Nutrient and Metal Accumulation in a Freshwater Tidal Marsh

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ABSTRACT: Stratigraphic records from sediment cores collected in a freshwater tidal marsh and in the estuary upstream and downstream from the marsh were used to determine the accumulation of nutrients and trace metals over long time periods. Analysis of pollen and seeds show that the high marsh has formed only within the past 100 yr, following increased sedimentation rates in the area. Variations in nutrient and trace metal accumulations over several decades show that pollutants from agricultural runoff and wastewater discharge are stored to a greater extent in high-marsh than in low-marsh sediments. Greater accumulation rates in the high marsh are probably related to its greater sedimentary organic carbon concentration.

Introduction

The importance of wetlands, including freshwater marshes, in improving water quality in the nation's rivers, lakes, and estuaries has been a subject of considerable research since the 1970s, when clean water became a high national priority (Grant and Patrick 1970; Whigham and Simpson 1976, 1980; Simpson et al. 1983; Hemond and Benoit 1988).

Many studies report that nutrients and metals are taken up by marsh vegetation during the growing season but are exported to the adjoining waters during winter decomposition and flushing of litter, so that retention is only temporary (Whigham and Simpson 1976; Simpson et al. 1983; Wolaver et al. 1983; Johnston et al. 1984). Other studies have found that nutrient retention occurs in organic surface sediments of freshwater marshes. A Florida freshwater marsh receiving wastewater effluent assimilated over 97% of the phosphorus input, 69.2% of which was taken up by its highly organic surface sediment (Dolan et al. 1981). Others have also suggested that longer term nutrient and metal retention occurs in organic sediments where nutrients and metals are either immobilized in or sorbed onto the organic material (Whigham and Simpson 1980; Howard-Williams 1985; DeLaune et al. 1986; Dubinski et al. 1986; Orson et al. 1992a). However, some studies have shown no noticeable accumulation of nutrients and metals in freshwater marsh sediments (Simpson et al. 1983).

Even though most agree that marshes are important in maintaining water quality for a few years, there is no consensus about their effectiveness over longer periods of time. This is largely due to the paucity of long-term data on the fate of pollutants in freshwater wetlands. Therefore this study was designed to determine the fate of pollutants entering a freshwater tidal marsh over long time periods by analyzing nutrient and trace metal accumulations in dated sediment cores. The hypothesis was that storms, deforestation, agriculture, and urbanization affect marsh sedimentation rates, vegetation, and substrate, and hence nutrient and metal retention. High sediment influx resulting from watershed deforestation and storms can increase the area of high marsh, where tidal flooding is less and of shorter duration than in the low marsh. Since high-marsh sediments often retain more organic matter than low marsh-sediments (Odum et al. 1984), the ability of the marsh to entrap nutrients and metals on a permanent basis may partly depend on the proportion of high to low marsh.

The stratigraphic record preserved in sediments provides a means of reconstructing long-term chemical and ecological conditions in ecosystems (Goldberg et al. 1978; Birks and Birks 1980; Cooper and Brush 1991). In addition to geochemical indicators including nitrogen, phosphorus, total organic carbon (TOC), and trace metals, fossil pollen and seeds of plants were analyzed to test the above hypothesis.

Many studies have successfully used nitrogen and phosphorus content of sediments as a surrogate record of nutrient loading in estuaries and lakes (Shapiro et al. 1971; Bortleson and Lee 1972; Hirata 1985; Cooper and Brush 1991), and sedimentary TOC as a measure of the organic matter preserved in sediments (Cooper and Brush 1991). The feasibility of interpreting changes in the sedimentary accumulation of trace metals in terms of anthropogenic influence has also been demonstrated. For example, enrichment of trace metals was found in recently deposited sediments in many polluted coastal regions (Bruland et al. 1974; Goldberg et al. 1978; Hirata 1985).

Fossil pollen grains preserved in the sediment are widely used to reconstruct vegetation history in various habitats, including estuaries and marshes (Carmichael 1980; Brush and DeFries 1981; Clark and Patterson 1985; Orson et al. 1992b). Many marsh and terrestrial plants produce pollen in sufficient quantities so that it can be used to observe temporal and spatial trends in vegetation. Moreover, pollen grains are easily retrieved and their resistant outer layer allows good preservation, especially in acidic sediments.

