Sources, input pathways, and distributions of Fe, Cu, and Zn in a Chesapeake Bay tidal freshwater marsh

M.A. Knight · G.B. Pasternack

Abstract Tidal freshwater marshes exist at the interface between watersheds and estuaries, and thus may serve as critical buffers protecting estuaries from anthropogenic metal pollution. Bi-weekly samples of newly deposited marsh sediments were collected and analyzed for Cu, Zn, and Fe concentrations over 21 months from July 1995 to March 1997 in five distinct habitats at the head of Bush River, Maryland. Bi-weekly anthropogenic metal enrichments ranged from 0.9–4.7. Anthropogenic excess metal loadings averaged over 1996 ranged from 6–306 and 25–1302 μg cm^{-2} $year^{-1}$ between sites for Cu and Zn, respectively. Based on Fe-normalized trace metal signatures, Susquehanna River sediment does not significantly contribute to upper Bush River. Organic matter was found to dilute total metal concentrations, whereas past studies suggested organics enhance labile metal content. Analysis of metal input pathways shows that marsh metals are primarily imported from nearby subtidal accumulations of historic watershed material by tidal flushing.

Key words Chesapeake Bay · Marsh sedimentation · Metal accumulation · Trace metals

Received: 29 April 1999 / Accepted: 7 December 1999

M.A. Knight
Department of Geography,
University of Maryland Baltimore County, 1000 Hilltop Circle, Baltimore, MD 21250, USA

G.B. Pasternack (✉)
Department of Land, Air, and Water Resources,
University of California, One Shields Avenue, Davis, CA 95616-8626, USA
e-mail: gpast@ucdavis.edu
Tel.: +1-530-7549243
Fax: +1-530-7525262

Introduction

Coastal wetlands have long been characterized as sinks for metals and other potential pollutants (Windom 1975; Simpson and others 1983a; Odum 1988). Strong evidence for the buffering role of wetlands comes from core studies that show excess concentrations of metals in modern sediment strata relative to low background levels in pre-industrialization strata (Varekamp and others 1992; Bricker 1993; Valette-Silver 1993; Khan and Brush 1994). The sediment transport and geochemical mechanisms by which this buffering occurs have been widely studied for salt marshes (e.g. De Groot and Allersma 1975; Hedges 1977; Millward and Moore 1982; Zwolsman and others 1983; Allen and others 1990; Varekamp 1991), whereas the processes affecting metal chemistry in tidal freshwater marshes have received little attention, except for work carried out in Delaware Bay (Simpson and others 1983b,c; Orson and others 1992).

Metal accumulation and retention in tidal freshwater marshes can occur by both sediment transport and solute transport. The former encompasses input and burial of metals already incorporated into or onto fine inorganic and organic particles (Warren 1981; Olsen and others 1982; Olsenholler 1991). Along urbanized coasts, direct urban runoff and tidally redistributed urban pollution can significantly contribute to metal accumulation in tidal freshwater wetland soils (Simpson and others 1983c; Velinski and others 1994). For example, Orson and others (1992) reported sharp increases in metal concentrations coincident with the introduction of tidal flow to study sites. Solute transport mechanisms, on the other hand, involve adsorption of metals onto soil and decomposing plant litter (Millward and Moore 1982; Simpson and others 1983b,c, Orson and others 1992), downward migration of free metals into sedimentary strata (Simpson and others 1983b; Dubinski and others 1986), and plant uptake (Sculthorpe 1967; Banus and others 1975; Dowdy and Larson 1975).

Excluding geochemical studies involving direct application of sewage sludge that contains known amounts of heavy metals (Giblin and others 1980, 1986; Dubinski and others 1986), few data have been collected on short-term changes in metal accumulation on the surface of a tidal freshwater wetland. In this investigation, the concentrations of Cu, Zn, and Fe in new marsh surface deposits were monitored on a bi-weekly basis. As indicated by the sampling and analysis methods used, this study primarily addresses changes in surface deposit metal concentrations caused by sediment transport in an upper Chesapeake Bay tidal freshwater marsh. Data were used to evaluate on-going metal loading, the role of anthropogenic versus natural inputs, and the relative roles of tidal flushing versus other processes as input pathways. In addition, sediment metal contents in five distinct marsh habitats were compared to determine the significance of spatio-temporal differences in short-term metal accumulation.

Study site

HaHa Branch Wetland is located on the north flank of Otter Point Creek in Harford County, MD. Otter Point Creek feeds into the head of Bush River, which is located one tributary down from Susquehanna River on the western shore of upper Chesapeake Bay (Fig. 1). HaHa Branch Wetland consists of 3.8 ha of tidal freshwater marsh and 1.4 ha of riparian forest (Fig. 2). Water inputs to the wetland include direct precipitation, direct urban runoff from the adjacent townhouse community, Chesapeake Bay tidal pumping, HaHa Branch stream flow, groundwater, and some Winters Run stream flow. HaHa Branch drains the 5.5-km^2 watershed whose terminus is

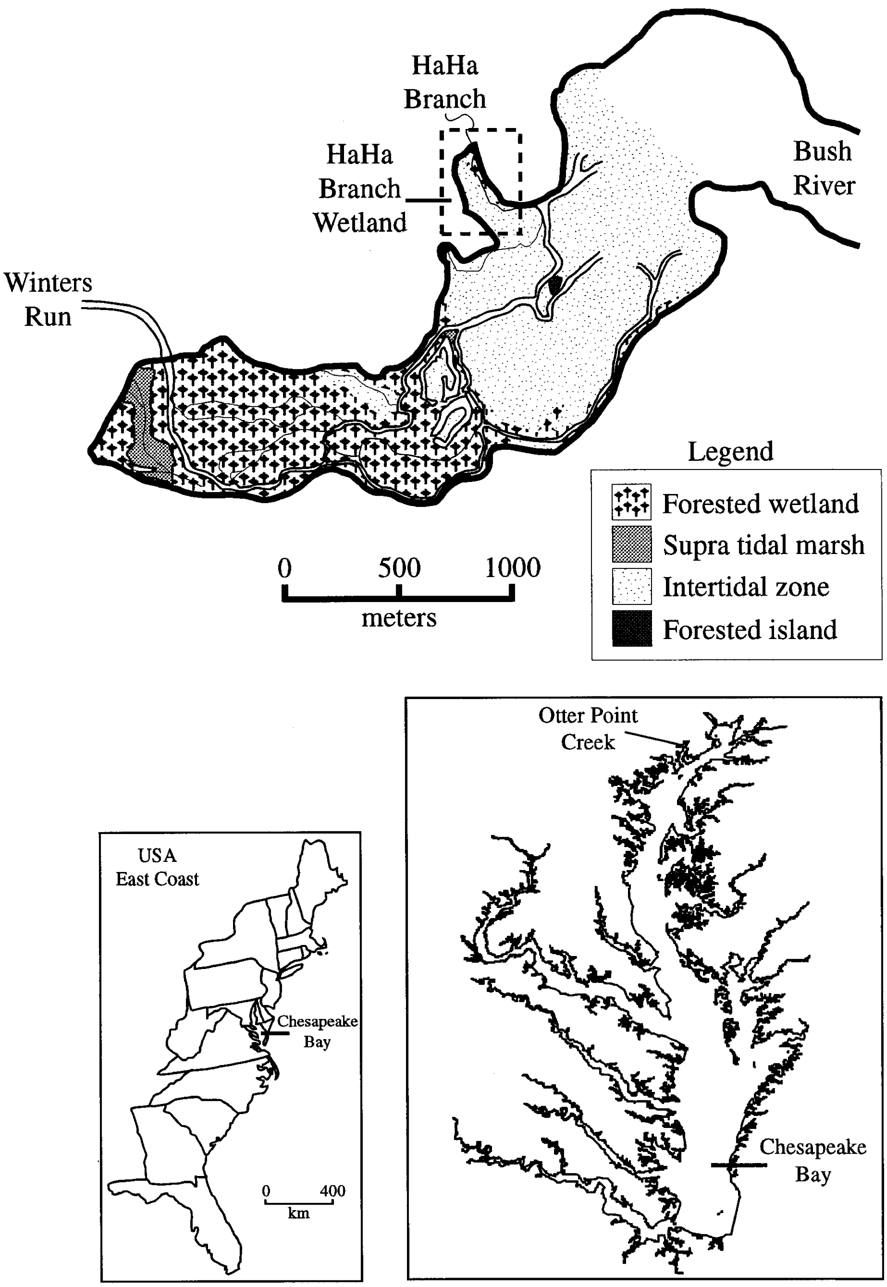

Fig. 1
Map of Chesapeake Bay showing the location and delta zonation of Otter Point Creek at the head of Bush River. HaHa Branch Wetland is on the northern flank of Otter Point Creek

