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Impact of Piers on Tidal Marshes: Accumulation of Wood Preservative Metals in Water and Soils

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Abstract: Wood treated with chromated copper arsenate (CCA) is a common material for pier pilings. Research on CCA impacts in estuarine systems indicates that the magnitude of the biological effect is variable and dependent on sediment and water characteristics. To assist environmental agencies in assessing pier impacts a project was conducted in the U.S.A. to investigate the spatial distribution and magnitude of As, Cr, and Cu accumulation in waters and soils near old and new piers. For new piers, soluble metal levels were highest within 2.9 m of the piers. Total As and Cu levels approached background levels at distances of 2.9 m and 1.4 m, respectively. For old piers, total As and Cu approached background levels at a distance of 9.0 m. Total Cr never exceeded background levels. Threshold effects concentrations were exceeded by sedimented As and Cu within 3.6 m of old piers and 2.1 m of new piers. Apparent effects thresholds were never reached. The only water chemistry variable impacted by piers was As with new piers. It was concluded that leachates accumulate only close to piers and at levels below critical biological thresholds, and would be expected to have negligible ecological effects in reasonably flushed areas.

Key words: Tidal marshes, piers, arsenic, chromium, copper.

1. Introduction

Leaching of chemicals from pier pilings can decrease water quality. In the past, piers were often comprised of wood treated with creosote or PCP's, both of which are toxic to biological systems. They have since been banned in most states. Wood pressure-treated with chromated copper arsenate (CCA) is now a common material for pier pilings and decking. CCA type C, most often used on the Atlantic coastline of the United States, is 47.5% hexavalent chromic oxide, 18.5% cupric oxide, and 34% arsenic pentoxide [1]. Leaching of CCA from pilings does occur in saline or brackish water [2]. Almost all (99%) of the leaching occurs in the first 90 days [3, 4] and leaching decreases 50% daily once treated wood is immersed in saltwater [2, 5]. Contaminants from CCA-treated bulkheads can be found in sediments up to 10 m from the bulkhead in areas of low water flow (e.g. canals), although the highest levels are found within one meter of the pilings [6, 7].

Heavy metal accumulation in tidal marsh sediments is governed by inputs, tide characteristics, and the capacity of the sediments to bind and release the metals. Sorption and desorption are dependent on redox conditions, pH, and cation exchange capacity which is

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favored by clays and organic matter [8-10]. A large percentage of the leached heavy metals is adsorbed onto nearby fine-grained sediments (silts and clays), which act as both a sink and a source [11]. Sand-sized particles have a much lower adsorption capacity. Therefore, soil texture will affect the proportion of leachates that stay in the vicinity of the pier. Energy of the tidal flow affects this as tidal flushing moves metals offsite.

Du Laing et al. [12] reported that heavy metal content in tidal marsh sediments decreased with depth (0-20 cm range). They attributed this to a corresponding decrease in clay and organic matter. De Lacerda et al. [13] reported higher heavy metal content in the upper sediment layer (5-15 cm depth) of a site vegetated by *Spartina alterniflora* than in an adjacent un-vegetated mudflat. Decreasing organic matter with depth at sites like these is probably related to herbaceous plant rooting and litter accumulation in the upper sediments. Cacador et al. [14] reported similar results for sites vegetated with *Spartina maritime*. They attributed this to oxidized rhizospheres and complex organic compounds released by roots. Sundby et al. [15] suggested that increased metal content in shallow sediments is promoted by iron plaque in the oxidized rhizosphere. The decomposition of plant litter may also promote heavy metal enrichment in shallow sediments [16].

Copper, As, and Cr are toxic to estuarine organisms [17] and leachate from CCA-treated wood has been shown to be toxic to estuarine species [2]. Research on CCA impacts in estuarine systems indicates that the magnitude of the effect on biological systems is quite variable the effect is dependent on time, sediment chemistry, organic matter levels, dissolved oxygen levels, and water flow [18]. Therefore, potential impacts should be addressed on a regional basis. Because of the potential negative environmental impacts of long piers, and the recognized regional nature of these impacts, environmental regulatory agencies are seeking impact data to assist in the evaluation of their pier construction permitting programs. To facilitate that process this study was conducted to evaluate the impacts of piers on soil and water quality. We specifically wanted to address the following questions: (1) What is the effective range in pollution? (2) Do the elevated levels of Cu, As, and Cr exceed safe biological thresholds? (3) Do the elevated levels of Cu, As, and Cr decrease over time?