Fossil seeds of terrestrial and aquatic plants have also been employed in documenting historical changes in vegetation (Watts and Winter 1966; Carmichael 1980; Brush and Davis 1984; Davis 1985; Jackson et al. 1988). It has been shown that buried seeds in surface sediments of freshwater tidal marshes closely reflect the surface vegetation (Leck and Graveline 1979; Leck and Simpson 1987). In the present study, both fossil pollen and seeds of indicator high and low marsh plants were used to trace marsh development through time.

The Study Site

Jug Bay is a freshwater tidal marsh located on the Patuxent River estuary in the Coastal Plain of Maryland (Fig. 1). The marsh is bordered on the north and west by the Patuxent River estuary and on the cast by forested lowland (Fig. 1). To its south lies a shallow embayment, Jug Bay proper. Jug Bay consists of a low marsh that is flooded to an average depth of 30 cm on higher areas and 65 cm on lower areas for 8-9 h during a tidal cycle, and a high marsh that is inundated to an average depth of 5 cm on higher areas and 20 cm on lower areas for 2-4 h during each tidal cycle (personal observation). The low marsh is vegetated mainly by Nuphar advena (spatterdock), Pontederia cordata (pickerclweed), and Peltandra virginica (arrowarum), while thick Zizania aquatica (wild rice) stands occur at the landward edge. The dominant vegetation of the high marsh is Typha angustifolia (narrow-leaved cattail) and T. latifolia (broadleaved cattail). Other common high-marsh species include Polygonum arifolium (tearthumb), Rosa palustris (marsh rose), Sagittaria latifolia (arrowhead), Acorus calamus (sweetflag), Bidens laevis (burmarigold), and Phragmites communis (common reed). Fringing the marsh are arboreals including Acer rubrum (red maple), Betula nigra (river birch), Fagus grandifolia (American beech), Liquidambar styraciflua (sweetgum), Nyssa aquatica (blackgum), Quercus rubra (red oak), and Q. palustris (pin oak).

The area has been inhabited by humans continuously for at least 8,000 yr. Agriculture was practiced by Indian tribes, but deforestation and soil erosion were limited (DeFrics 1980). Extensive land clearing for tobacco and corn cultivation began with European settlement in the 17th Century. Deforestation reached its peak in the mid- to late-1800s, when 70-80% of total land was cleared (Froomer 1978). Around that time, fertilizers began to be heavily used in agriculture. In 1895 a railroad bed was laid across the marsh, dividing it into two parts. The railroad provided a transportation route between Washington, D.C. and Chesapeake Bay beaches. By the 1930s the rail company was operating at a loss, and in 1935 the railroad was closed (Williams 1981). The Jug Bay area was largely abandoned until 1985 when it became a wetlands sanctuary for scientific research. Within the last three decades, portions of the watershed close to Jug Bay have undergone a greater degree of urbanization than most other watersheds in the Chesapeake Bay area. Numerous wastewater treatment plants, constructed upstream from the marsh, together discharge 152 million liters of nutrient-rich sewage effluent into the river daily, a 1,300% increase over the volume of effluent discharged in 1963 (Alliance for the Chesapeake Bay 1988). The closest one, the Western Branch Treatment Plant, 1 km upstream from Jug Bay, began discharging effluent into the estuary in 1970. At present its average daily flow is 49-53 million liters (Western Branch staff personal communication). Along with nutrients, wastewater cffluent usually. contains trace metals, including copper, lead, and zinc (Helz et al. 1975). Thus sediment, nutrient and metal loads into the estuary have changed dramatically within the last century as a result of anthropogenic activities.

Methods

Sediment cores, ranging from 1 to 2 m in length, were collected in the high and low marshes at Jug Bay, and in the estuary upstream and downstream from the marsh (Fig. 1). All cores were collected

Fig. 1. Map of Jug Bay showing location of sediment cores. Core HM was collected in the high-marsh, and core LM in the lowmarsh. Cores UE and DE were collected in the estuary upstream and downstream from the marsh, respectively.



using a piston vibrocorer with an internal diameter of 8 cm. The cores were cut into 1-cm sections and a chronology was constructed for each 1-cm section using sedimentation rates based on carbon-14 and pollen analysis (Brush 1989). Radiocarbon dates were obtained for the bottom sediments of three cores and ranged from $1,300 \pm 100$ yr to $1,800 \pm 150$ yr before present (B.P.). Two other horizons, recognized by a sharp increase in ragweed pollen and decrease in the oak ragweed pollen ratio, represent post-European agriculture (Brush 1984) and were dated 1650 A.D. and 1840 A.D. based on historical records of land clearance in the region. Another horizon was the top sediment of each core, representing the date the core was collected.

