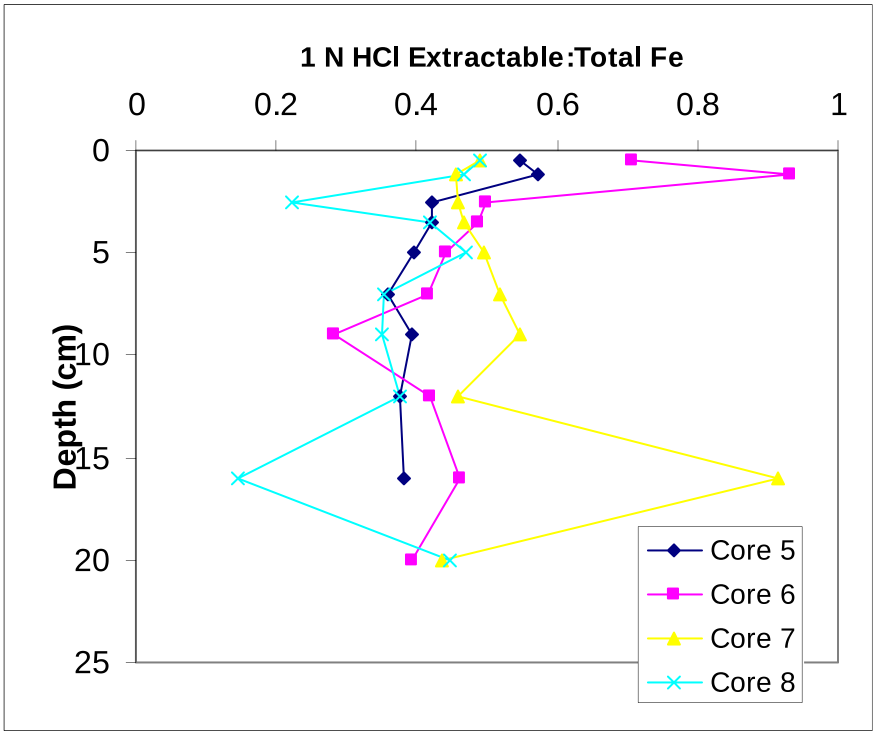


Fig. 48. Ratio of easily extractable to total Fe in Inner West Falmouth Harbor sediments.

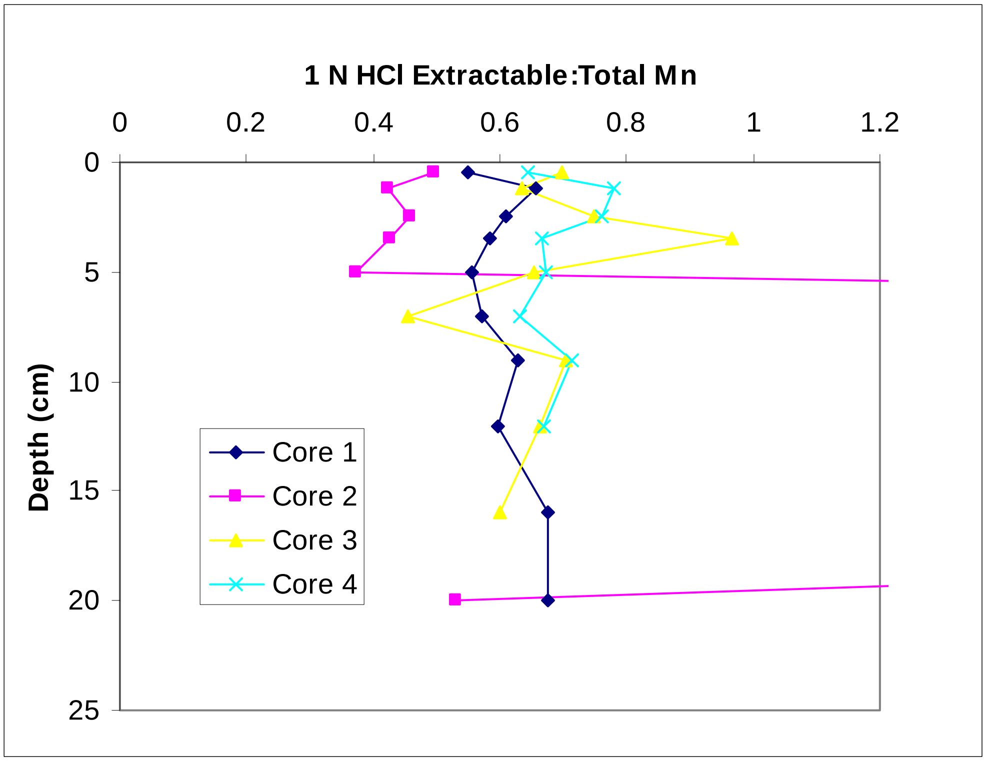


Fig. 49. Ratio of easily extractable to total Mn in Outer West Falmouth Harbor sediments.