2. Materials and Methods

2.1 Site Selection

Pier length ranged from 30 m to 210 m. The surrounding tidal vegetated marsh areas were $\geq$ 30 m (perpendicular to the piers). Research sites were concentrated in the northern half of Worcester County, Maryland U.S.A. where development is heaviest, but also included a handful of sites in the southern half of the county. We tried to pair control sites and pier sites within drainages. We had additional criteria: pier extends to open water, natural vegetation, access, and marsh size. Marsh size was critical to allow for transects away from the pier without crossing into the range of an adjacent pier. There were eleven pier sites and eleven control sites (no piers). Eight of the piers were > 3 years in age (designated “old piers”), three piers were $\leq$ 1 year old (designated “new piers”). We targeted new piers with the assumption that water chemistry effects were more likely to show up near new piers. We targeted old piers with the objective of identifying sediment effects after equilibrium had been reached. Most data were collected from the three new piers and five of the old piers. The remaining six old pier sites and the control sites were used to establish baseline levels for As, Cu, and Cr in water and soils.

2.2 Soils Characterizations

Soil characteristics such as texture, and organic matter content and distribution have been shown to impact the retention and transport of heavy metals. Therefore to facilitate extrapolation over a wider geographic range, soils were identified and classified to

the series level at each site. One pedon per site was described according to USDA, NRCS standards [19]. For pier sites the sampling point was 15 m from the mid-point of the pier and perpendicular to the pier. For control sites the sampling point was located midway between the landward base of the marsh and open water.

2.3 Collection of Water and Soil Samples

All samples were collected at low tide. Water samples (one sampling depth) were collected from unlined bore holes created with a stainless steel bucket auger. Water samples were collected directly into sample bottles (I-CHEM certified). Soil samples were taken from spade slices extracted with a stainless steel tiling spade. Sub-samples were extracted from the spade slice with a stainless steel knife. No attempt was made to separate live roots and rhizomes from detritus or soil organic matter. These samples will be referred to as “soils”, although a more accurate term might be “root mat”. All samples were kept on ice for transport to the lab where they were refrigerated prior to analysis.

2.4 Comparison of Pier Sites and Control Sites

This analysis was conducted to establish baseline levels for As, Cu, and Cr, and to identify sites with elevated heavy metal levels from sources other than piers. Water and soil samples were collected from eleven pier sites and eleven control sites and analyzed for chemical composition. At pier sites the samples were collected at a distance from the pier of at least 30 m to minimize any pier impact. Each sample was a composite of six sub-samples collected at random. Soil samples were taken at a depth of 0-20 cm; all were collected from surface organic horizons (Oe, hemic materials). F-tests were run to compare variances for each data sub-set (control, pier); in each cases variances were not significantly different at $P < 0.05$; therefore unpaired two-tailed t-tests were run to separate means.

2.5 Effect of Distance from Pier

For three new piers, two transects were run per pier with sampling point distances starting at 0.6 m and with 0.75 m intervals up to 9.0 m (twelve sampling points). For five old piers there were two transects per pier with three sampling points per transect at distances of 0.6 m, 3.6 m, and 9.0 m for water, and four sampling points per transect at distances of 0.6 m, 2.1 m, 3.6 m, and 9.0 m for soil samples. Soil samples were collected from two depths (0-10 cm, 10-20 cm) for new piers and four depths (0-10 cm, 10-20 cm, 20-30 cm, and 30-40 cm) for old piers. Sampling depths 0-10 cm and 10-20 cm represent organic horizons; sampling depths 20-30 cm and 30-40 cm represent mineral horizons. We chose different sampling schemes for old piers and new piers to minimize laboratory costs and labor demands, yet still meet our primary objectives. We felt that a more intensive horizontal sampling for new piers was necessary to characterize the initial distribution of heavy metal leachates from pilings. However, we felt that the metals probably would not have sufficient time to work deeper into the profile in one year so we only sampled the upper 20 cm. For new piers, distance and depth effects were analyzed by multiple linear regression, SAS v. 9.1 [20], with distance and depth as independent variables and As, Cr, and Cu as dependent variables. For old piers distance and depth effects on soil metal concentrations were assessed by ANOVA, SAS v. 9.1 PROC:GLM [20] blocked on depth since we considered distance to be the more important variable.

2.6 Comparison of Old Piers and New Piers

Data were collected as above: three new piers, five old piers; two transects per pier; at distances of 0.6 m, 3.6 m, and 9.0 m; and two sampling depths, 0-10 and 10-20 cm. Soil metal concentrations were assessed by ANOVA, SAS v. 9.1 PROC:GLM [20] blocked on depth to increase the sensitivity of new pier to old pier comparisons. Each distance was analyzed separately.