Average sedimentation rates were calculated by dividing the depth in cm between dated horizons by the number of years represented between those horizons. Sedimentation rates for each 1-cm interval were then obtained by adjusting average rates between horizons according to the pollen concentration in each interval between the dated horizons. Individual rates were then used to date every 1-cm interval in the cores. Mass rates of sediment accumulation (g cm⁻² yr⁻¹) were computed by multiplying the bulk density of sediment in each interval by the individual sedimentation rate.

Pollen was extracted from each 1-cm interval by drying 1.5 ml of wet sediment from each interval at 80–90°C, treating the dried sediment with hydrochloric and hydrofluoric acids to remove calcareous and siliceous matter, and with a mixture of sulfuric acid and acetic anhydride to break up cellulose in leaves and rootlets (Faegri and Iversen 1989). The treated samples were stored in 25 ml of tertiary butanol. Two 0.1-ml aliquots from each subsample were examined under a light microscope at $\times 200$ –400. All pollen in each aliquot was counted and identified with the help of reference slides and guides. On average, 600 pollen grains were counted per aliquot.

Seeds were extracted by soaking 19–20 g of wet sediment from selected intervals in a solution of 10% nitric acid (Birks and Birks 1980). The volume of sediment was determined from the volume of displaced acid. After soaking for 24–36 h, the sediment was washed with running water into a sieve and collected in a petri dish. Seeds were then examined under a binocular microscope and, in most cases, identified to the species level.

TOC in selected intervals was measured by the method of Krom and Berner (1983). Samples were first dried overnight at 100°C and then finely ground. About 2 g from each sample were placed in ceramic dishes and combusted for 12 h at 450°C in a mufile furnace. Both the dried and ashed sam-

ples, along with blanks and standards, were run for total carbon and nitrogen on a N-2000 Carlo Erba CNS analyzer. The difference between total carbon and nitrogen values for dried and ashed samples from the same interval gave the total organic carbon and nitrogen values for that interval. Phosphorus was measured by adding 3 ml of 70% perchloric acid to 0.2 g of dried and ground sediment, and digesting it for 75-90 min at 200°C. The digestant was then diluted with distilled water to make up to 50 ml of solution from which aliquots were neutralized with NaOH using p-nitrophenol as an indicator (Sommers and Nelson 1972). Total phosphorus was determined on a spectrophotometer using the method of Murphy and Riley (1962).

To measure the trace metals, 0.2 g of dried and ground sediment was placed in a graphite crucible containing 1 g of lithium metaborate. The mixture was fused at 950–1,000°C for 15 min in a muffle furnace and the borate bead was dissolved in 100 ml of 5% nitric acid (Cantillo et al. 1984). Aliquots from the solution were analyzed on an atomic absorption spectrophotometer to obtain metal concentrations.

Since sediment deposition in an estuarine environment is variable, both temporally and spatially, all concentrations of fossils and chemicals (number or mg cm⁻³) were converted to accumulation rates (number or mg cm⁻² yr⁻¹) by multiplying the former by the appropriate sedimentation rates (cm yr⁻¹). This allowed a more meaningful comparison between different time intervals in and among the cores (Brush 1989).

Results

SEDIMENTATION PATTERNS AT JUG BAY

Sedimentation rates and chronologies for selected intervals in the high and low marsh and the upstream and downstream estuarine cores are shown in Tables 1-4. In pre-European time, sedimentation rates in both the marsh and estuarine cores range between 0.05 cm yr^{-1} and 0.08 cm yr^{-1} . After European settlement, however, rates increase in all cores, reaching an average of 0.50 cm yr⁻¹ in the mid-1800s, over 5 times higher than pre-European rates (Tables 1-3). In the marsh cores sedimentation increases again in the late-1890s to early-1900s, at times reaching as high as 0.64 cm yr^{-1} . This turn-of-the-century increase is not present in the estuarine cores (compare Tables 1 and 2 with Tables 3 and 4). All cores register a sharp increase in sedimentation rates in the mid-1960s through the mid-1970s, and again in the early-1980s. Since then rates have decreased somewhat. Single peaks are also present in the mid-1930s, mid-1950s, and