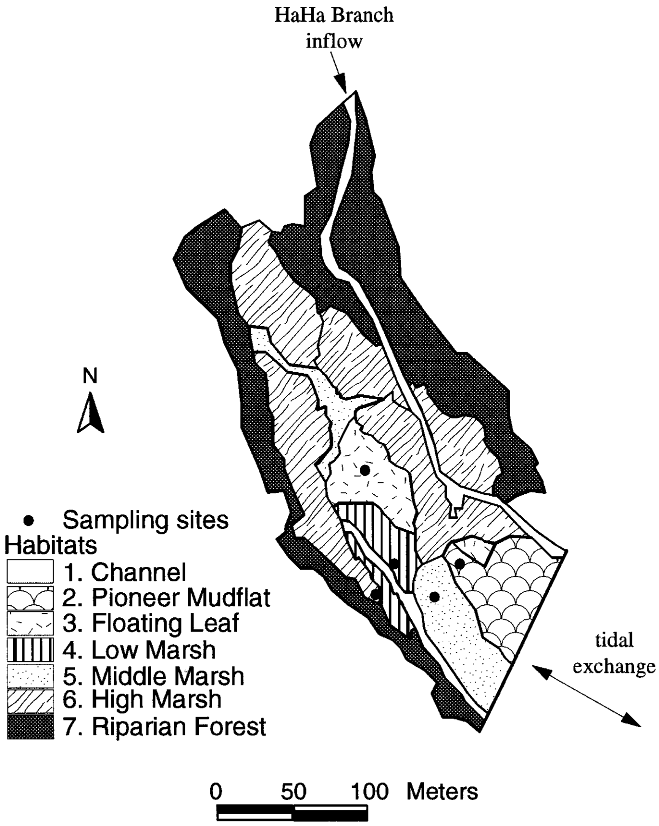

Fig. 2
HaHa Branch Wetland habitats identified by plant species and abundances. Sampling sites used for this study are shown (*circles*)

the study area, whereas Winters Run drains 150 km^2 into Otter Point Creek. The area surrounding the wetland consists of a townhouse community to the west, Maryland Route 40 to the north, and a trailer park to the east. Seasonal cycles in sediment deposition and erosion in this system were reported by Pasternack and Brush (1998). The 88-week average accumulation rate was found to be 1.21 g cm^{-2} year^{-1}, with bi-weekly point rates ranging from -7.43 to 29.96 g cm^{-2} year^{-1}. The vegetation at Otter Point Creek and HaHa Branch Wetland has been mapped and analyzed (Hilgartner 1995; Pasternack 1998). Nine distinct plant associations are present in seven tidal freshwater wetland habitat types at Otter Point Creek. Six of the habitat types are present in HaHa Branch Wetland, including pioneer mudflat, floating leaf, low marsh, middle marsh, high marsh, and shrub marsh (Fig. 2). In addition to being delineated by plant associations, habitats show statistically significant differences in sedimentation and organic content (Pasternack and Brush 1998).

Methods

Between 7 July 1995 and 13 March 1997, bi-weekly surface sediment samples were collected in preweighed, prewashed glass jars from detachable 20×20 cm^2 ceramic tiles that were anchored and mounted flush with the marsh surface (see Pasternack and Brush 1998 for full procedure). Collections were discontinued from mid-December to mid-March because colder than normal conditions, including a record-setting blizzard, resulted in the marsh freezing over with up to 15 cm of ice for most of the winter. Winter observations indicated that no sediment transport occurred when the marsh was frozen. Bi-weekly sediment samples from one site representative of each habitat (high marsh, middle marsh, low marsh, floating leaf, pioneer mudflat; see Fig. 2) were analyzed for metal content for the period 18 March 1996–21 November 1996. Past research has suggested that the high marsh would show the greatest temporal variability, so additional samples from 7 July 1995–18 March 1996 and 21 November 1996–13 March 1997 were analyzed, even though there were gaps in the sampling record as described above. Unless otherwise noted, all data analyses are reported for the common 1996 period. Because it is well known that metals preferentially occur in the finest grain-size fractions (De Groot and Allersma 1975; Förstner and Wittmann 1983; Varekamp 1991), surficial sediments adjacent to the bi-weekly sampling sites were collected and analyzed for their grain-size distributions according to Folk (1974) after organics were removed by reaction with 30 % H_2O_2 (full grain-size methodology reported in Pasternack 1998). Adjacent sediments had to be used because bi-weekly samples were too small to carry out this analysis along with all of the others. As it turned out, almost no material larger than 63 μmwas present at any of the sites, so sand content was not a significant factor in reported metal concentrations. Grain-size variations among fines were accounted for using a standard geochemical normalization technique (Loring 1991).

All retrieved samples were processed in the laboratory to obtain wet weight, dry weight, water content, organic content, and sedimentation rate. Exteriors of jars were washed and dried to remove excess material. Jars and samples were weighed wet, opened and heated in an oven at 80 °C until completely dry, and weighed again. Even though samples were collected bi-weekly, dry weights per tile were adjusted to units of g cm^{-2} year^{-1} to facilitate comparison with other studies. A fraction of each sample was assessed for organic content by combusting in a muffle furnace for 8 h at 450 °C and calculating weight loss-on-ignition. No adjustment of loss-on-ignition was made to account for sulfur oxidation to SO_2, because this element is not a significant constituent in the freshwater environment (Odum 1988). The ashed material was further used in metal analyses as described below. In addition to the field samples, the National Institute of Standards and Technology Standard Reference Material #1646a (“estuarine sediment” dredged from Chesapeake

Bay in the vicinity of the York River) was prepared using the same procedure in order to assess completeness of metal recovery given the sample handling procedure used and for use as a reference for determining excess metal inventories.

Sediment samples and the standard reference material were subjected to metal analysis using microwave digestion in concentrated HNO_3. The extraction technique used here does not yield total digestion because HF was not used; however, the harsh treatment accounted for a majority of metals in the sediment. Approximately 1-g samples were placed in 120-ml Teflon PFA vessels, and 10 ml of 14 M analytical grade HNO_3 was added before vessels were capped, reproducibly tightened (using a CEM Corporation capping station), and loaded onto a turntable. Venting tubes were connected to an MDS-81D exhaust fan at maximum fan speed. A CEM Microwave Digestion System, Model MDS-81D was programmed to run for 2.5 min at 100 % power (full power output rated at 630 ± 70 W), followed by 10 min at 80 % power. Vessels were allowed to cool and manually vented; 5 ml H_2O_2 was added dropwise. Solutions were filtered and brought to 100 ml with distilled water after the ensuing reaction was completed. All sample solutions were analyzed for Cu, Zn, and Fe using a Hewlett–Packard Model 5400 Inductively Coupled Plasma Mass Spectrometer.

Table 1
Time-averages and ranges of metal concentrations (μg g^{-1} dry weight for Cu and Zn; % of dry weight for Fe) for each metal in each habitat at HaHa Branch Wetland

Sampling site	Mean[a]	Range	n[b]
Copper			
High marsh[a]	24.2 ± 7.87	9.68–39.7	29
High marsh[b]	23.3 ± 7.97	9.68–39.7	17
Middle marsh	25.2 ± 5.15	15.3–31.4	16
Low marsh	31.5 ± 5.33	21.2–38.9	15
Floating leaf	22.3 ± 3.22	15.4–26.6	14
Pioneer mudflat	25.5 ± 4.84	20.3–37.7	16
Zinc			
High marsh[a]	102 ± 30.0	49.5–159	29
High marsh[b]	96.3 ± 25.6	51.6–140	17
Middle marsh	111 ± 28.6	66.0–146	16
Low marsh	127 ± 19.6	98.7–152	15
Floating leaf	97.0 ± 11.1	80.4–117	14
Pioneer mudflat	105 ± 18.4	85.8–140	16
Iron			
High marsh[c]	3.30 ± 1.29	0.86–5.31	29
High marsh[d]	2.94 ± 0.99	0.86–4.28	17
Middle marsh	3.68 ± 1.24	2.22–5.54	16
Low marsh	3.89 ± 0.66	2.85–4.67	15
Floating leaf	2.96 ± 0.59	2.18–4.02	14
Pioneer mudflat	2.66 ± 1.58	1.87–8.51	16

[a]Mean ± 1 SD of temporal variability in data reported to 3 significant figures
[b]Number of samples available for metal analysis
[c]Calculated using all data for the high marsh site
[d]Calculated using same 1996 data window as available for all sites

Results

Metal concentrations

Using the National Institute of Standards and Technology (NIST) as a basis, Fe, Cu, and Zn recoveries were > 95, 77, and 59 %, respectively. These recoveries compare very favorably with those from other sediment geochemistry studies, such as the recent analysis by Velinski and others (1994), who had 75 % Fe, 41 % Cu, and 63 % Zn recoveries. The chemical composition of each site studied is reported in Table 1 without extrapolation to 100 % recovery and on a dry weight basis to account for metal contributions from organic material. Despite these conservative estimates, copper and zinc concentrations in HaHa Branch Wetland were two to three times higher than those reported for a similar tidal freshwater marsh in the region under pristine sediment conditions at the beginning of the industrial revolution as determined by metal analysis of core samples (Khan and Brush 1994). When non-parametric Mann–Whitney U-Tests were performed to statistically compare habitat mean values, 1996 time-averaged Cu and Zn concentrations showed no significant differences among habitats at the 95 % confidence level, except for the low marsh, which was significantly higher than all other habitats for both trace metals. With respect to Fe, the pioneer mudflat was found to have a significantly lower concentration than the other habitats, and the low marsh was significantly higher than the floating leaf habitat.