2.7 Laboratory Analyses

Soil samples were dried and ground to pass a 2 mm sieve. Water and soil samples were analyzed for total As, Cu, and Cr. Soil samples were also analyzed for soluble As, Cu, and Cr. Total metals in soil and water samples were determined by microwave acid digestion followed by Inductively Coupled (argon) Plasma-Optical Emission Spectrometry (ICP-OES); method SMWW 3030k and 3120B [21]. Detection limits ($mg \cdot kg^{-1}$) were 0.003 for soluble Cu and Cu in water, and 0.5 for total sedimented Cu; 0.004 for soluble Cr and Cr in water, and 0.8 for total sedimented Cr; 0.008 for soluble As and As in water, and 2.0 for total sedimented As. Concentrations of As, Cu, and Cr in soil are expressed on a dry weight basis.

3. Results and Discussion

3.1 Marsh Characteristics

The selected marshes can, in general, be defined as mature, low energy, hard marshes. They are located on tidal creeks or bays. All marshes were located on the east side of the county near the Atlantic Ocean. The dominant soil series (based on on-site determinations) were Broadkill (Typic Sulfaquents), Boxiron (Histic Sulfaquents), and Mispillion (Terric Sulfihemists). Occasionally found was Transquaking (Typic Sulfihemists). Broadkill was the most common series at the old pier sites; Misspillion was most common at new pier sites. Most of the sites were mapped as undifferentiated groups ("Transquaking and Mispillion", map unit TP, and "Boxiron and Broadkill", map unit BX) [22]. These series represent a large percentage (area basis) of the tidal marsh soils in the Mid-Atlantic Region [22]. All four series are predominately fine textured (loams and silt loams). They differ in the thickness of the organic horizons (Broadkill, < 20 cm; Boxiron, 20-40 cm; Mispillion, 40-130 cm; Transquaking, > 130 cm). Dominant plant species were *Spartina alterniflora* Loisel, S*partina patens* (Aiton) Muhl., and *Distichlis spicata* (L.) Greene.

3.2 Pier Sites Versus Control Sites

Table 1 presents water and soil chemistry data for control sites and pier sites outside the perceived range of pier effects (> 30 m). There were no statistically significant differences for any of the variables. Therefore, from a chemical standpoint the two sets of ecosystems were similar, and any enhanced chemical levels in the vicinity of the piers can be attributed to the presence of the piers.

3.3 New Piers: Effect of Distance

Table 2 presents the effect of distance from pier (new piers) on water chemistry. Only As was significant (Fig. 1) and distance accounted for little of the variability (R^2 = 0.0606). Concentrations were highest within 1.4 m of the piers but there was also a spike at 5.2 m. The presence of piers had no effect on water chemistry with respect to Cu or Cr concentrations. These results are not surprising when viewed in context of the literature. Brooks [23] investigated leaching losses of As, Cr, and Cu from CCA-treated wood immersed in freshwater under controlled environmental conditions (pH, temperature). Copper losses were more than twice that of As; Cr losses were the lowest. Copper loss rate per day dropped dramatically over the first three days, then

Table 1 Comparison of As, Cr, and Cu content in soils and water at 11 control sites and 11 pier sites.

	Control sites		Pier sites		
Metal	$\bar{X}$	SE	$\bar{X}$	SE	P
	Soil-total ($mg \cdot kg^{-1}$ DM)				
As	4.61	2.540	6.13	4.291	0.3304
Cr	27.41	13.487	27.53	10.177	0.9817
Cu	14.90	7.011	18.37	6.961	0.2574
	Soil-soluble ($mg \cdot kg^{-1}$ DM)				
As	0.0614	0.04460	0.0958	0.05371	0.1322
Cr	0.3543	0.19618	0.3664	0.15277	0.8726
Cu	0.1984	0.12449	0.2523	0.12686	0.3241
	Water ($mg \cdot kg^{-1}$)				
As	0.0680	0.05096	0.0470	0.03844	0.2781
Cr	< dl[a]		< dl		
Cu	0.0044	0.00305	0.0051	0.00308	0.6314

[a] Below detection limits (0.004 $mg \cdot kg^{-1}$).

Table 2 Simple regression statistics for relationship between distance from new piers and As, Cr, and Cu concentration in water (mg·kg^{-1}).