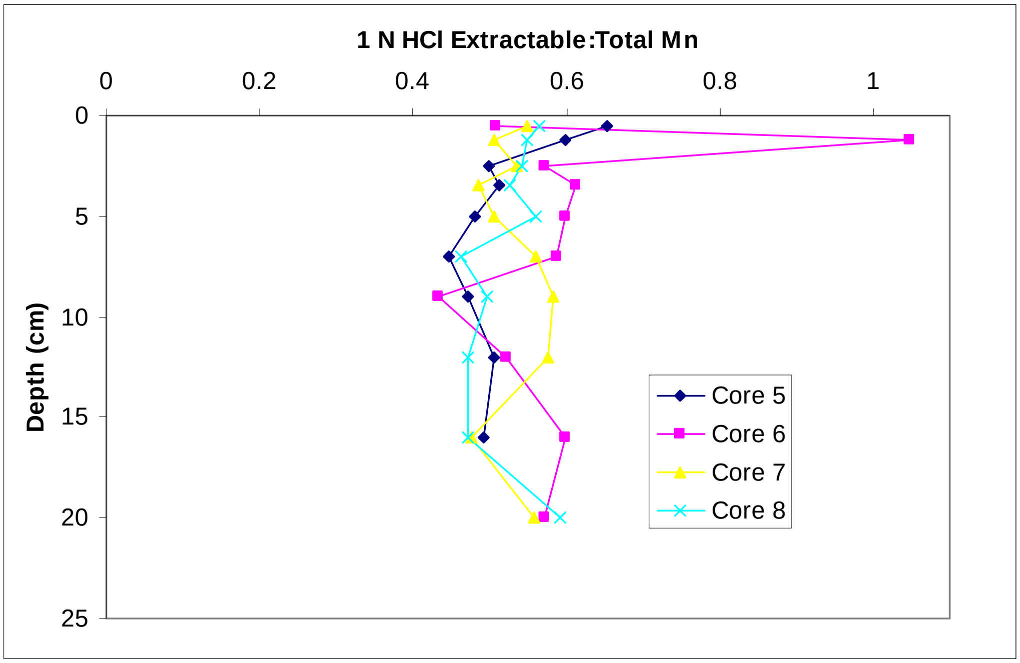


Fig. 50. Ratio of easily extractable to total Mn in Inner West Falmouth Harbor sediments.

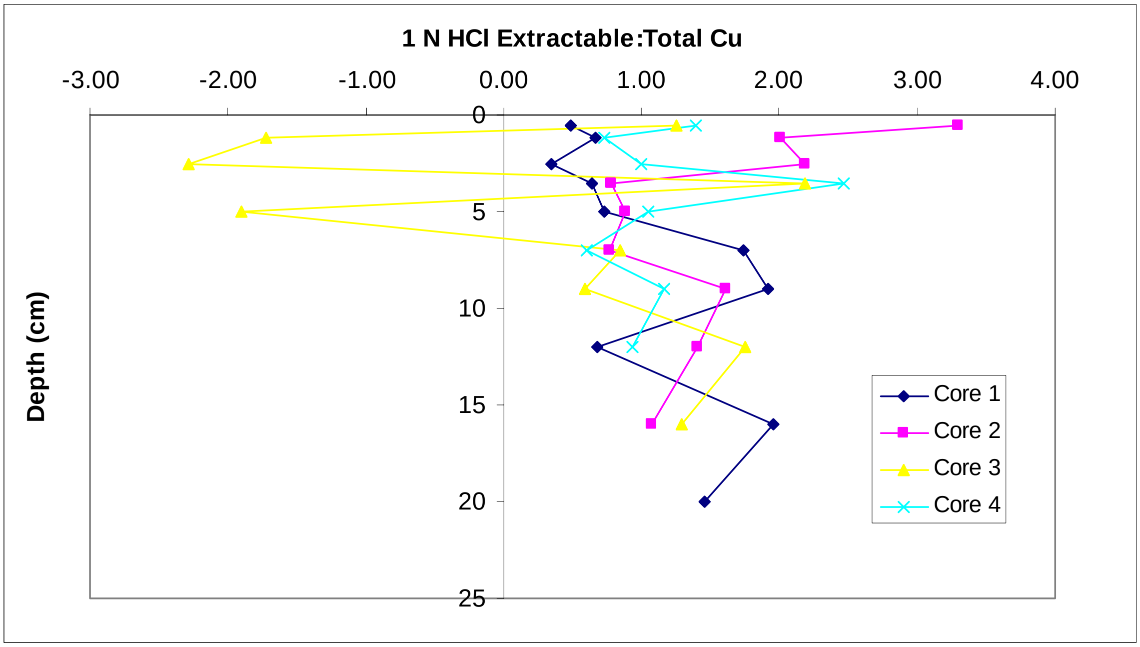


Fig. 51. Ratio of easily extractable to total Cu in Outer West Falmouth Harbor sediments.