Metal sources

The degree to which trace metals stem from anthropogenic sources as opposed to their natural association with inorganic sediment was determined using a standard geochemical normalization approach (Helz and others 1985; Windom and others 1989; Loring 1991). To validate the use of iron as the normalizing element, linear relationships between the trace metals and iron were established and statistical tests performed. Taken together, the data from all 1995–1997 samples showed positive correlations for both Cu and Zn, as indicated by Pearson's r (Fig. 3). F-tests for each case showed that the correlations were statistically significant above the 99.99 % confidence level. The Durbin–Watson statistic yielded insignificant serial correlations, which confirmed that the data consist of random samples of independent observations. When the data were habitat stratified, all habitats except the pioneer mudflat showed statistically significant positive correlations ($p < 0.01$) between trace metal concentrations and iron concentrations (Table 2). In the floating leaf habitat, Zn was strongly related to Fe, but Cu was not. In the pioneer mudflat, the slopes of the regressions are notably greater than those for the other habitats, excluding the one anomalously high Fe value.

Time-averaged Fe-normalized trace metal values are shown in Table 3 along with those from other studies for comparison. Fe-normalized trace metal values may be divided by those from an appropriate regional reference

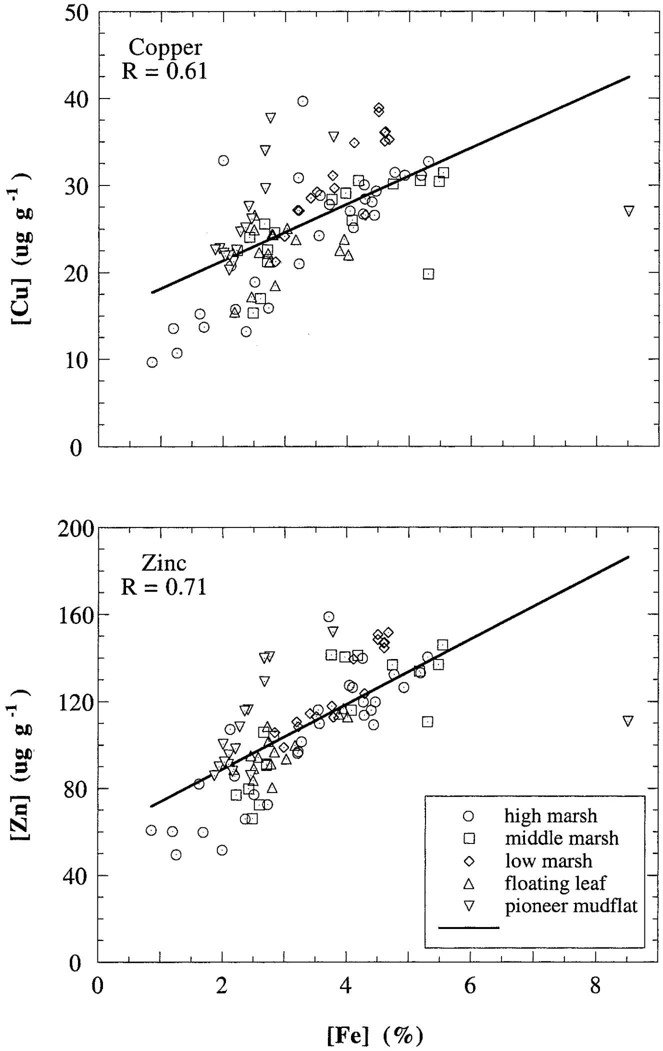

Fig. 3
Cu and Zn concentrations versus Fe concentrations in HaHa Brach Wetland sediments among all sampling locations for all sampling time intervals

to obtain enrichment factors that express the contribution of anthropogenic sources (Sinex and Helz 1981; Loring 1991; Velinski and others 1994). These calculations were carried out using the Chesapeake Bay estuarine mud NIST standard reference, but are not tabled separately because they are difficult to compare across studies, as different reference materials are often used for the same region. Moreover, it is unlikely that the NIST material is representative of truly pristine conditions, so enrichment factors are conservative estimates. Enrichment factors for HaHa Branch Wetland habitats were ~2, indicating that half of the Cu and Zn present is of anthropogenic origin on average. Although there was no spatial trend among habitats, the pioneer mudflat had the greatest average enrichment factors, while the high marsh had the highest individual enrichment factors. These maximum Fe-normalized metal values exceeded the NIST reference by factors of 4–5 (Table 3).

Table 2
Correlation coefficients and F-test results indicating statistically significant linear increases in Cu and Zn concentrations with increasing Fe for most habitats

Sampling site	Cu versus Fe	*p*	Zn versus Fe	*p*
High marsh	0.775	< 0.00001	0.869	< 0.00001
Middle marsh	0.651	< 0.005	0.814	< 0.0001
Low marsh	0.882	< 0.00001	0.945	< 0.00001
Floating leaf	0.269	0.332	0.794	< 0.0005
Pioneer mudflat	0.283	0.270	0.276	0.284

Table 3
Time-averaged ratios of Cu : Fe and Zn : Fe based on μg g^{-1} dry weight

	$10^4 \times$ Copper : iron		$10^3 \times$ Zinc : iron	
Site	Mean	Max	Mean	Max
High marsh	8.4 ± 2.8	16.4	3.5 ± 1.2	7.1
Middle marsh	7.3 ± 1.8	10.1	3.1 ± 0.5	4.0
Low marsh	8.1 ± 0.4	8.6	3.3 ± 0.2	3.7
Floating leaf	7.7 ± 1.5	10.6	3.3 ± 0.4	4.1
Pioneer mudflat	10.6 ± 2.2	13.7	4.4 ± 0.9	5.2
NIST Chesapeake Bay saline mud	4.0		1.5	
Bush River mouth brackish bed[a]			8.0	
Harford County shoreline[a]	14.7		1.2	
Deer Creek freshwater bed[b]	8.4		2.5	
Conowingo Reservoir[b]	12.8		8.0	
South River, MD, brackish bed[c]	0.9		0.6	
Potomac River, MD, freshwater bed[d]	13.4		8.2	
Upper St. Lawrence River mudflat[e]	11.8		6.0	
Pataguanset, CT, salt marsh[f]	25.4		1.9	
Griswold Point, CT, saline mudflat[g]	29.5		6.8	

[a]Helz and others (1985)
[b]USGS (personal communication, 1992 data)
[c]Marcus and others (1993)
[d]Velinski and others (1994)
[e]Coakley and others (1993)
[f]Scholand (1992)
[g]Varekamp (1991)

Bi-weekly metal profiles

Bi-weekly concentrations of Cu, Zn, and Fe in the five habitats showed some random variability and some nonrandom trends. The 88-week record obtained for the high marsh provides the most information for assessing temporal trends (Fig. 4). All three metals showed a seasonal cycle with high concentrations in early summer that decreased until October when a spike input occurred. The spike was followed by a winter minimum and then a rise through spring. Comparing 1995 to 1996, the summer decrease was not as dramatic in the earlier year, but an October peak was clearly present. In terms of Fe-normalized trace metal values, both Cu and Zn showed significant anthropogenic inputs in autumn and early spring. The October spike in metal concentrations is only