Variable	Est. (×10^{-5}) (m)	SE (×10^{-5})	P	R^2
As	-53.504	25.3717	0.0386	0.0606
Cr	-0.612	3.7632	0.8713	0.0004
Cu	-13.849	13.0625	0.2927	0.0160

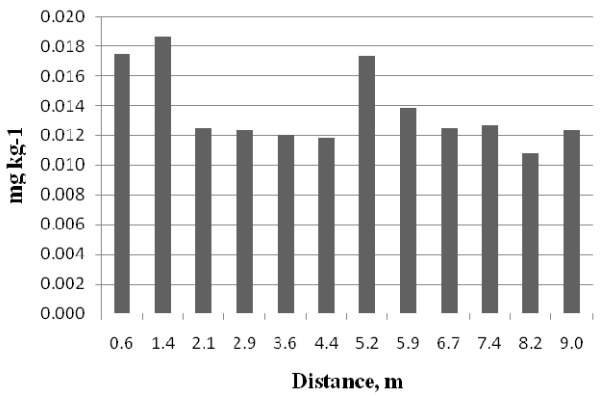

Fig. 1 Effect of distance from new piers on [As] in water.

stabilized and remained the highest of the three metals from day 15 to day 120. Of the three metals, As losses were the highest from day 2 to day 15. Chromium losses were negligible after day 5. Water pH, salinity, and temperature, and current speed can affect leaching losses. Therefore, the absolute numbers from Brooks' work are not directly applicable to our work but the trends supply insight to our data. EPA has heavy metal standards for salt water (not brackish water) with respect to aquatic organisms [24]. For chronic exposure, the standards for As, Cr, and Cu are 36, 50, and 3.1 μg·L^{-1}, respectively. In no case did the levels of As, Cr, and Cu in water exceed those standards in this study.

Figs. 2-7 and Table 3 present the effect of distance from the pier on two soil levels (0-10 cm and 10-20 cm) on soluble and total As, Cr, and Cu. All samples were collected from O horizons. Total As levels were three magnitudes higher than soluble levels. Total Cr and Cu levels were four magnitudes higher than soluble levels. These results indicate that most of the heavy metal pool is sequestered in plant biomass, detritus, or soil organic matter. Samples were collected in late summer. The dominant plant species were herbaceous perennials.

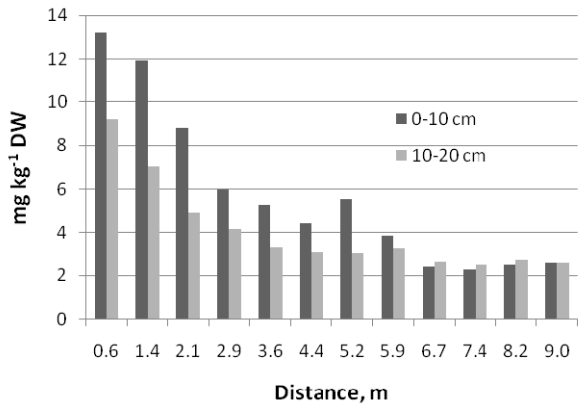

Fig. 2 Effect of distance from new piers on total As in soil at 2 depths.

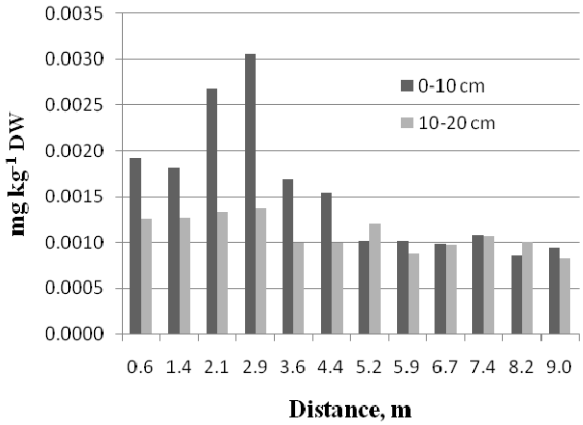

Fig. 3 Effect of distance from new piers on soluble As in soil at 2 depths.