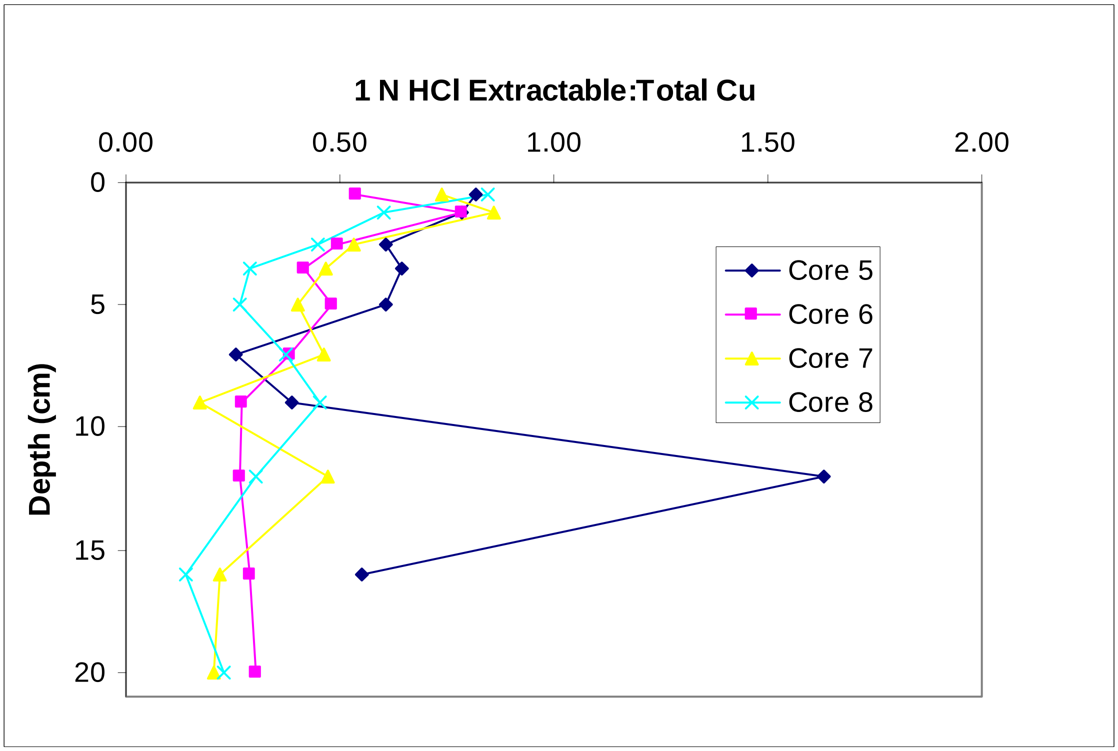


Fig. 52. Ratio of easily extractable to total Cu in Inner West Falmouth Harbor sediments.