Depth (cm)	Sedimentation Rate (cm yr ⁻¹)	Mass Accumulation Rate (g cm ² yr 1)	Years (A.D.)
0-1	0.43	0.11	1990-1988
3-4	0.48	0.14	1982-1980
7–8	0.89	0.52	1973-1972
11-12	0.53	0.21	1966-1964
16-17	0.74	0.41	1955-1954
19-20	0.40	0.11	1949-1946
24-25	0.70	0.38	1934-1933
27-28	0.37	0.12	1927-1924
33-34	0.60	0.28	1910-1908
36–37	0.64	0.31	1904-1902
41-42	0.51	0.21	1894-1892
49-50	0.38	0.16	1878-1875
53-54	0.61	0.29	18681866
60-61	0.54	0.26	1854-1852
71-72	0.38	0.19	1830-1827
83-84	0.27	0.14	1795-1791
101-102	0.15	0.09	1697-1690
110-111	0.07	0.03	1603-1589
131-132	0.08	0.04	1250-1237
151-152	0.05	0.03	990-970
168-169	0.06	0.03	630-613

in 1972 in all cores (Tables 1–4). Patterns of mass rates of sediment accumulation, $g \text{ cm}^{-2} \text{ yr}^{-1}$, are similar to linear sedimentation rates in all four cores (Tables 1–4).

POLLEN AND SEED INFLUXES

Typha pollen appears for the first time in the high marsh core in the mid-1800s (Fig. 2A), and increases thereafter, reaching its greatest influx from the early-1900s onward. Similar trends are shown by pollen of Impatiens, Sagittaria, Bidens, and Rosa. During the same time period, however, pollen influxes of Nuphar and Cyperaceae decrease substantially. Seed profiles of this core show that Polygonum arifolium, Bidens laevis, and Sagittaria latifolia are absent before the mid-1800s (Fig. 2B). From then on there is a huge influx of seeds of these species, with the sharpest increase occurring in the early-1900s. Seed influxes of Pontederia cordata, Zizania aquatica, and Carex spp. drop significantly from the late-1800s to the present.

In the core from the present low marsh, the most dramatic change occurs in pollen influxes of *Nuphar* and Cyperaceae (Fig. 3A). An increase occurs in the mid-1800s and again in the early-1900s, and influxes stay high to the present. Influxes of *Typha, Impatiens, Sagittaria, Bidens*, and *Rosa* pollen are sporadic and much lower than in the high marsh core, and totally absent before the mid- to

TABLE 2. Sedimentation rates for selected 1-cm intervals in the low marsh core. Highest sedimentation rates are recorded in the mid-1800s, early-1900s, 1933, 1954–1955, and 1972. The double line indicates the beginning of European agriculture in the region.

Depth (cm)	Sedimentation Rate (cm yr ¹)	Mass Accumulation Rate (g cm ⁻² yr ⁻¹)	Years (A.D.)
0-1	0.42	0.19	1990-1988
3-4	0.49	0.20	1982-1980
7–8	0.68	0.56	1973-1972
11-12	0.49	0.22	1966-1964
15-16	0.70	0.52	1956-1955
1819	0.35	0.15	1949-1946
24-25	0.65	0.43	1934-1932
28-29	0.45	0.20	1926-1924
36-37	0.61	0.29	1910-1908
39-40	0.62	0.31	1904-1902
44-45	0.52	0.20	1894-1892
52-53	0.55	0.20	1878-1876
57-58	0.48	0.24	1868-1866
64-65	0.52	0.25	1854-1852
75–76	0.39	0.18	1831-1828
86-87	0.25	0.12	1795-1791
105-106	0.18	0.09	1697–1691
119-120	0.10	0.05	1596-1586
141-142	0.12	0.06	1244-1236
158-159	0.07	0.04	976-962
174-175	0.04	0.03	676-651

late-19th Century. Seed influx patterns show abundant submerged aquatic vegetation (SAV) until the late-1800s (Fig. 3B), followed by a rapid decline as influxes of *Pontederia cordata, Zizania aquatica*, and *Carex* spp. seeds increase.

SEDIMENT CHEMISTRY

Accumulation rates of TOC, nitrogen, and phosphorus (Fig. 4A–C) show more or less constant rates in all cores prior to the mid-19th Century. However, accumulation rates begin to rise in the high marsh core around 1850 A.D., and register a sharp increase in the carly-1900s. This upward trend continues throughout the 20th Century. TOC and nutrient accumulations increase slightly in the low marsh core, and values are much lower than in the high marsh core.