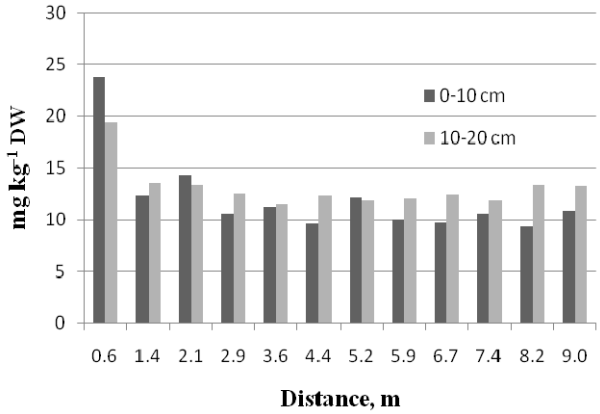

Fig. 4 Effect of distance from new piers on total Cr in soil at 2 depths.

We would expect soluble levels of these metals to increase later in the year as plant litter decomposes. With the exception of Cu and Cr at the 10-20 cm depth, pier distance had a significant effect on soluble levels. Soluble As and Cr levels were highest within 2.9 m of

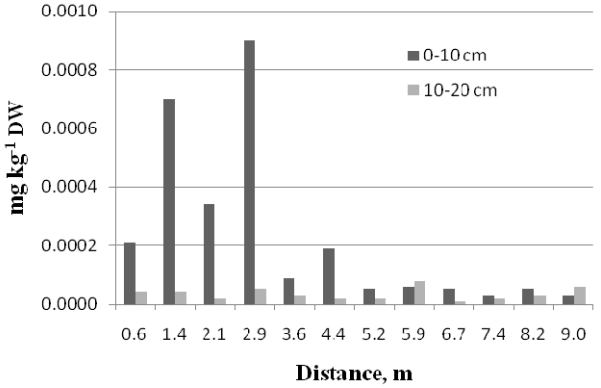

Fig. 5 Effect of distance from new piers on soluble Cr in soil at 2 depths.

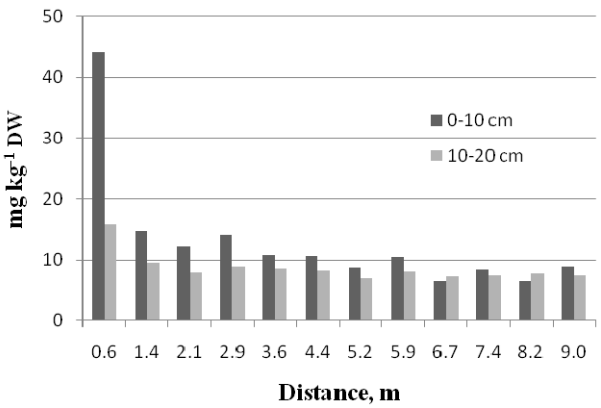

Fig. 6 Effect of distance from new piers on total Cu in soil at 2 depths.

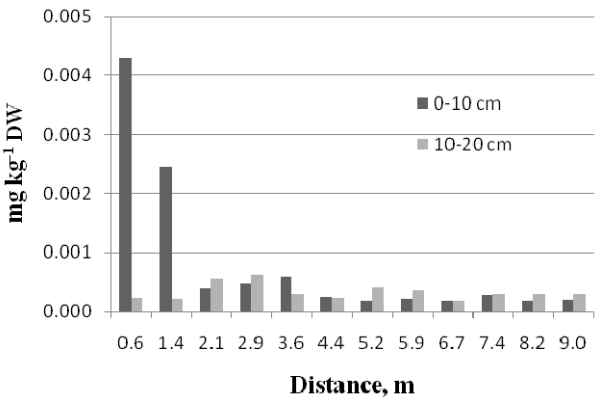

Fig. 7 Effect of distance from new piers on soluble Cu in soil at 2 depths.

the piers, Cu levels within 1.4 m of the piers. Heavy metal levels clearly dropped off at greater distances. Although we feel that these trends are real, we advise caution in the interpretation of the magnitude of the soluble levels as the mean values presented here, in most cases, fall below detection limits.

Table 3 Simple regression statistics for relationship between distance from new piers and Cu, Cr, and As content (mg·kg^{-1} DM) of soils at two depths.