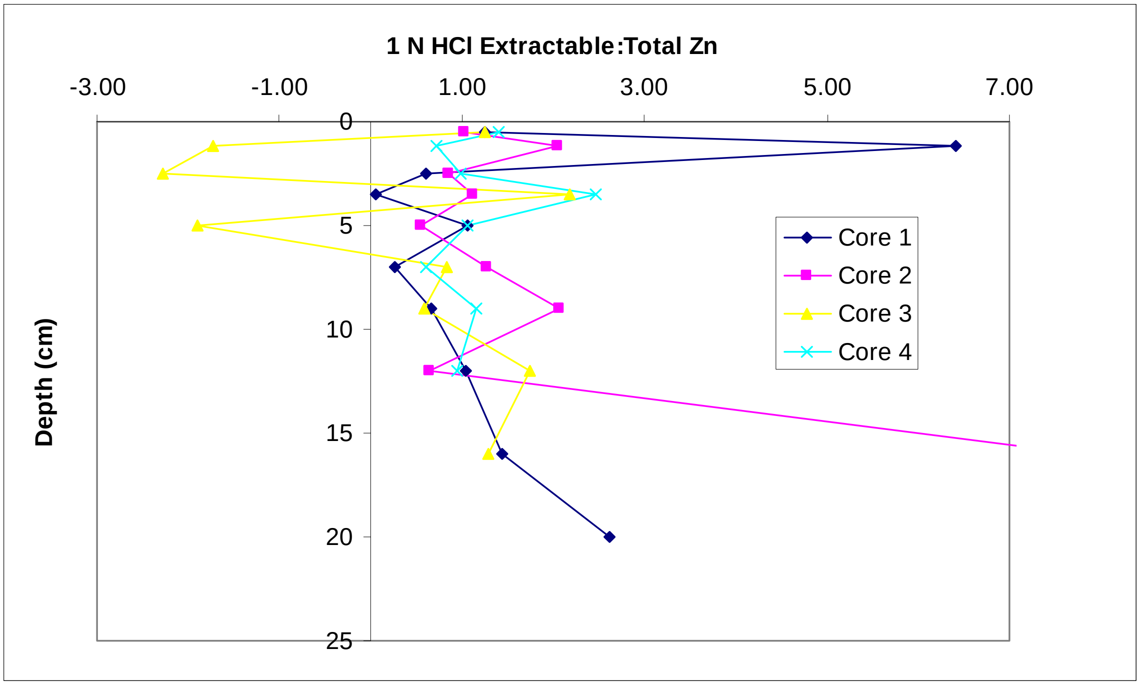


Fig. 53. Ratio of easily extractable to total Zn in Outer West Falmouth Harbor sediments.

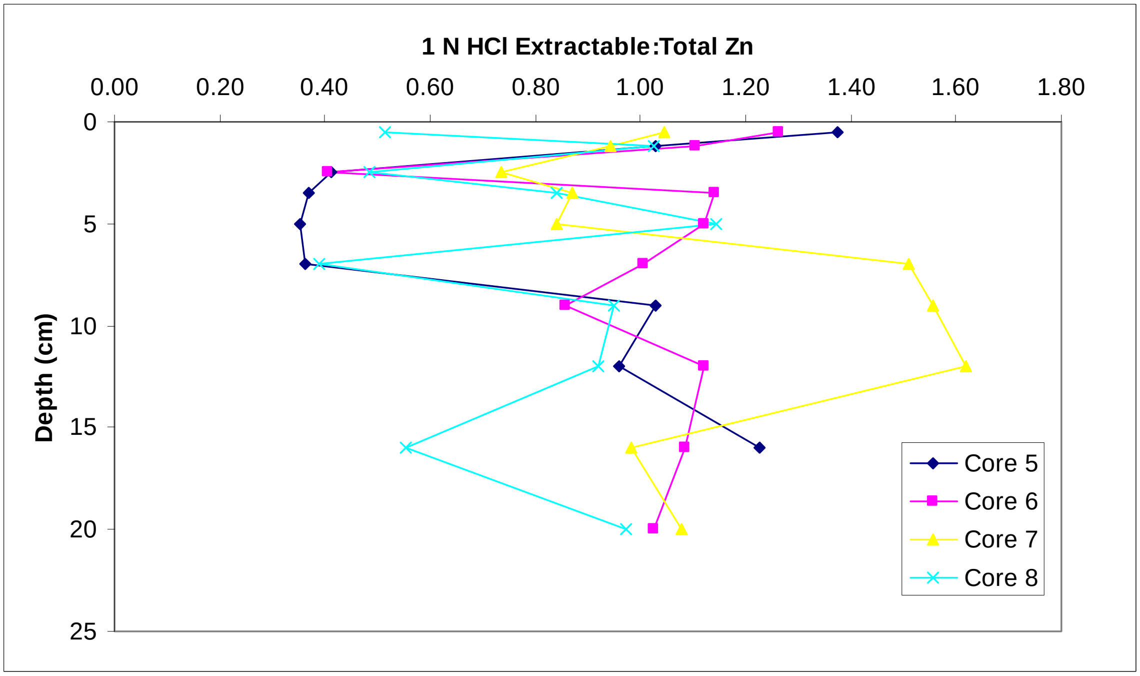


Fig. 54. Ratio of easily extractable to total Zn in Inner West Falmouth Harbor sediments.