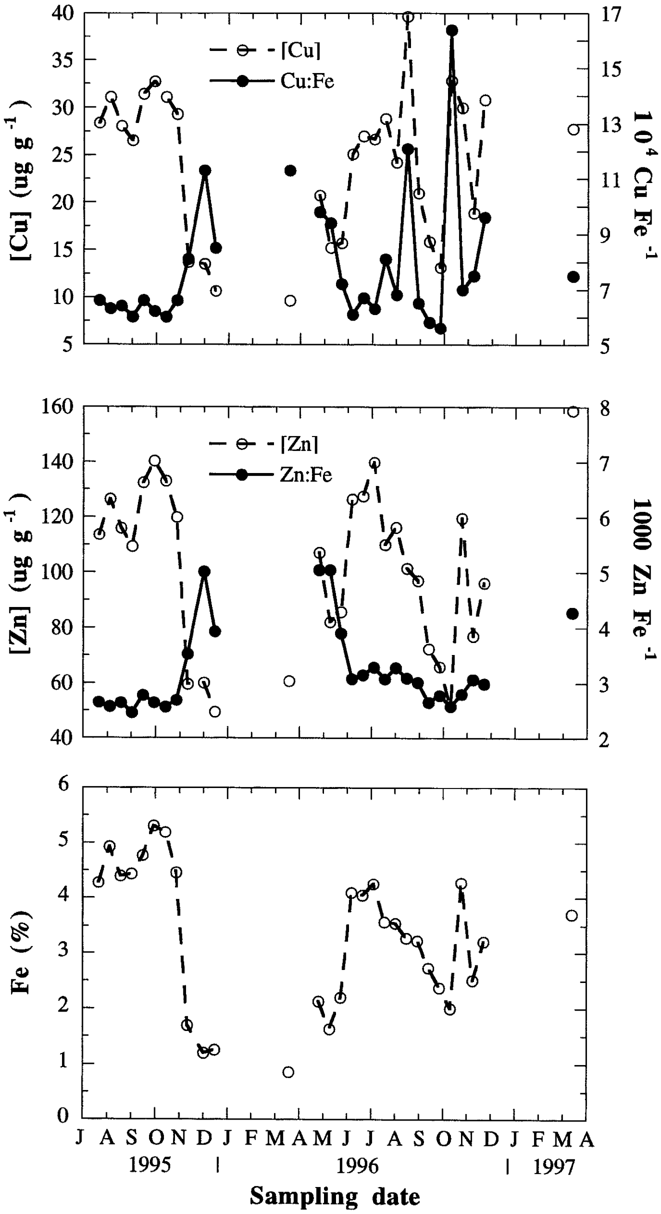

Fig. 4
Time series of high marsh bi-weekly surface sediment metal concentrations and Fe-normalized trace metal values

indicative of anthropogenic excess for Cu. Also, Cu experienced a spike of excess input in mid-August.

Metal concentrations in the remaining four habitats are reported for 1996 and show similar patterns among the three metals (Fig. 5). In terms of iron concentrations, the middle marsh had a summer plateau at double the background level, the low marsh and floating leaf habitats showed an overall decreasing trend from 4 to less than 3 %, and the pioneer mudflat had a nearly constant value except for an anomalous spike in autumn. The sediment sample that generated the spike was homogenized and tested twice to insure that the anomaly was not a laboratory artifact; the same high iron concentration was found both times. Copper and zinc concentrations in the middle marsh followed the same pattern as iron overall. In the low marsh, both experienced rapid drops during August and peaks in early autumn. In the floating leaf habitat copper had no trend, whereas zinc showed a steady decrease that paralleled iron. The pioneer mudflat had nearly constant trace metal concentrations until both copper and zinc shot up in September. These sharp increases were not associated with the anomalous iron spike. No impacts of the three 1996 hurricanes (Bertha, Fran, and Edouard) that passed the region and significantly affected water levels (Pasternack 1998) registered in any metal data.

When trace metal concentrations were normalized by Fe, they showed quite different temporal patterns (Fig. 5). In the middle marsh the values were highest in spring and late autumn, as was observed in the high marsh. The low marsh and floating leaf habitats showed no trends, but the latter had greater variability. In the pioneer mudflat, both normalized trace metals showed early autumn peaks followed by strong drops. The drops were caused by the anomalous iron value.

Role of organic matter

Previous studies have supported differing conclusions as to whether increases in sediment organic matter yield higher metal concentrations. Pasternack and Brush (1998) observed seasonal cycles in bi-weekly measurements of organic content for HaHa Branch Wetland habitats, so it was necessary to determine how those cycles impacted metal concentrations. The presence of organic matter can potentially increase soil metal concentrations by adsorption of metals from surrounding media onto plant litter, as well as contribution of the metals directly contained in the particulate organics. In this study, the only statistically significant correlations between metal concentration and percentage of organic matter were observed in the middle marsh and high marsh. The correlation coefficients for these cases were negative, indicating a dilution effect (Table 4).

Metal loadings

March through November metal loadings (μg cm^{-2} $year^{-1}$) were determined for total load and anthropogenic excess (Table 5). Total loads were calculated by multiplying metal concentrations by corresponding bi-weekly sediment accumulation rates, whereas anthropogenic loadings were estimated by adjusting total loads according to the following equations:

$$\text{Anthropogenic}+\text{natural}=\text{total} \qquad (1)$$

$$\text{Anthropogenic}\cdot\text{natural}^{-1}=\text{EF} \qquad (2)$$

$$\text{Anthropogenic}=\text{total}\cdot\text{EF}\cdot(\text{EF}+1)^{-1} \qquad (3)$$

where EF denotes the enrichment factor. These calculations assume that accumulated sediment would not remobilize at any time during the study period had it been left in place. The assumption is reasonable because no HaHa Branch Wetland sites showed erosion from March

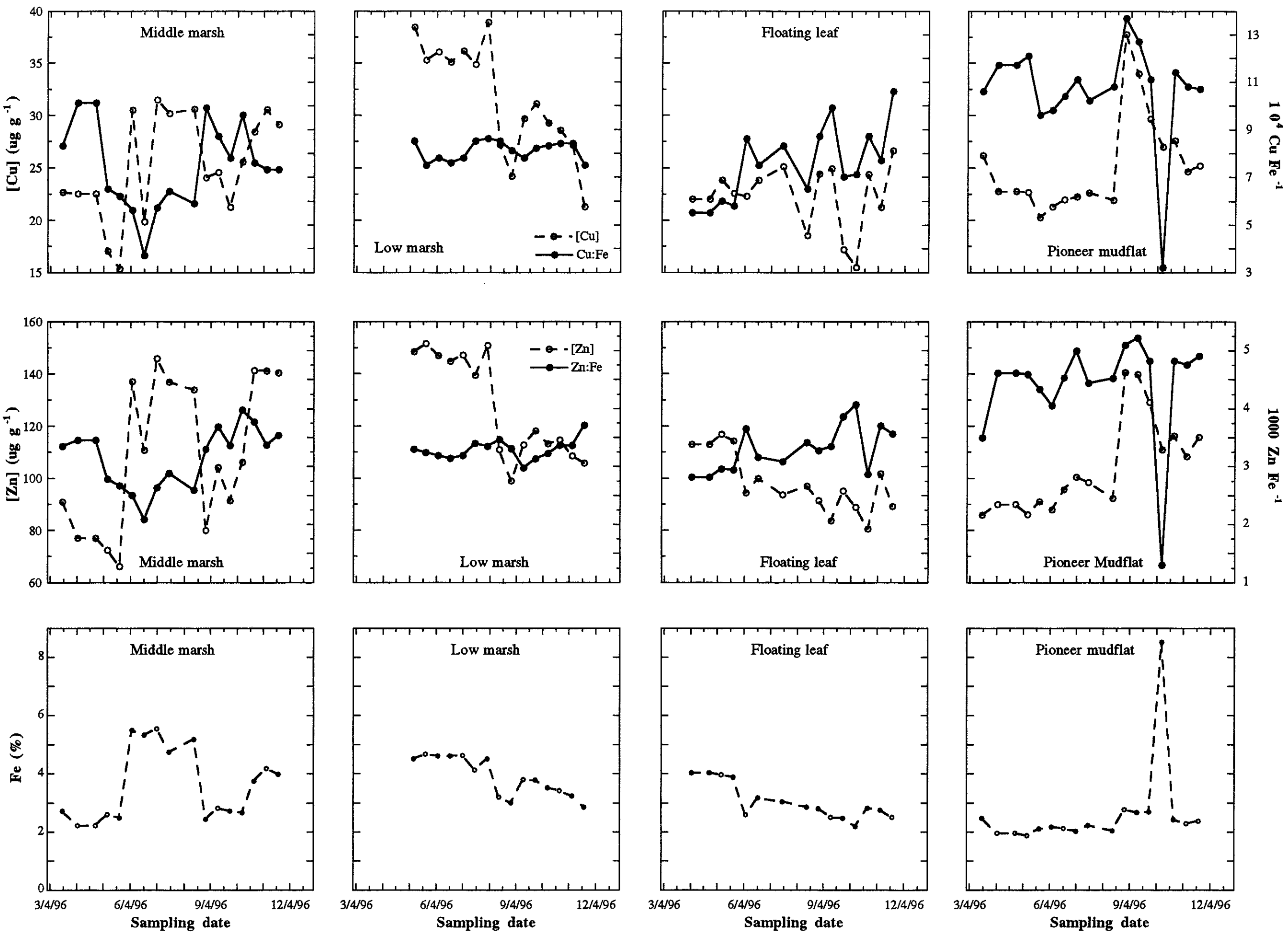

Fig. 5
1996 bi-weekly surface sediment metal concentrations and Fe-normalized trace metal values for middle marsh, low marsh, floating leaf, and pioneer mudflat sites