The upstream estuarine core shows an increase in TOC and nutrient accumulation around the mid-1800s, which continues up to the 1960s (Fig. 4A–C). In the early 1970s another large increase occurs, which persists to the present. However, a small decrease in the phosphorus profile is visible at the very top of the core (Fig. 4C). The TOC and nutrient profiles of the downstream estuarine core are similar to those of the upstream core until the early-1900s (Fig. 4A–C). Thereafter, accumulation rates in the downstream core become lower than rates in the upstream core for the next several de-

TABLE 3. Sedimentation rates for selected 1-cm intervals in the downstream estuarine core. Highest sedimentation rates are recorded in the mid-1800s, 1933, 1954–1955, and 1972. The double line indicates the beginning of European agriculture in the region.

Depth (cm)	Sedimentation Rate (cm yr ³)	Mass Accumulation Rate (g cm ^{-x} yr ⁻¹)	Years (A.D.)
0-1	0.50	0.24	1990–1988
4-5	0.57	0.27	1982-1980
8-9	0.77	0.56	1973-1972
12-13	0.49	0.24	19661964
16-17	0.67	0.44	1956-1954
19-20	0.38	0.18	1948-1945
24-25	0.65	0.43	1934-1932
28-29	0.49	0.23	1926-1924
36-37	0.52	0.22	1909-1907
38-39	0.51	0.24	1905-1903
43-44	0.51	0.25	1895-1893
51 - 52	0.40	0.20	1879-1876
56-57	0.49	0.24	1868-1866
63-64	0.50	0.27	1854-1852
74-75	0.38	0.20	1832-1829
85-86	0.28	0.15	17961793
105-106	0.13	0.07	1694-1686
115-116	0.05	0.02	1608-1588
134-135	0.05	0.02	1240-1220
151-152	0.04	0.02	980-955
166-167	0.08	0.05	680-667

cades. Between about 1984 and 1990 they rise again and become virtually identical to those in the upstream core.

Accumulation rates of trace metals in all cores are presented in Fig. 5A–C. In the high marsh core these rates begin to rise dramatically in the 1950s. In the low marsh core, lower rates of metal accumulation are observed, with smaller increases beginning in the 1950s.

The upstream estuarine core shows an appreciable increase in metal accumulation after 1950. In the downstream core metal accumulation also increases for the same time period, but, except for lead, this increase is considerably smaller than that observed in the upstream core.

Discussion

HISTORICAL DEVELOPMENT OF JUG BAY

As forests were cut down in southern Maryland in post-European time for farming, soil erosion from the land increased and sedimentation in rivers and estuarics rose, reaching very high levels in the mid- to late-1800s, the time of maximum land clearance. Sedimentation tends to be highest in the upper and middle portions of an estuary, where the freshwater wetlands are situated, and much lower further downstream (Brush 1984; Donoghue 1990). Roberts and Pierce (1976) report that in the Patuxent River estuary sediment

TABLE 4. Sedimentation rates for selected 1-cm intervals in the upstream estuarine core. Highest sedimentation rates are recorded in the mid-1800s, 1933, 1954–1955, and 1972. Pre-European dates are not available for this core.

Depth (cm)	Sedimentation Rate (cm yr ⁻¹)	Mass Accumulation Rat e (g <m th="" yr="" ²="" ¹)<=""><th>Ycars (A.D.)</th></m>	Ycars (A.D.)
0-1	0.45	0.27	1990-1988
4–5	0.59	0.31	1982-1980
8-9	0.75	0.59	1973-1972
12-13	0.50	0.30	1966-1964
16-17	0.69	0.47	1955-1954
19-20	0.45	0.21	1949-1947
24–25	0.66	0.47	1935-1933
28–29	0.42	0.26	1926-1924
36-37	0.55	0.24	1910-1908
39-40	0.55	0.22	1904-1902
44-45	0.56	0.26	1894-1892
52–53	0.54	0.26	1878–1876
57–58	0.59	0.29	1868-1866
64-65	0.52	0.27	1854-1852
74–75	0.45	0.21	1831-1829
86–87	0.20	0.16	1795-1790
103-104	0.12	0.09	1696-1688

deposition is highest just around its confluence with the Western Branch, the site of Jug Bay (Fig. 1).

At the turn of the century, sediment deposition as high as 0.64 cm yr⁻¹ occurred, coinciding with the construction of the railroad bed. The bed could have obstructed water flow in the marsh thereby increasing sedimentation. Other studies also provide evidence of increased sedimentation around railroads and roads (Jackson et al. 1988; Hilgartner, Johns Hopkins University, personal communication). The lack of a concurrent increase in sedimentation rates in the estuarine cores during this time is additional evidence that this peak in sedimentation is a local response in the marsh because of its proximity to the railroad bed.