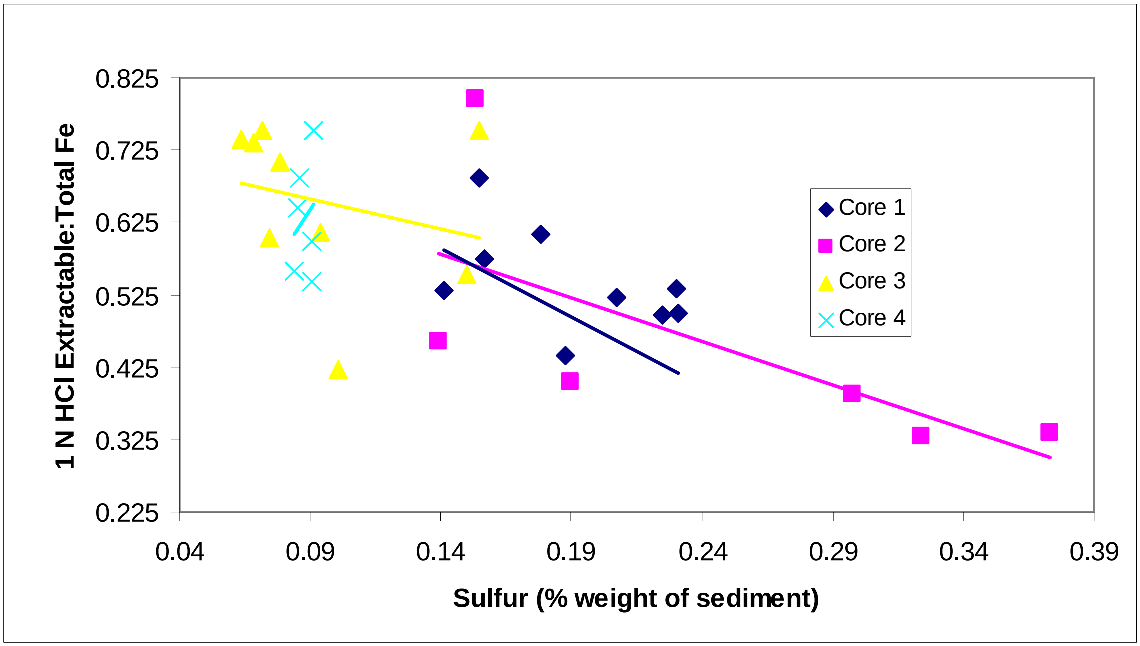


Fig. 55. Relationship of easily extractable Fe to total S in Outer West Famouth Harbor sediment core sections.

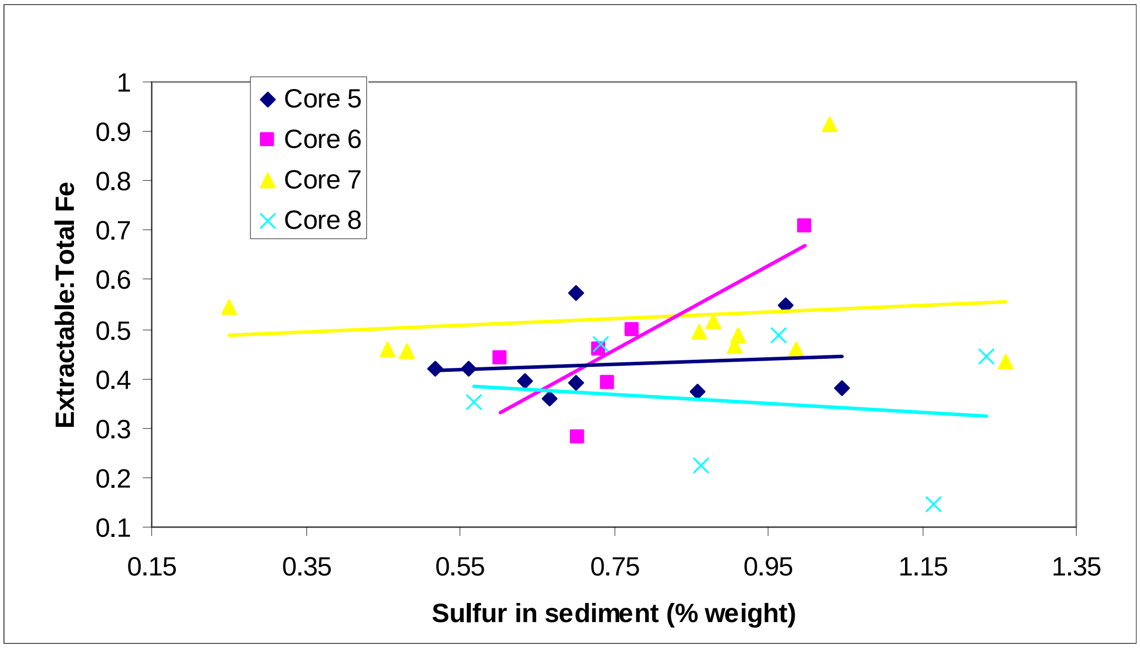


Fig. 56. Relationship of easily extractable Fe to total S in Inner West Famouth Harbor sediment core sections.