through November (Pasternack 1998). To the contrary, sedimentation rates were extremely high and sampled sediment would have been quickly buried. Pasternack and Brush (1998) reported erosion for the high and low marsh sites during winter 1997, but when averaged over a whole year, even these sites experienced substantial net deposition. On average, March through November sediment loading values overestimate net annual sediment loadings by 31 %, and this percentage is probably close to the overestimate in each metal loading. Reported metal loadings based on bi-weekly measurements should not be extrapolated over years to decades because they do not include changes via compaction, solute transport, extreme events, etc. Nevertheless, sub-estuarine deltas are unique among coastal systems because of the strong coupling with watershed processes and impacts of human activities (Brush 1984).

Time-averaged loads for all three metals show an exponential decrease as habitat (and elevation) increases, assuming a linear habitat gradient, with the low marsh having a higher than expected value (Fig. 6). The anthropogenic excesses had the same trends as the totals. The exponential decreases in metal loadings reflect the large range in sedimentation rates among the habitats (Paster-

Table 4
Correlation coefficients and F-test results indicating statistically significant inverse relationships between metal concentrations and organic content for some sites

Sampling site	Cu versus organic	p	Zn versus organic	p	Fe versus organic	p
High marsh	−0.584	0.014	−0.506	0.038	−0.795	0.0001
Middle marsh	−0.656	0.006	−0.642	0.007	−0.528	0.036
Low marsh	−0.423	0.116	−0.404	0.135	−0.453	0.090
Floating leaf	−0.108	0.714	−0.411	0.144	−0.509	0.063
Pioneer mudflat	0.184	0.496	0.377	0.150	0.103	0.704

Table 5
Metal loadings ($\mu g\ cm^{-2}\ year^{-1}$) in HaHa Branch Wetland and comparable depositional systems

Total metal loadings	Copper		Zinc		Iron	
Sampling site	Mean	Range	Mean	Range	Mean	Range
High marsh	8.72 ± 7.52	0.54–32.8	39.7 ± 39.8	3.37–172	12,200 ± 12,300	476–52,300
Middle marsh	27.2 ± 18.9	8.32–78.9	117 ± 80.5	40.1–334	38,400 ± 25,800	11,400–95,100
Low marsh	152 ± 129	3.75–475	620 ± 546	18.7–2040	192,000 ± 170,000	5030–630,000
Floating leaf	114 ± 81.8	35.0–341	510 ± 390	131–1670	158,000 ± 133,000	37,000–565,000
Pioneer mudflat	419 ± 279	1.72–1130	1750 ± 1100	5.66–4210	415,000 ± 271,000	1620–994,000
Jug Bay, MD, middle marsh[a]	15		42.5			
Jug Bay, MD, floating leaf[a]	8.75		26.5			
Bush River mouth[b]			140		18300	
South River, MD, marsh[c]	1.4		10.1			
Upper Narragansett Bay, RI salt marsh[d]	46.2		31.8			

Excess metal loadings[h]	Copper		Zinc	
Sampling site	Mean	Range	Mean	Range
High marsh	5.65 ± 4.60	0.40–20.2	27.4 ± 27.4	2.78–118
Middle marsh	17.7 ± 13.2	5.41–54.3	78.9 ± 56.4	28.2–238
Low marsh	102 ± 84.5	2.46–312	423 ± 372	13.3–1400
Floating leaf	74.1 ± 51.2	23.7–206	349 ± 259	87.9–1100
Pioneer mudflat	306 ± 217	1.26–877	1300 ± 864	3.95–3250
Jug Bay, MD middle marsh[a]	7.5		17,5	
Jug Bay, MD floating leaf[a]	1.25		2.5	
Griswold Point, CT mudflat[e]	7		17.1	
Pataguanset, CT salt marsh[f]	0.18		−0.05	
Shelter Island, NY salt marsh[g]	0.5		0.4	
Alley Pond, NY salt marsh[g]	27		12	

[a]Khan and Brush (1994)
[b]Helz and others (1985)
[c]Marcus and others (1993)
[d]Bricker (1993)
[e]Varekamp (1991)
[f]Scholand (1992)
[g]Cochran and others (1998)
[h]See text for equations

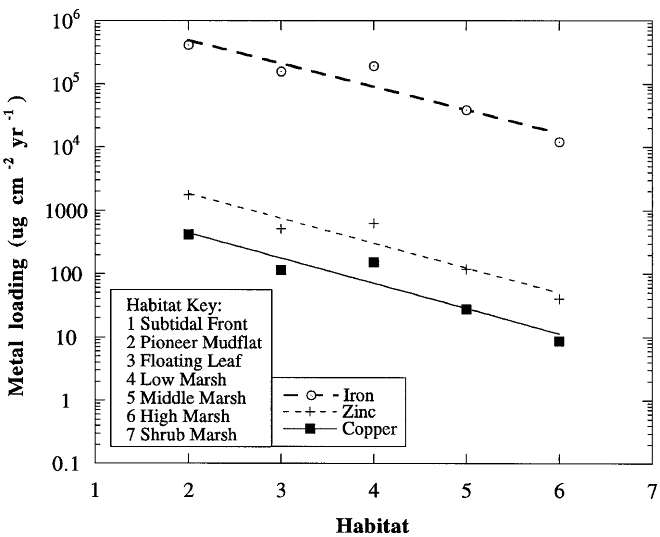

Fig. 6
Metal loadings along an assumed linear habitat gradient showing the unexpectedly high amounts in the low marsh

nack 1998). As exemplified for zinc (Fig. 7), variation in sedimentation far outweighs differences in metal concentrations in determining the loading, so changes in metal loading over time mimic changes in sedimentation. Time-averaged metal loadings for the 1996 data were combined with the area of each habitat within HaHa Branch Wetland to obtain an estimate of total annual wetland metal influx (Table 6). In contrast to the unit area metal loadings of Table 5, habitat-wide influxes show a different spatial pattern. Despite the higher unit area loading for the middle marsh, the larger area of high marsh habitat yields a greater total metal contribution to the wetland. The extreme annual accretion rate in the pioneer mudflat is still responsible for the greatest metal influx among habitats for all three metals studied.

Metal pathways

Although several potential metal deposition pathways exist, including sediment transport via runoff, atmospheric deposition, and tidal redistribution, it is difficult to rank and quantify contributions without measuring the mass balance for each metal. As an alternative approach, the relative roles of tidal flushing versus other processes as input pathways were investigated by taking advantage of the variability of metal concentrations as a

