Marsh sediments as records of sedimentation, eutrophication and metal pollution in the urban Delaware Estuary

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Received in revised form 11 October 2005; accepted 11 October 2005

Abstract

The tidal freshwater portion of the Delaware Estuary has historically been an area of intense urban and industrial activities including dredging, point discharges, petroleum refineries, and shipyards. Multiple cores were collected in fringing marshes across from the urban area and used here to investigate historical records of these associated activities. Two cores in the most industrialized portion exhibited regular and congruent geochronology (0.6 cm/year downstream and an average of 1.2 cm/year upstream) based on both natural 210-Pb and fallout 137-Cs radionuclides. Thus, these sedimentary records should reflect sedimentary pollution histories over much of the latter past century.

Recorded in the freshwater marsh sediment upstream is a dramatic increase in total phosphorus (TP) starting in 1950–1960, and, as in the Delaware River water, tracks the introduction of P detergent use. Although this might include increased use of P fertilizers, there is a substantial decrease after removal of the P detergent source in the mid-1970s. Carbon stable isotopes (δ^{13}C) track P changes after 1955. The heavier carbon isotope (^{13}C) corresponds to higher levels of P in the sediments (and water), while the lighter carbon (^{12}C) isotope in recent times corresponds to decreased use or discharge of P. In more recent times since the 1970s, there is a significant relationship ($p < 0.05$) between δ^{13}C and sediment P, while before 1965 there is a significant but different relationship. As such, the lower δ^{13}C of the sediment organic matter may record decreased growth/eutrophication when P loadings and concentrations are reduced. The N stable isotope record shows a marked increase in δ^{15}N (ca. 3.5‰ to 7.5‰) starting in the early 1960s. This corresponds to a substantial increase in the concentration of dissolved nitrogen (mainly as nitrate) from population growth, fertilizer applications, or changes in the processing of wastewater leading to reduction in chemical oxygen demand.

The industrial metals fall into at least two transient records:

(1) The Ag, As, Co, Cd, Cr, and Co show 2- to 4-fold increases after 1950, with steady inventories over the past 20–30 years. This reflects periods of increased industrialization, followed by better sewage treatment, industrial stagnation, relict sources, or continued urban run-off from atmospheric deposition. Episodic remobilization of sedimentary inventories is not indicated in the regular geochronologies and lack of porosity change.

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(2) The Pb and Sn show similar, but a much larger (10-fold) increase after 1950. This reflects the use and then legislative controls of anthropogenic organo-metallic compounds. The lead transient peak corresponds to the use (and local manufacture) of tetra ethyl lead as a gasoline additive, but phased out starting 30 years ago. Likewise, industrial organo-tins include tri-butyl tin (TBT), anti-fouling additives used in ship bottom paints. The sustained modern levels of organo-tins indicate some continued relict inputs. The decreasing order of butyl-tin concentrations is mono- to di- to tri-butyl species, implicating degradation of TBT via trans-alkylation. This also suggests the order of product stability, rather than that of independent source loading. The conservative correlation of linear butyl tins (linear order mono→di→tri-) with both total and butyl-tins, also strongly implicates TBT as the unique input. Although TBT use was banned about 20 years ago, there appear to be continued sources and diagenesis of buried TBT with mobilization of butyl-tin products into the tidal Delaware Estuary.

1. Introduction

1.1. Tidal marshes and biogeochemical processes

Most marshes accumulate at a rate that approximates the rate of local sea level rise, becoming the repository of much of the fine sediment in estuaries that occupy drowned river valleys on passive-margin coasts (Church et al., 1981). As a result, these intertidal areas surround many transgressive coasts as a product of sedimentation, sea level rise and local subsidence (Nichols, 1989).

Marshes sustain a biologically active surface in the form of macrophyte grasses that host a complex eco-system. These grasses also act as a sediment trap for not only much of the fine material, but also associated organic material and trace metals that enter marshes on flooding tides. Marsh sediments have an upper oxidized zone characterized by aeration via the root systems, and a reducing zone below. The result is the burial of abundant organic material partially decomposed over time, since only some of this organic matter is seasonally regenerated (Church, 1991).

1.2. Marsh geochronology and metal records

Since the area of salt marshes is exposed longer to the atmosphere than to lunar tidewaters, atmospheric deposition of pollutants can be as important in the tidal exchange of lunar contaminants (Church and Scudlark, 1998). In freshwater tidal marshes, a mechanism proposed for the accumulation and retention of metals involves incorporation in above or below ground plant material, respectively (Orson et al., 1992a). Thus, in spite of intense diagenesis at the zone of redox transition, marshes appear to retain and record ambient trace element levels on annual time scales. This has been confirmed in the salt marsh studies of Long Island Sound (Cochran et al., 1998) and lower Delaware Bay (Kim et al., 2004) as compared with marshes on the west coast of France (Velde et al., 2003).

1.3. Objectives of the study

The objectives of this study attempt to answer the following questions concerning the historical pollution of the upper Delaware Estuary, relative to past industrial practices and discharges.