Similar trends in mass rates of sediment accumulation, which adjust for the water content of sediment, and the linear rates indicate that compaction of sediment is not significant and the increase in sedimentation rates in post-European time is real.

At Jug Bay, high sedimentation led to the infilling of the estuary and low-lying areas bordering it. Thus in the 17th Century, the water was deep enough for Jug Bay to be used as a harbor for ocean-going sailing ships (Barth 1978). Today the bay is extremely shallow; at low tide the average water depth is just about 1 m (personal observation). Areas that were previously low marsh at one site became high marsh, and open water was replaced by low marsh at another site. Pollen and seed records from the core taken in the present high marsh show replacement of low marsh by





Zizania aquatica



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Fig. 3. (A) Profile of pollen influx in low-marsh core. (B) Profile of seed influx in low-marsh core. Influxes were obtained by multiplying the concentration of pollen (grains cm^{-3}) and seeds (number 100 cm⁻³) in the sampled core intervals by the appropriate sedimentation rates (cm yr^{-1}).

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Fig. 4. (A) Accumulation of total organic carbon (TOC) in the marsh and estuarine cores.

high marsh within the last century. The high marsh plants Typha spp., Polygonum arifolium, Rosa palustris, Impatiens capensis, Sagittaria latifolia, and Bidens laevis were not present at the site before 1850 A.D., and increased sharply only after the late-1800s (Fig. 2A, B). The establishment of Typha in pond basins during post-European times has also been observed by others and attributed to eutrophication of waters and infilling of ponds from increased sediment runoff (Birks et al. 1976; Jackson et al. 1988). Both of these factors were probably responsible for the appearance of Typha at Jug Bay in the mid-1800s, although the simultaneous appearance of other typically high-marsh plants suggests that rising elevation of the previously lowmarsh areas was the dominant cause for this vegctation change. Furthermore, Nuphar advena, a low-marsh plant growing near mean low-water levels, decreased substantially during the period when high-marsh plants were expanding. This was accompanied by a significant decrease in Cyperaceae, Pontederia cordata, and Zizania aquatica, which also grow at lower elevations (Fig. 2A, B).

The pollen and seed profiles from the core collected in the present low marsh indicate that the area was open shallow water throughout the 1700s and most of the 1800s, with low marsh forming only within the past century. SAV was abundant at this site until the late-1800s, then declined rapidly as Nuphar advena, Pontederia cordata, Zizania aquat*ica*, and Cyperaceae increased sharply in the late-1800s (Fig. 3A, B). Today, SAV grows along the channel edges in water depths of 20-40 cm at low tide. It can grow in water depths of up to 4 m if turbidity is not high (Odum et al. 1984). Within the last 5 yr Nuphar advena has extended further into the main estuary because continued sediment input is lowering water depth there (Jug Bay Sanctuary staff personal communication).

The sharp change in marsh vegetation at both sites in the late-1800s to early-1900s shows that the transformation of open water into low marsh and



Fig. 4. (B) Accumulation of nitrogen in the cores.

low marsh into high marsh, which had begun in the mid-1800s, accelerated soon after the railroad bed was laid (Figs. 2A, B and 3A, B). Replacement of open water by marshes, following high sedimentation rates in post-European times, is reported in other tributaries on the western shore of the Chesapeake Bay in Maryland (Froomer 1980).

Large storms also influence marsh sedimentation. Orson et al. (1990) reported average sedimentation rates as high as 1.67 cm yr⁻¹ in a freshwater tidal marsh on the upper Delaware River estuary during the intense storm activity of 1954– 1965. In Jug Bay increased sedimentation, as shown in all cores, occurred during 1932–1934 and 1955–1956 and coincided with large storms events in southern Maryland (Ashbaugh and Brancato 1958; United States Geological Survey Water Resources Division, Towson, Maryland, personal communication). Sediment deposition of 0.89 cm yr⁻¹ on the high marsh resulted from Hurricane Agnes in 1972. Sedimentation rates at Jug Bay rose again in the mid-1960s and early-1980s when rapid urbanization occurred in the upstream watershed. Areas undergoing construction yield several hundred times more sediment than forested or farmed areas (Wolman 1967) because the loose soil at construction sites is very susceptible to erosion. The estuarine cores show similar patterns of sedimentation related to regional land use, but they have not recorded the sedimentation peaks seen in marsh cores around the turn of the century, following local railroad bed construction (Tables 3 and 4).