Variable	Depth (cm)	Estimate (m)	SE	P	R^2
Soluble Cu	0-10	-0.0003193	0.00006970	<0.0001	0.2308
Soluble Cu	10-20	-0.0000107	0.00001457	0.4647	0.0077
Total Cu	0-10	-2.4311515	0.35072368	<0.0001	0.4070
Total Cu	10-20	-0.5556579	0.09184210	<0.0001	0.3434
Soluble Cr	0-10	-0.0000666	0.00001957	0.0011	0.1441
Soluble Cr	10-20	-0.0000008	0.00000199	0.6777	0.0025
Total Cr	0-10	-0.9273026	0.16421053	<0.0001	0.3634
Total Cr	10-20	-0.3060987	0.10569079	0.0011	0.1446
Soluble As	0-10	-0.0002016	0.00002240	<0.0001	0.5362
Soluble As	10-20	-0.0000515	0.00000957	<0.0001	0.2923
Total As	0-10	-1.2364145	0.08075658	<0.0001	0.7700
Total As	10-20	-0.3601974	0.06516447	<0.0001	0.5702

For total As, Cu, and Cr the distance effect was always significant, however the impact of distance was not consistent for the three metals. Cu and Cr levels were appreciably higher at 0.6 m; the levels changed little with distance further out from the pier. Arsenic levels declined more gradually with distance and stabilized at 6.7 m. Any difference in metal concentration associated with sampling depth reflected distance effects, once levels at 0-10 cm stabilized there were no apparent depth effects. We are confident that the stabilized levels for all three metals represent background levels as they are within (or less than) $\bar{X}$±1 SE of the values found > 30 m from the piers (Table 1). Therefore, the spatial range in total metal enrichment of soils can be accurately determined from these figures. As and Cu levels near piers approached background levels at distances of 2.9 m and 1.4 m, respectively. Levels of Cr in the vicinity of piers were always below (but within 1 SE) of background levels. These results indicate that any heavy metal enrichment of soils is restricted to close proximity of the piers.

Table 4 presents toxicology benchmarks for assessing the biological response to sedimented As, Cu, and Cr in saltwater [25]. These are not standardized but represent cautionary thresholds used regionally in the U.S.. Because the magnitude of leaching losses from treated wood is greatest for Cu and because it is the

Table 4 Toxicology benchmarks for assessing the biological response to sedimented Cu, Cr, and As in saltwater, from Jones et al. [25].

Metal	AET	TEC	PEC	(TEC+PEC)/2
				($mg \cdot kg^{-1}$ DM)
Cu	390	18.7	108	63.4
Cr	260	52.3	160	106.2
As	57	7.24	41.6	24.4

AET: Apparent effects threshold. This is a benchmark above which adverse effects are observed as metal concentrations increase.
TEC: Threshold effects concentration. This is a benchmark below which adverse effects associated with the metal are not expected.
PEC: Probable effects concentration. Adverse effects are often found at levels above this benchmark.

most toxic of the three metals to estuarine organisms, it is the metal of highest concern [23]. Levels of As, Cr, and Cu never exceeded the apparent effects threshold or probable effects concentration. Levels exceeding the threshold effects concentration were limited to Cu at 0-10 cm depth within 0.6 m of the pier, As at 0-10 cm depth within 2.1 m of the pier, and As at 10-20 cm depth within 1.4 m of the pier. Sanger and Holland [26] concluded, "it is unlikely that the bioaccumulation of dock leachates by marine biota is having or likely to have an impact on living resources in South Carolina estuaries and tidal creeks". They cited the following reasons: most leaching occurs only when the dock is new, the affected area is small, and high rates of tidal flushing will dilute and flush accumulations in the water column. Weis et al. [17] also concluded "leachates from pilings, even new ones, in reasonably flushed areas have negligible ecological effects". In our study heavy metal levels were never high enough to expect detrimental effects on aquatic organisms.

3.4 Old Piers: Effect of Distance

There were no significant distance effects for water chemistry in the vicinity of old piers: As ($P = 0.6413$, grand $\bar{X} = 0.04033$ $mg \cdot kg^{-1}$), Cr ($P = 0.6740$, grand $\bar{X} = 0.03700$ $mg \cdot kg^{-1}$), Cu ($P = 0.9986$, grand $\bar{X} = 0.00403$ $mg \cdot kg^{-1}$). These values are similar to those found at a distance > 30 m from the piers or at control sites (Table 1). Therefore, we can conclude that the presence of old piers had no effect on water chemistry.

Tables 5 and 6 present the effects of distance and depth on metal concentrations in soils near old piers. Total Cu consistently decreased with depth and distance. For total Cr and As the magnitude of the decrease with depth was greater closer to the pier (significant interactions).

The depth effects are to a large extent due to the vertical distribution of detritus and soil organic matter. Sample depths 0-20 cm represent organic soil horizons; sample depths 20-40 cm represent mineral soil horizons. It has been reported that greater heavy metal levels in tidal marsh soils are associated with root zones and soil organic matter [9, 13]. A large percentage of the leached heavy metals is adsorbed onto nearby fine-grained sediments (silts and clays), which act as both a sink and a source [11]. Sand-sized particles have a much lower adsorption capacity. Therefore, soil texture will affect the proportion of leachates that stay in the vicinity of the pier. Mineral soil horizons sampled in this study were predominately loams and silt loams.