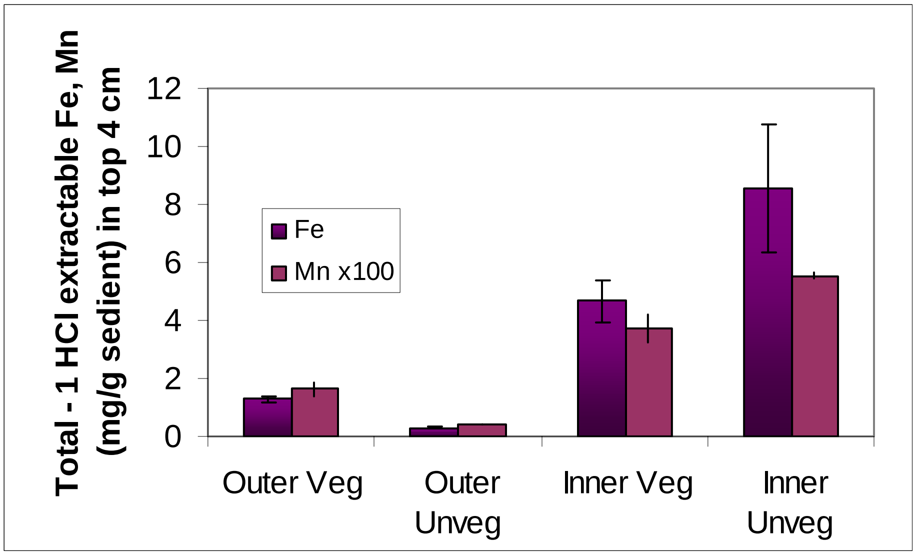


Fig. 57. Reduced Fe and Mn averaged over top 4 cm of West Falmouth Harbor sediments. Mn concentrations were multiplied by 100 to display them on the same scale as Fe.

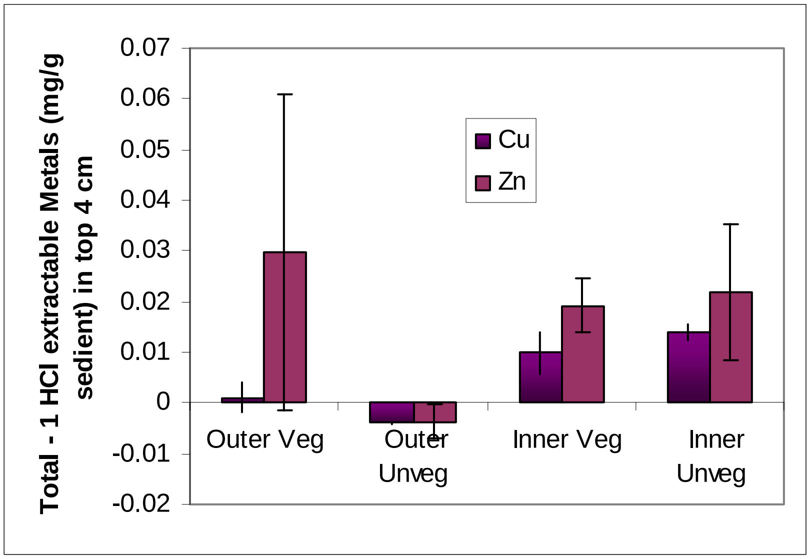


Fig. 57. Reduced Cu and Zn averaged over top 4 cm of West Falmouth Harbor sediments.