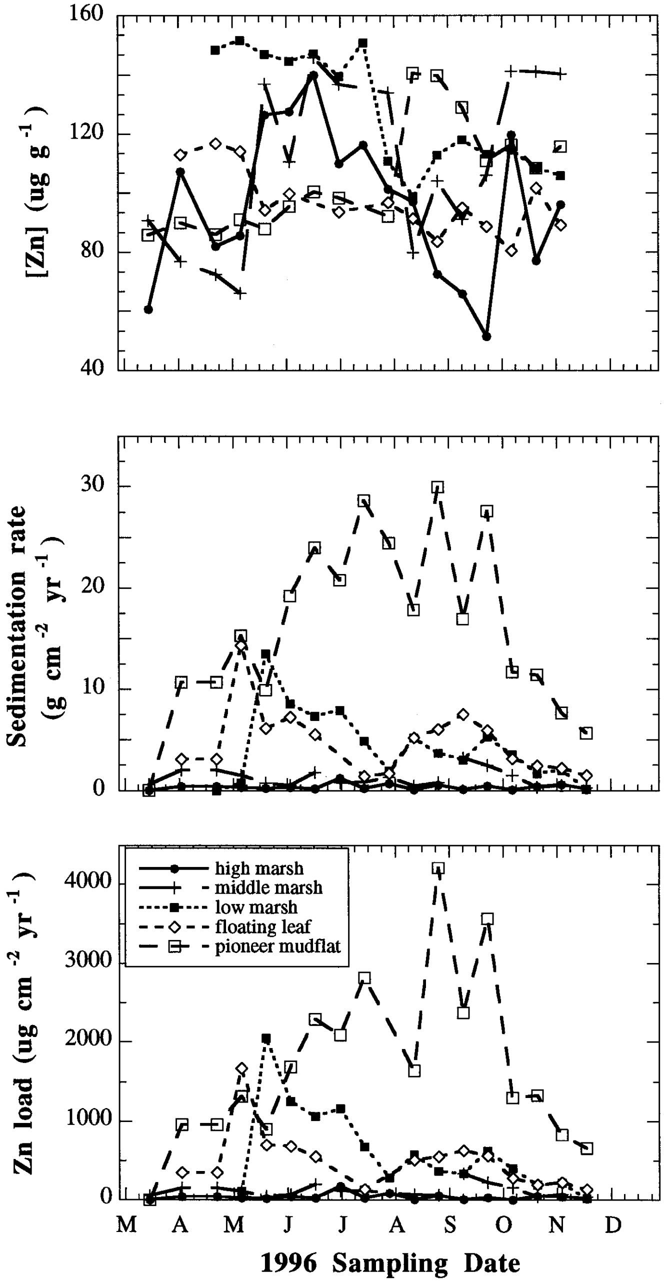

Fig. 7
Zinc concentrations, total sedimentation rates, and zinc loadings for the five habitats over the 1996 season

function of sedimentation rate. If a single input were responsible for transporting sediment and metals into the marsh, then metal concentrations would be constant regardless of sedimentation rate, assuming that the input had a constant composition. Such is the case for the pioneer mudflat, with respect to all three metals and organic content, except for some small variability in the data (Fig. 8). The dominant single input pathway of sediment, and thus of metals for the pioneer mudflat, has been observed to be tidal flushing of nearby subtidal muds (Pasternack 1998), so it is reasonable to assume that the metal concentrations in the pioneer mudflat are representative of those in the tidal pathway. The subtidal muds include metals derived from watershed erosion, atmospheric deposition, shoreline erosion, and estuarine transport. In contrast, if a metal pathway was independent of tidal flushing, then concentrations would vary independently of tidally-induced sedimentation. The high marsh demonstrates this fairly well, having no correlation between metal concentrations and sedimentation rate (Fig. 8). Non-tidal metal pathways include direct atmospheric deposition, urban runoff, influx of riparian debris, groundwater discharge, and in situ biomass accumulation. Using these two conceptual pathway endmembers, the relative quantities of metals transported by tides versus other processes were calculated using the following algorithm:

$$\begin{aligned} &\mathrm{IF}[\mathrm{M}] - [\mathrm{C}] > 0 \\ &\text{Then \% additional inputs} = 100\,\frac{[\mathrm{M}] - [\mathrm{C}]}{[\mathrm{M}]} \\ &\text{ELSE \% depletion} = 100\,\frac{[\mathrm{M}] - [\mathrm{C}]}{[\mathrm{C}]} \end{aligned} \tag{4}$$

where [M] is the measured metal concentration at a site and [C] is the tidal pathway metal concentration as represented by the mean value in the pioneer mudflat. Note, that it is irrelevant whether concentrations or mass loadings are used because the sedimentation rate cancels out of the equations. The test in the first line of equation (4) is necessary to determine whether the site is enriched or depleted relative to the tidal source. If it is enriched, then the additional amount is calculated relative to the total input, whereas, if it is depleted, then it is calculated relative to the expected tidal baseline.

When relative source contributions were calculated and time-averaged, significant habitat trends were evident

Table 6
Annual fluxes to HaHa Branch Wetland habitats, expressed in kg year^{-1} to 3 significant figures

Sampling site	Cu	Zn	Fe	Organics	Total sediment
High marsh	1.33	6.08	1,860	16,300	58,300
Middle marsh	1.18	5.11	1,670	9,620	52,600
Low marsh	3.20	13.0	4,030	11,200	90,700
Floating leaf	2.71	12.1	3,760	14,800	113,000
Pioneer mudflat	15.8	65.9	15,700	49,800	613,000
Marsh total	24.3	102	27,000	102,000	928,000

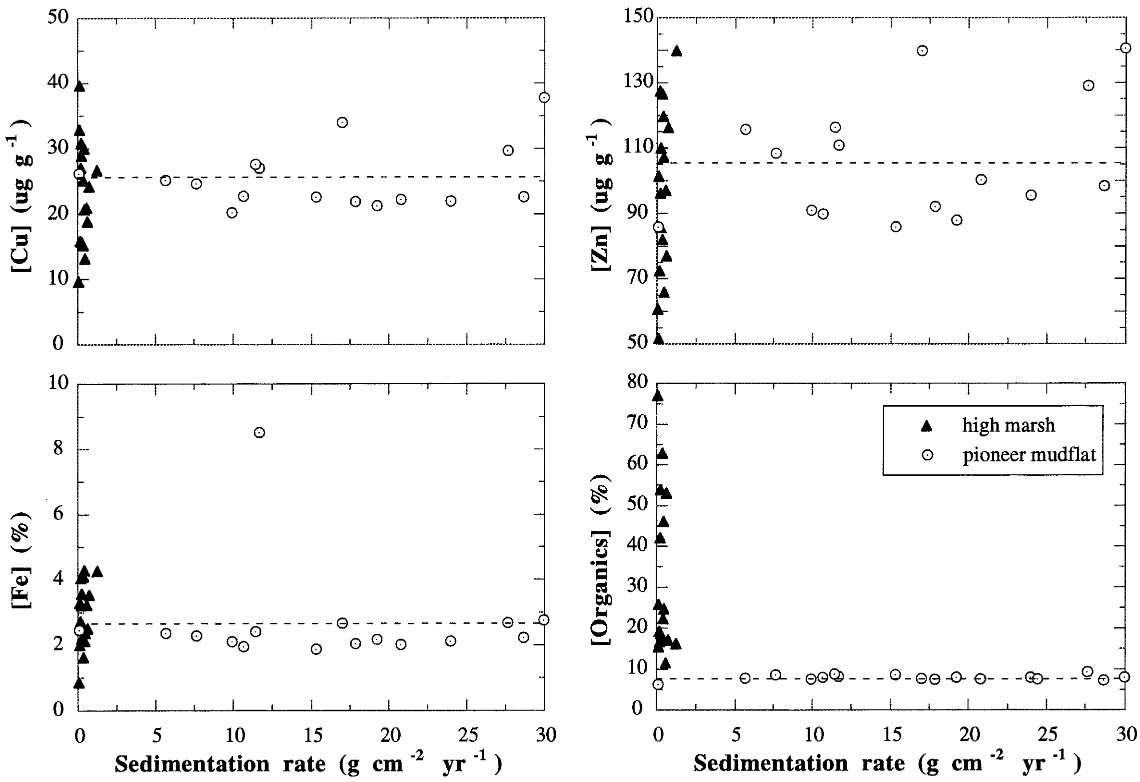

Fig. 8
Metal concentrations and organic content versus sedimentation rate for the high marsh and pioneer mudflat sites. *Dashed line* is the average pioneer mudflat value, which is taken to be the concentration of the tidal input pathway

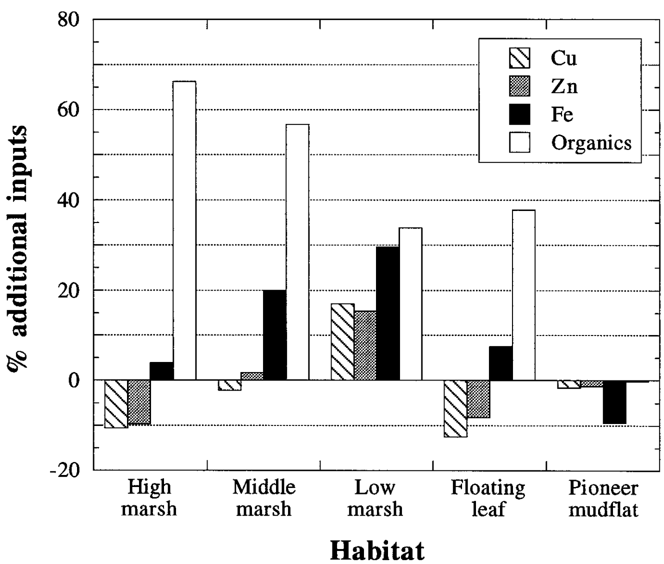

Fig. 9
Percent of metal and organic concentrations not accounted for by the tidal input pathway. *Negative values* indicate depletion relative to the expected concentration derived from the tidal input

(Fig. 9). All habitats except the pioneer mudflat, which was mostly devoid of standing vegetation, received organic material from sources other than tidal flushing. Both the high marsh and middle marsh received more than half of their organic contents from non-tidal sources, with bi-weekly maximum non-tidal inputs accounting for as much as 90 and 70 % of the total content at each site, respectively. In terms of iron, the peak time-averaged non-tidal input occurred in the low marsh, with diminishing inputs away from it. The pioneer mudflat appears depleted, but this is mostly an artifact caused by the single anomalous data point that pulls the baseline concentration line above most pioneer mudflat iron values (Fig. 8). Ideally, the pioneer mudflat should have zero values for all constituents, but scatter in the data leaves small residuals, which were negative in this case. Copper and zinc showed similar spatial trends, with significant depletion in the high marsh and floating leaf habitats, and significant additional sources in the low marsh (Fig. 9).