Both As and Cu levels exceeded threshold effects concentration values at 0-10 and 10-20 cm depths at a distance of 0.6 m from the piers, and 0-10 cm depth at distances of 2.1 and 3.6 m. Chromium levels never reached threshold effects concentrations. The elevated levels of As, Cr, and Cu never exceeded the apparent effects threshold or probable effects concentration.

Table 5 Results of ANOVA for effects of distance and depth for total and soluble metal content in soils near old piers.

Factor		As	Cr	Cu
	Df	P		
		Total		
Distance	3	<0.0001	0.0614	0.0305
Depth	3	<0.0001	<0.0001	<0.0001
Distance × Depth	9	<0.0001	0.0430	0.2837
		Soluble		
Distance	3	0.0053	0.0016	0.8545
Depth	3	0.0500	0.9084	0.0930
Distance × Depth	9	0.0132	0.9546	0.1872

Table 6 Total and soluble metal concentrations in soils as affected by depth and distance from old piers.

Distance (m)	Depth (cm)	Total ($mg \cdot kg^{-1}$ DW)			Soluble $mg \cdot kg^{-1}$
		As	Cr	Cu	As
0.6	0-10	17.56	26.63	25.87	0.02184
0.6	10-20	7.59	17.27	19.95	0.00942
0.6	20-30	4.90	12.14	14.95	0.00618
0.6	30-40	4.13	8.43	9.59	0.00676
2.1	0-10	10.49	19.19	23.54	0.01215
2.1	10-20	6.09	15.04	15.52	0.01104
2.1	20-30	3.48	9.40	11.95	0.01434
2.1	30-40	2.95	7.62	7.49	0.01113
3.6	0-10	9.07	16.65	19.66	0.03668
3.6	10-20	5.44	15.23	18.03	0.03030
3.6	20-30	4.66	12.95	11.76	0.02511
3.6	30-40	3.83	11.14	10.29	0.01855
9.0	0-10	5.33	14.05	15.58	0.06668
9.0	10-20	3.72	9.21	11.60	0.03978
9.0	20-30	3.88	9.70	10.60	0.04619
9.0	30-40	3.42	10.83	11.18	0.02698

By comparing the values in Table 6 with background values (Table 1) we can estimate the spatial extent of sedimented total metal content enrichment. As and Cu levels (0-10 cm depth) near old piers approached background levels at a distance of 9.0 m from the piers. For new piers As and Cu levels approached background levels at distances of 2.9 m and 1.4 m, respectively (see previous section). Therefore, As and Cu enrichment of soils does expand away from the pier over time. Chromium, which did not show a significant distance, was consistently at or below background levels. However, they were always within 1 SE.

At soil depths of 20-40 cm, concentrations of total As, Cr, and Cu in the vicinity of piers were at background levels (Table 1). It should be pointed out that the values in Table 1 were derived from samples collected at a depth of 0-20 cm; however our data show that metal concentrations tend to decrease with depth. So clearly the leached metals are accumulating in the upper 20 cm of the soil and probably in plant biomass and soil organic matter. Although we do not have data directly support it, we feel that this would hold true for the new piers as well. Obviously, with the new piers there is less time for the metals to work deeper into the profile and initial assimilation into plant biomass would occur through the younger plant roots which tend to be shallow. Du Laing et al. [12] reported that heavy metal content in tidal marsh sediments decreased with depth (0-20 cm range). They attributed this to a corresponding decrease in clay and organic matter. De Lacerda et al. [13] reported higher heavy metal content in the upper sediment layer (5-15 cm depth) of a site vegetated by *Spartina alterniflora* than in an adjacent un-vegetated mudflat. Decreasing organic matter with depth at sites like these is probably related to herbaceous plant rooting and litter accumulation in the upper sediments. The decomposition of plant litter may also promote heavy metal enrichment in shallow sediments [16].