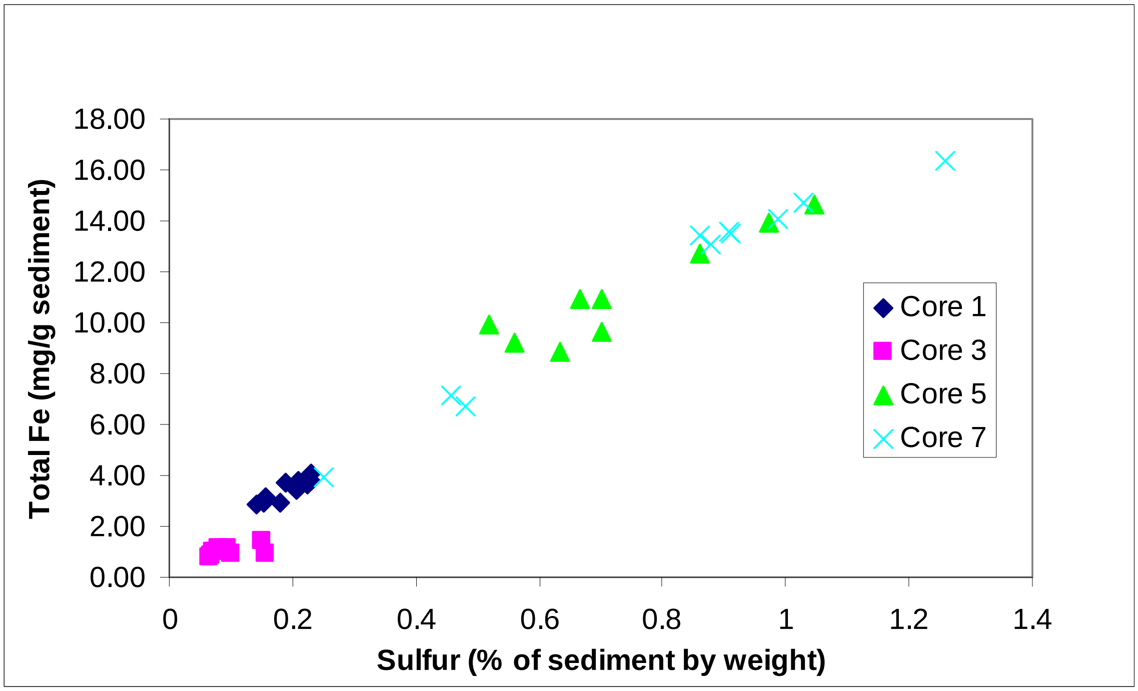


Fig. 58. Relationship of total Fe to S in individual sections of West Falmouth Harbor sediment cores.

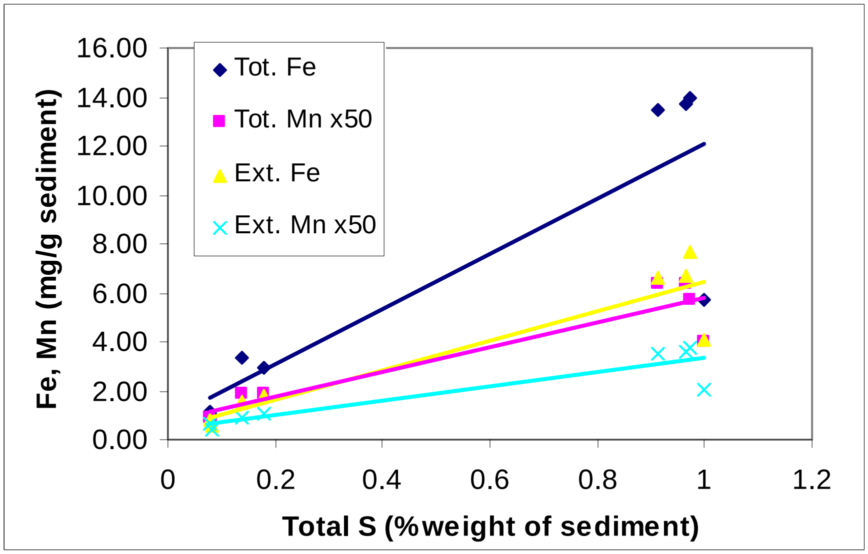


Fig. 59. Relationship of total and 1 N HCl extractable Fe and Mn to S in top centimeter of West Falmouth Harbor sediments. Mn concentrations were multiplied by 50 to permit display on the same scale as Fe.