Discussion

Tidal freshwater marsh sites investigated in this study had significant spatio-temporal patterns in bi-weekly metal chemistry. In the spatial domain, the low marsh stood out among habitats for being enriched in time-averaged trace metal concentrations, but its Fe-normalized trace metal values were not significantly different from the other habitats (Tables 1 and 3). Unlike these difficult to distinguish parameters, metal loadings did changed significantly along the habitat gradient (Fig. 6) because of the spatial distribution of sedimentation rates (Pasternack 1998; Pasternack and Brush 1998). As sedimentation rates decrease with increasing elevation, decreased flood duration, and high bottom roughness (caused by high plant stem density), the mass of metal imported decreases.

Metal concentrations versus organic content also showed statistically significant differences among habitats. The high and middle marsh habitats have significant negative correlation coefficients (Table 4), indicating that organic matter dilutes soil metal concentrations at this time scale. Moreover, because the relationships between metal concentration and organic content are not significant for the other marsh habitats, organic matter does not play a role in sorbing significant quantities of metals. In contrast to previous findings, the negative tendencies for the low marsh and floating leaf habitats support some degree of metal dilution by organic matter, even though the organic content of these zones may be insufficient to create a statistically significant effect. The measurement of total metal content and the focus on sediment processes in this study help to account for this observed dilution effect by organic matter; organics primarily affect solute sorption and are, therefore, more associated with labile metal concentrations. Dilution by organic content when considering total metals is consistent with the reported result that several tidal freshwater marsh plants have metal concentrations five to ten times lower than those in the surrounding soil (Simpson and others 1983b,c). The “sponge” effect of litter cannot be adequately assessed in this system without measuring labile metal content, but since the total decomposition time of plant species in tidal freshwater marsh systems ranges from less than 2 weeks for the wettest species to several years for the most robust (Simpson and others 1983b; Findlay and others 1990), any ultimate impact of litter in long-term sequestration would likely be habitat dependent.

In the time domain, all three metals showed seasonal cycles in concentration. The cycles in Cu and Zn largely mimicked those of Fe and overall sedimentation. Fe-normalized trace metal values showed an inverted cycle, with early spring and late autumn peaks. These excess inputs corresponded with times when vegetation was either decaying or not present at all in the marsh. Pasternack and Brush (1998) reported autumn peaks in high marsh and middle marsh organic content caused by the influx of riparian foliage with the change of seasons. This influx was evident in the high percentage of organic matter for non-tidal input pathways overall (Fig. 9) and in autumn specifically. However, this riparian influx is unlikely to account for Fe-normalized trace metal peaks because of the previously discussed dilution effect by organic matter. Moreover, the high marsh showed a depletion of metals relative to the concentration of the tidal source and the middle marsh showed no deviation from it (Fig. 9). Other possible pathways that could account for the excess spring and autumn metals are stream-flow, groundwater discharge, and urban runoff. The three highest runoff events after January 1996 in the Winters Run basin all occurred in autumn, and they all significantly raised water level elevations in the marsh (Pasternack, unpublished data). If these floods and corresponding direct urban runoffs carried significant anthropogenically-derived Cu and Zn in their suspended sediments, which is likely, the high water levels in the marsh would have enabled them to access higher elevation areas. Unfortunately, no final answer can be obtained without event-based water quality measurements, which were beyond the scope of our program.

Comparing HaHa Branch Wetland Fe-normalized metal values (Table 3) and metal loads (Table 5) to other areas of Chesapeake Bay and beyond indicates that this system is in the middle range of values reported in the literature. Helz and others (1985) studied bed material along the longitudinal axis of Chesapeake Bay and reported Zn:Fe ratios at the mouth of Bush River double the average for HaHa Branch Wetland. Similarly, the US Geological Survey reports that the bed material behind Conowingo Reservoir on Susquehanna River has a Cu:Fe ratio of nearly 13 and Zn:Fe of 8. These data are very important because they suggest that the metal-enriched suspended load from Susquehanna River is not a major contributor to sedimentation in the marshes of upper bay tributaries, or else the metal ratios in the sediments there would reflect the ratios of Susquehanna-derived material. In contrast to those of the Susquehanna River, the trace metal signatures of Bush river marsh sediments very closely resemble those reported for Deer Creek bed material sampled near Gorsuch Mills, Maryland, located just west of northern Harford County (USGS, personal communication). The Deer Creek basin is adjacent to the Winters Run basin, so this sample is likely indicative of the source material supplying Otter Point Creek and HaHa Branch Wetland. Elsewhere around the bay, Potomac river bed material is substantially more polluted, whereas South River bed material is depleted with respect to natural loadings of Cu and Zn. Tidal freshwater mudflats in upper St. Lawrence River turn out to be somewhat more polluted than HaHa Branch Wetland, but within the spread of the spatio-temporal variability reported here (Table 3). Cores from Connecticut River salt marshes and mudflats are substantially more enriched in Cu and somewhat more enriched in Zn (Table 3).

In terms of metal loading, the high spatio-temporal variability in HaHa Branch Wetland makes it difficult to compare against other systems, where typically just one or two cores are analyzed with 5- to 20-year resolution. Nevertheless, it appears that there are significant differences between HaHa Branch Wetland and another Chesapeake Bay tidal freshwater marsh, Jug Bay on the Patuxent River. In the latter, modern Cu and Zn loadings for a middle marsh site and a floating leaf site were 2–15 times lower as determined from cores (Table 5). Part of this difference stems from lower metal concentrations in the Jug Bay study, but much of the difference is a result of the higher sedimentation rates reported here. Since this study investigated short-term accretion, it excluded processes that significantly reduce sedimentation rates when averaged over the long term, such as compaction and diagenesis. Also, although most sediment was observed to be true deposition and not simply resuspension within the individual habitats, there were some isolated cases of early spring and late autumn erosion, which did not leave sediment behind for laboratory metal analysis of eroded material. Beyond Chesapeake Bay, metal loadings in salt marshes and mudflats show a range of values that are lower than those in HaHa Branch Wetland (Table 5). Material entering HaHa Branch Wetland may be transported by tidal flushing or a variety of other carriers (e.g. atmospheric deposition, rain, urban runoff, groundwater, and river floods). The total load of iron entering HaHa Branch Wetland exceeded that reaching the mouth of Bush River from Susquehanna River by an order of magnitude. This difference is accounted for by the abundance of low level metal pollution stored in Otter Point Creek subtidal mud that is constantly transported into HaHa Branch Wetland from March to November, whereas upper Chesapeake Bay receives the majority of its metal inputs during infrequent hurricanes (Helz and others 1985). Pasternack (1998) showed that wind-enhanced tidal flooding was the predominant mechanism for sediment influx into the wetland from the subtidal zone. These data indicate that tidal flushing plays a major role in metal influx (Fig. 9), but it must be emphasized that the main bay is not acting as the metal source. Rather, watershed-derived sediment that was historically stored in Bush River is being redistributed via this process. Also, the new approach reported here for estimating constituent input pathways based on source sediment concentrations and fluxes shows that tidal flooding alone cannot account for the observed concentrations (Fig. 9). Additional sources of organic material have been observed in the field to derive from a combination of in situ emergent plants and influxes of riparian debris. Additional pathways of metals in the law marsh habitat, as well as the depletion of Cu and Zn from the tidal input pathway in the floating leaf and high marsh habitats, cannot be readily explained, as many potential pathways, such as atmospheric deposition cannot account for the observed spatial variability.