Depth effects can also be attributed to physiological processes of the plants. Cacador et al. [14] reported similar results with sites vegetated with *Spartina maritime*. They attributed this to oxidized rhizospheres and complex organic compounds released by roots. Oxidation of rhizospheres by transport of oxygen through arenchyma raises the soil redox potential [27]. Under the reducing conditions prevalent in salt marshes heavy metals tend to be immobilized as insoluble metal sulfides [28]. In the oxidized rhizosphere the metals become more bioavailable which promotes cycling. Sundby et al. [15] suggested that increased metal content in shallow sediments is promoted by iron plaque in the oxidized rhizosphere. *Spartina alterniflora* has been shown to excrete heavy metals through salt glands [15]. Thus marsh plants such as *Spartina* impact heavy metal accumulation in soils directly through normal physiological processes, indirectly by modifying soil redox conditions, and through the decomposition of detritus.

There were no significant distance or depth effects for soluble Cu (grand $\bar{X}$ = 0.00731 $mg \cdot kg^{-1}$). For soluble Cr only distance was significant: 2.1 m ($\bar{X}$= 0.02110 $mg \cdot kg^{-1}$ DM) was highest; the other Cr values < dl. For soluble As distance, depth, and distance × depth were

significant. At distances of 0.6 m and 9.0 m As decreased with depth, but not at the other two distances. Also, soluble As values in general increased with distance from the pier 0.01105, 0.01216, 0.02766, and 0.04491 mg·kg^{-1} DW. We have no explanation for this as total As clearly decreased with distance from pier.

3.5 New Piers Versus Old Piers

We compared new piers with old piers to determine if sedimented heavy metal levels change over time. Table 7 presents As, Cr, and Cu levels at 0-20 cm soil depth at distances of 0.6 m, 3.6 m, and 9.0 m from new and old piers. Total sedimented metal levels were similar for old piers and new piers (Cr, 0.6 and 9.0 m) or higher for old piers with the exception of Cu at 0.6 m. This would indicate that Cu was still leaching from the new piers. We assume that most of the leached material quickly leaves the vicinity of the piers through tidal action. For metals to remain in the vicinity of the piers they must be quickly assimilated into plant biomass. At greater distances the higher levels for old piers probably reflect transport of metals after their release through mineralization. We should consider the possibility that differences between new and old piers may just reflect inherent differences at time zero caused by inherent differences in piling characteristics. However, we feel that these results indicate that the wood preservative metals continue to move away from the piers over time and the range in pollution increases over time. J.S. Weis and P. Weis [29] compared heavy metal levels in soils and plants directly below and near two CCA-treated walkways over tidal marshes. The walkways were 3 and 15 years in age. They found elevated levels of sedimented metals were found to a distance of 10 m from the piers. Sedimented metal concentrations under the walkways were higher for the new walkway but the metals dispersed to a greater distance from the old walkway. Dispersal of metals near the old walkway was greater in the low marsh than the high marsh which they attributed to differences in tidal inundation.

Table 7 Comparison of As, Cr, and Cu content (total, mg·kg^{-1} DW) of soils (0-20 cm depth) at three distances from old piers and new piers.

Metal	Old piers	New piers	Pr>F
		Means	
		0.6 m	
As	12.337	11.188	0.5010
Cr	21.953	21.628	0.8819
Cu	22.913	29.973	0.0434
		3.6 m	
As	8.292	4.293	0.0073
Cr	17.119	11.333	0.0253
Cu	19.529	9.692	0.0003
		9.0 m	
As	7.256	2.566	<0.0001
Cr	15.939	12.063	0.0557
Cu	18.848	8.233	<0.0001

Although soluble heavy metal levels were higher with old piers than new piers (usually < dl), there were only two statistically significant comparisons: Cr at 2.1 m (P = 0.0429) and As at 0.6 m (P = 0.0204). Chromium (2.1 m) was 0.0177 mg·kg^{-1} DW for old piers and < dl for new piers. Arsenic (0.6 m) was 0.0335 mg·kg^{-1} DW for old piers and < dl for new piers. These results indicate that soluble levels reflect equilibrium between metal release to the water column through mineralization (primarily decomposition of plant litter) and off-site removal through tidal action. If that is indeed the case we would not expect soluble levels to change appreciably over time after 2-3 years.

4. Conclusions

For new piers, soluble metal levels were highest within 2.9 m of the piers. Total As and Cu levels approached background levels at distances of 2.9 m and 1.4 m, respectively. For old piers, total As and Cu approached background levels at a distance of 9.0 m. Total Cr never exceeded background levels. Threshold effects concentrations were exceeded by sedimented As and Cu within 3.6 m of old piers and 2.1 m of new piers. Apparent effects thresholds were never reached. The only water chemistry variable impacted by piers was As with new piers. It was concluded that leachates accumulate only close to piers and at levels below

critical biological thresholds, and would be expected to have negligible ecological effects in reasonably flushed areas.

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