NUTRIENT AND METAL ACCUMULATION IN THE MARSH

Small increases in organic carbon accumulation were observed in the low-marsh core as this site changed from open water to low marsh over the last 100 yr (Fig. 4A). Decomposition of plant litter tends to be rapid in the low marsh (Odum 1988; Whigham et al. 1989; Findlay et al. 1990), disappearing within weeks after the death of low-marsh plants. From November through March the low-



Fig. 4. (C) Accumulation of phosphorus in the cores. These values were computed by multiplying the concentration (mg cm⁻³) of TOC, nitrogen, and phosphorus in the sampled core intervals by the appropriate sedimentation rates (cm yr⁻¹).

marsh surface at Jug Bay becomes a totally bare mudflat with no plant litter in sight (H. Khan, personal observation). Rapid decomposition is due to the high nitrogen and low cellulose content of lowmarsh plants, which increases their nutritional value to detritus consumers (Odum 1988). More effective diurnal flushing of the low marsh by tidal action also results in a greater removal of organic material. Accumulations of other measured chemical parameters in the low-marsh core also show only a slight increase over time, indicating little accumulation of nutrients and trace metals in the low marsh over long time periods (Figs. 4B, C and 5A, B, C). However, this part of the marsh may serve as a seasonal sink for nutrients and metals, with uptake by plants in summer and export to the estuary via flushing of litter during fall and winter.

Sediment chemistry of the high-marsh core shows a considerable increase in TOC as the site changed from low to high marsh (Fig. 4A). Highmarsh plants, such as *Typha* and *Phragmites*, contain less nitrogen and large amounts of resistant material such as cellulose and lignin, resulting in low consumption by detritus feeders and hence slower decomposition (Odum 1988). Litter from the high-marsh surface is also flushed less frequently than in the low marsh because of lower and shorter tidal inundation. At Jug Bay a considerable amount of dead plant material, especially that of Typha, remains on the high-marsh surface in the fall, and is steadily covered by incoming sediment and other plant debris (II. Khan, personal observation). These two factors, combined with the relatively high rates of allochthonous sediment input at this site, allow burial of much of the organic matter in high-marsh sediments. TOC accumulation in highmarsh sediments is on average 4 times as much as in low-marsh sediments. Results from the two marsh cores confirm the suggestion of Odum et al. (1984) that, in a freshwater tidal marsh, sedimentary organic content increases from low to high marsh.

Results also indicate that there is greater nutrient and metal accumulation in high-marsh than in



Fig. 5. (A) Accumulation of copper in the marsh and estuarine cores.

low-marsh sediments. In the high-marsh core, nutrient accumulation increased as this site changed from low marsh to high marsh (Fig. 4B, C). This may be related, at least partly, to the large sedimentary organic carbon accumulation in the high marsh. Since a significant amount of litter is buried in the high marsh, nutrients and trace metals immobilized by living vegetation are also incorporated into the sediment. Microbes on decomposing litter itself accumulate significant amounts of nutrients and metals from the flooding waters as well as those leached from freshly fallen litter (Bowden 1987; Whigham et al. 1989). With litter burial, these substances are incorporated in the sediment and immobilized more or less permanently.

The ability of organic matter, especially humic compounds, to adsorb trace metals directly is also well documented (Nriagu and Coker 1980; Hirner et al. 1990). The major mechanism by which humic compounds react with metals is chelation in which strong bonds exist between the humic molecules and metal ions. Cation exchange and physical adsorption of metal ions on the colloidal organic surface are other important mechanisms of organo-metallic reactions (Rashid 1974; Horowitz 1991). Organic soils have also been reported to adsorb a considerable amount of phosphorus (Dolan et al. 1981; Howard-Williams 1985). Some have attributed this to chelation of iron and aluminum by the organic matter. However, Vijayachandran and Harter (1975) found that little iron or aluminum was chelated by organic matter, and suggested that anion adsorption sites on the organic matter itself were responsible for the correlation between the observed phosphorus adsorption and organic carbon.

Therefore, mechanisms of nutrient and metal storage in the high marsh may include vegetation and litter uptake and immobilization of these substances as well as direct adsorption of nutrients and metals onto sedimentary organic matter. In the low marsh, on the other hand, rapid decomposition and flushing of litter and little sedimentary organic carbon presumably result in less nutrient and metal accumulation.

However, the amount of nutrients and metals ac-



Fig. 5. (B) Accumulation of zinc in the cores.

cumulated per unit of organic carbon is consistently greater in the low marsh than in the high marsh, despite the fact that total accumulation of nutrients and metals is higher in the high marsh. A likely explanation is that since the low marsh is submerged for much longer periods than the high marsh, there is prolonged contact between organic matter in the low-marsh surface sediments and the flooding waters. This leads to a greater likelihood for reaction between nutrients and metals in the water and sedimentary organic carbon, and hence greater efficiency of adsorption by organic carbon in the low marsh.