Conclusion

HaHa Branch Wetland is a tidal freshwater wetland located at the critical interface between an Atlantic coastal plain stream and a Chesapeake Bay sub-estuary. Field monitoring of sedimentation and metal chemistry has shown that the wetland is taking in anthropogenically-derived Cu, Zn, and Fe in similar quantities to other polluted coastal wetlands along the Atlantic seaboard, but significantly less than the most polluted tributaries, such as the Potomac River near Washington, DC, the East River near New York City, and the Patapsco River near Baltimore, Maryland. Based on Fe-normalized trace metal values for HaHa Branch Wetland and upper Chesapeake Bay, the sediments accumulating at the head of Bush River do not include a significant Susquehanna River component, and are principally derived from the soils of Harford County. The spatio-temporal patterns in metal accumulation are primarily driven by spatio-temporal patterns in tidally-derived sedimentation, but during spring and autumn additional input pathways, perhaps storms and direct urban runoff, play an important role.

Acknowledgements This research was supported by NOAA and Maryland Department of Natural Resources. Laboratory geochemical analyses were funded by a University of Maryland Baltimore County Provost Undergraduate Research Award to M. Knight. We gratefully acknowledge Dr. George Murray (The Johns Hopkins University Applied Physics Laboratory) and Amanda Jenkins (University of Maryland Baltimore County) for providing access to lab equipment at Johns Hopkins University Applied Physics Laboratory and for assistance with using the mass spectrometer. We thank Dr. Grace Brush and Dr. Alan Stone (The Johns Hopkins University) as well as Dr. Andrew Miller (University of Maryland Baltimore County), Suzanne Bricker (National Ocean Service), and anonymous reviewers for discussions and reviews. Numerous students and community volunteers assisted in our field sampling program.

References

Allen JRL, Rae JE, Zanin PE (1990) Metal speciation (Cu, Zn, Pb) and organic matter in an oxic salt marsh, Severn Estuary, southwest Britain. Mar Pollut Bull 21 : 574–580

Banus MD, Valiela I, Teal JM (1975) Lead, zinc, and cadmium budgets in experimentally enriched salt marsh ecosystems. Estuarine Coast Mar Sci 3 : 421–430

Bricker SB (1993) The history of Cu, Pb, and Zn inputs to Narragansett Bay, Rhode Island as recorded by salt-marsh sediments. Estuaries 16 : 589–607

Brush GS (1984) Patterns of recent sediment accumulation in Chesapeake Bay (Virginia–Maryland, USA) tributaries. Chem Geol 44 : 227–242

Coakley JP, Nagy E, Sérodes J-B (1993) Spatial and vertical trends in sediment-phase contaminants in the upper estuary of the St Lawrence River. Estuaries 16 : 653–669

Cochran JK, Hirschberg DJ, Wang J, Dere C (1998) Atmospheric deposition of metals to coastal waters (Long Island Sound, New York USA): evidence from saltmarsh deposits. Estuarine Coast Shelf Sci 46 : 503–522

De Groot AJ, Allersma E (1975) Field observations on the transport of heavy metals in sediments. In: Krenkel PA (ed) Heavy metals in the aquatic environment. Pergamon Press, New York, pp 85–101

Dowdy RH, Larson WE (1975) Metal uptake by barley seedlings grown on soils amended with sewage sludge. J Environ Qual 4 : 229–233

Dubinski BJ, Simpson RL, Good RE (1986) The retention of heavy metals in sewage sludge applied to a freshwater tidal wetland. Estuaries 9 : 102–111

Findlay S, Howe K, Austin HK (1990) Comparison of detritus dynamics in two tidal freshwater wetlands. Ecology 71 : 288–295

Folk RL (1974) Petrology of sedimentary rocks. Hemphill Publishing Company, Austin

Förstner U, Wittmann GTW (1983) Metal pollution in the aquatic environment. Springer, Berlin Heidelberg New York

Giblin AE, Bourg A, Valiela, I, Teal JM (1980) Uptake and losses of heavy metals in sewage sludge by a New England salt marsh. Am J Bot 67 : 1059–1068

Giblin AE, Luther GW, Valiela I (1986) Trace metal solubility in salt marsh sediments contaminated with sewage sludge. Estuarine Coast Shelf Sci 23 : 477–498

Hedges JI (1977) The association of organic molecules with clay minerals in aqueous solutions. Geochim Cosmochim Acta 41 : 1119–1123

Helz GR, Sinex SA, Ferri KL, Nichols M (1985) Processes controlling Fe, Mn, and Zn in sediments of northern Chesapeake Bay. Estuarine Coast Shelf Sci 21 : 1–16

Hilgartner WB (1995) Habitat development in a freshwater tidal wetland: a paleoecological study of human and natural influences. PhD Thesis, Johns Hopkins Univ, Baltimore

Khan H, Brush GS (1994) Nutrient and metal accumulation in a freshwater tidal marsh. Estuaries 17 : 345–360

Loring DH (1991) Normalization of heavy-metal data from estuarine and coastal sediments. ICES J Mar Sci 48 : 101–115

Marcus WA, Nielsen CC, Cornwell JC (1993) Sediment budget-based estimates of trace metal inputs to a Chesapeake estuary. Environ Geol 22 : 1–9

Millward GE, Moore RM (1982) The adsorption of Cu, Mn, and Zn by Fe-oxyhydroxides in model estuarine solutions. Water Res 16 : 981–985

Odum WE (1988) Comparative ecology of tidal freshwater and salt marshes. Annu Rev Ecol Sys 19 : 147–176

Olsen CR, Cutshall NH, Larson IL (1982) Pollutant-particle associations and dynamics in coastal marine environments: a review. Mar Chem 11 : 501–533

Olsenholler SM (1991) Annual loading estimates of urban toxic pollutants in the Chesapeake Bay basin. Final report to USEPA, Chesapeake Bay Program, Metropolitan Washington Council of Governments, Washington, DC

Orson RA, Simpson RL, Good RE (1992) A mechanism for the accumulation and retention of heavy metals in tidal freshwater marshes of the upper Delaware River estuary. Estu Coast Shelf Sci 34 : 171–186

Pasternack GB (1998) Physical dynamics of tidal freshwater delta evolution. PhD Thesis, Johns Hopkins Univ, Baltimore

Pasternack GB, Brush GS (1998) Sedimentation cycles in a river-mouth tidal freshwater marsh. Estuaries 21 : 407–415

Scholand SJ (1992) Salt marsh geochemical records and paleoenvironmental change. Honors Thesis, Wesleyan Univ, Middletown, CT

Sculthorpe CD (1967) The biology of aquatic vascular plants. Edward Arnold, London

Simpson RL, Good RE, Leck MA, Whigham DF (1983a) The ecology of freshwater tidal wetlands. Bioscience 33 : 255–59

Simpson RL, Good RE, Dubinski BJ, Pasquale JJ, Philipp KR (1983b) Fluxes of heavy metals in Delaware River freshwater tidal wetlands. Final Report. Center for Coastal and Environmental Studies, Rutgers University, New Brunswick, NJ

Simpson RL, Good RE, Walker R, Frasco BR (1983c) The role of Delaware River freshwater tidal wetlands in the retention of nutrients and heavy metals. J Environ Qual 12 : 41–48

Sinex SA, Helz GR (1981) Regional geochemistry of trace elements in Chesapeake Bay sediments. Environ Geol 3 : 315–323

Valette-Silver NJ (1993) The use of sediment cores to reconstruct historical trends in contamination of estuarine and coastal sediments. Estuaries 16 : 577–588

Varekamp JC (1991) Trace element geochemistry and pollution history of mudflat and marsh sediments from the Connecticut coastline. J Coast Res Spec Issue 11 : 105–123

Varekamp JC, Thomas E, Van de Plassche O (1992) Relative sea-level rise and climate change over the last 1500 years. Terra Nova 4 : 293–304

Velinsky DJ, Wade TL, Schlekat CE, McGee BI, Presley BJ (1994) Tidal river sediments in the Washington DC area. I. Distribution and sources of trace metals. Estuaries 17 : 305–320

Warren LJ (1981) Contamination of sediments by lead, zinc, and cadmium; a review. Environ Pollut (Ser B) 2 : 401–436

Windom HL (1975) Heavy metal fluxes through salt-marsh estuaries. In: Cronin LE (ed) Estuarine research, vol. 1. Academic Press, New York, pp 137–152

Windom HL, Schropp SJ, Calder FD, Ryan JD, Smith RG Jr, Burney LC, Lewis FG, Rawlinson CH (1989) Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States. Environ Sci Tech 23 : 314–320

Zwolsman JJG, Berger GW, Van Eck GTM (1993) Sediment accumulation rates, historical input, post-depositional mobility and retention of major elements and trace metals in salt marsh sediments of the Scheldt estuary, SW Netherlands. Mar Chem 44 : 73–94