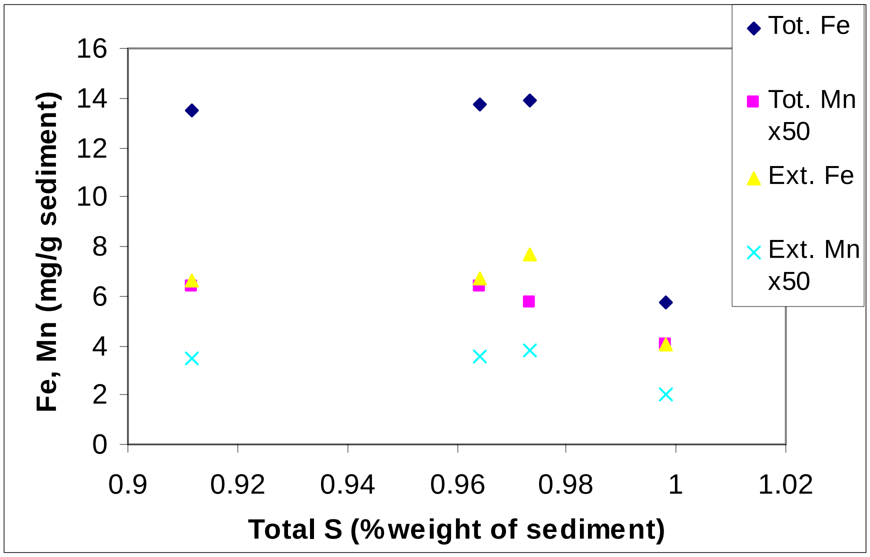
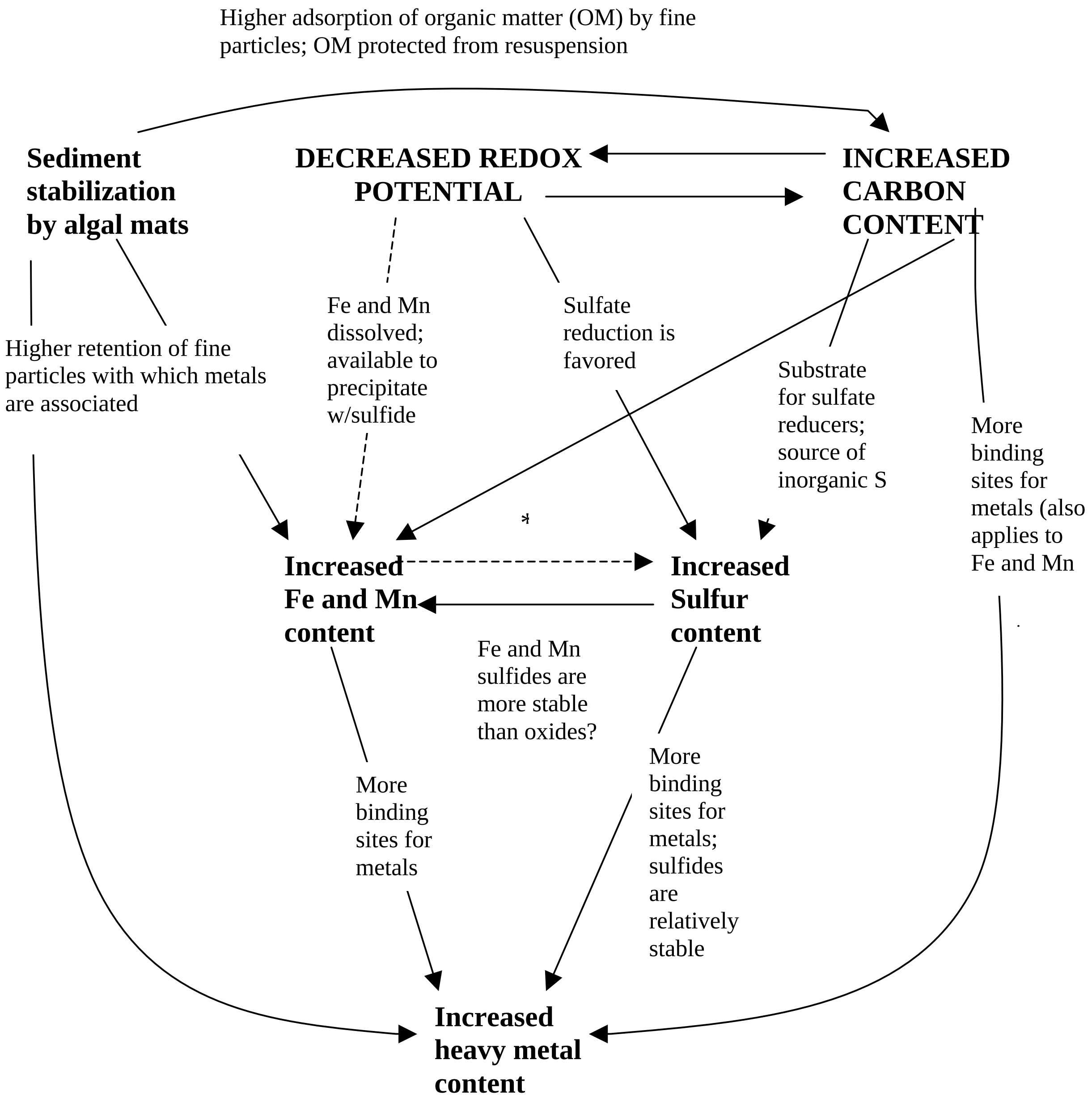


Fig. 60. Relationship of total and 1 N HCl extractable Fe and Mn to S in top centimeter of Inner West Falmouth Harbor sediments. Mn concentrations were multiplied by 50 to allow them to be displayed on the same scale as Fe.

Table 2. Comparison of West Falmouth Harbor heavy metal loads to other New England estuaries.

	Cu (ug/g)	Zn (ug/g)	Pb (ug/g)
Outer WFH	6	27	4
Inner WFH	31	79	23
Waquoit Bay	~50	~115	~60
Eel Pond Shallow	~300-575	~130-190	~180
Eel Pond Deep	~300	~200-230	~180
Boston Harbor moderately polluted	79	98	
Boston Harbor highly polluted	241	327	



*High capture of newly released sulfides in precipitates. Dotted lines represent mechanisms in which Fe and Mn concentrations are assumed to control the precipitation of sulfides.

Fig. 61. Conceptual model of eutrophication's effects on heavy metal retention by estuary sediments.