NUTRIENT AND METAL ACCUMULATION IN THE ESTUARY

The upstream estuarine core shows good correspondence between sediment chemistry and the historical record of eutrophication (Fig. 4A–C). Nutrient and TOC accumulations in the core increased in the mid-19th Century with the widespread use of fertilizers regionally. They rose again sharply during the past two decades when effluent from wastewater treatment plants and runoff from nonpoint sources, such as lawn chemicals, greatly increased pollution in the estuary. Some decrease in phosphorus accumulation is visible at the top of the core, reflecting the Maryland ban on phosphorus in detergents and its removal from the Western Branch sewage effluent since 1985.

The chemical profile of the downstream estuarine core also reflects the trend of increased nutrient accumulation and water-quality deterioration observed in the upstream core in the mid- to late-1800s. Differences in nutrient accumulation rates between the two cores are less than 8%, suggesting that upstream and downstream water quality was essentially similar. Most of the area at Jug Bay was either shallow open water or low marsh at that time, and nutrients were not trapped except perhaps seasonally. However, between 1920 and 1980, a time of increasing nutrient input upstream, nitrogen accumulation in the downstream core is 50–67% lower and phosphorus accumulation 60–70% lower than in the upstream core



Fig. 5. (C) Accumulation of lead in the cores. These values were computed by multiplying the concentration ($\mu g \text{ cm}^{-3}$) of copper, zinc, and lead in the sampled core intervals by the appropriate sedimentation rates (cm yr⁻¹).

(Fig. 4B, C). Given the proximity of the two estuarine sites (1.5 km) and their mostly similar environmental variables, such a large difference in accumulation rates in all likelihood indicates less nutrient pollution downstream, and is not simply the result of some spatial variability. This decrease in nutrient accumulation downstream coincides with the development of high marsh at Jug Bay in the 1920s, and suggests that the storage of nutrients in the high marsh was most likely responsible for improving downstream water quality. Storage of copper and zinc in high-marsh sediments in recent years has also tended to buffer the downstream estuary against increased upstream metal loads (Fig. 5A, B). Therefore, downstream water quality was most probably affected mainly by marsh development over time.

However, upstream and downstream accumulation of lead was similar (less than 8% difference) during the 1960s and 1970s, even though large amounts were being trapped in the high marsh (Fig. 5C). During this time exhaust fumes of automobiles using leaded gasoline were the source of a large atmospheric component of lead. The marsh would not affect downstream influx from an atmospheric source. In the 1980s, when leaded gas was no longer used, lead accumulation decreased both upstream and downstream, though more so in the latter. This was most likely the result of storage in the high marsh of a large portion of the still relatively high lead influx in the upstream estuary. In contrast, there has been considerably less metal accumulation in the low marsh during this time.

Since about 1984, similar nutrient and TOC accumulation rates in the upstream and downstream estuarine cores (within 5% of each other) indicate that at present there is no noticeable difference between upstream and downstream water quality. This suggests a decrease in long-term nutrient storage in the high marsh. With a decrease of sediment input on the high marsh in recent decades, relative rates of decomposition of litter and subsequent leaching of mineralizing nutrients out of the marsh may have increased. It is also possible that the high-marsh vegetation is not taking up nutrients from incoming waters to the extent that it did in the past because there are now sufficient, recyclable nutrient stores in the sediment. In fact, Bowden (1987) has suggested that nitrogen stored in wetland sediments may become an adequate source for the plants and external uptake may decrease.

The results of this study show that marsh and estuarine sediments contain a well-preserved record of local ecological history. Mature marshes, that is, those with large areas of high marsh (Odum et al. 1984), serve as long-term stores for nutrients and metals, and that formation of high marsh is at least in some cases initiated by soil erosion within the watershed. However, prolonged exposure to heavy nutrient input can reduce the capacity of the marsh to trap nutrients permanently. On the other hand, low marsh areas appear to serve little function in the protection of water quality over long time periods, though they may be important seasonally.

These results have implications for estuarine management. Controlling sediment input into the estuary is beneficial for SAV and other benthic organisms in that turbidity is reduced in the water column. However, lower sediment input also slows the development of marsh areas that can act as permanent nutrient and metal sinks in the estuarine ecosystem.

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