1) Can urban tidal marshes provide historical sedimentary and pollutant records in the concordantly dated sediments?
2) Do marsh sedimentary records of C, N, P, together with C and N stable isotopes, respond to historical changes in eutrophication?
3) Might marsh sediment records provide dated pollutant histories of the onset and abatement of metal-based industrial activities?
4) Specifically, are there records of transient industrial organo-metallic pollutants (e.g. lead and tin alkyl compounds), now historically banned, confirmed in the marsh sediment record?

2. Area descriptions, methods and material studied

2.1. Regional setting

The Delaware Estuary is the flooded valley of the Delaware River, a partially stratified to well-mixed coastal plain estuary that extends from the head of tides at Trenton, New Jersey, 215 km from the mouth of Delaware Bay. The marsh study sites fall within the upper estuary between Wilmington, Delaware, and Philadelphia, Pennsylvania, approximately 15−45 km downstream from Trenton (Fig. 1). Between Trenton and Wilmington, the Delaware flows along the Fall
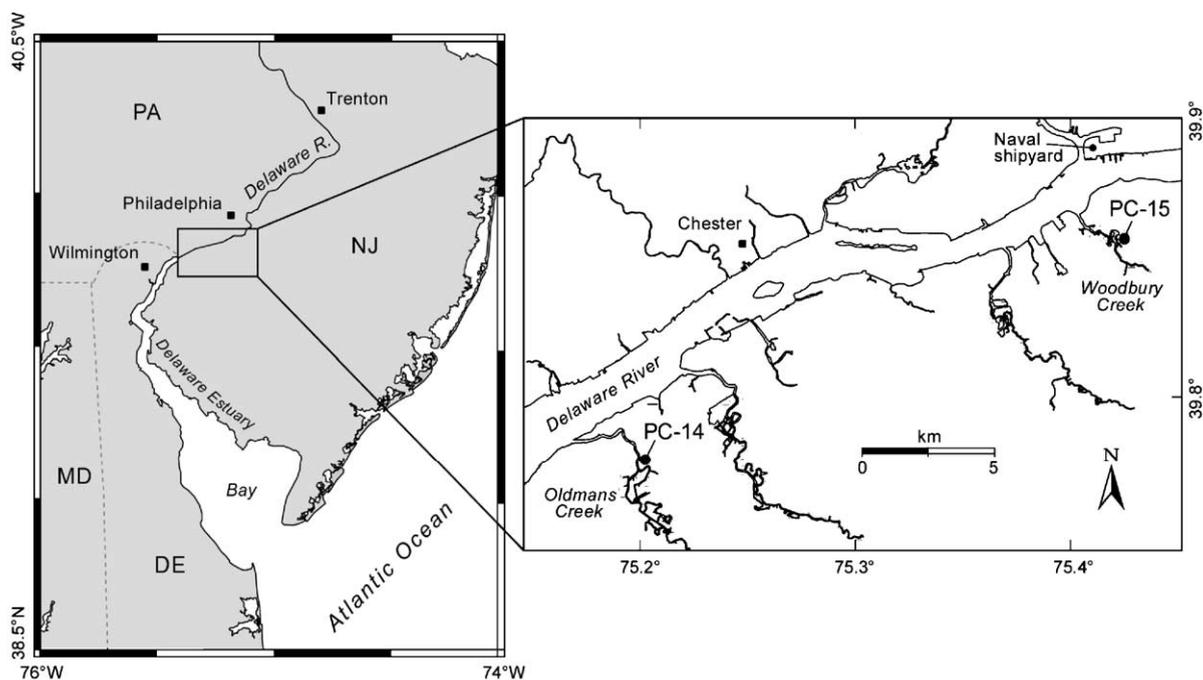
Fig. 1. Map of the upper Delaware Estuary in the greater Philadelphia urban corridor showing the locations of the Oldmans and Woodbury Creek marsh sites and coring locations therein (PC-14 and PC-15).

Line, the geologic boundary between the Piedmont Lowland and Atlantic Coastal Plain, physiographic provinces to the west and east, respectively. Here the river deeply incises crystalline bedrock and the unconsolidated sedimentary strata of the Delaware River Valley (Newell et al., 1998). This highly urbanized reach of the upper estuary is transitional between tidal fresh and estuarine waters with mean salinities typically less than 1 psu. Spring tidal range in the upper estuary is 1.8 m, and corresponding depth-averaged tidal currents reach 1 m/s in the channel (Cook, 2004). Suspended sediments are derived from three major sources: (1) river discharge from multiple Piedmont and Coastal Plain tributaries; (2) subaqueous erosion of Holocene and older alluvial deposits of the estuarine floor; and (3) landward advection from Delaware Bay and adjoining coastal ocean. An estimated 1.4 million metric tons of suspended silt and clay enter the estuary from rivers on an annual basis (Mansue and Commings, 1974), most of which is supplied by the Delaware River mainstem, particularly in association with spring freshets and summer rainstorms. The landward extent of the estuarine turbidity maximum falls between Wilmington, Delaware and Philadelphia, where suspended-sediment concentrations reach 100–775 mg/l near-bottom during spring tides (Cook, 2004). More typically, suspended-sedi-

ment concentrations in this part of the estuary are 25–75 mg/l in surface waters.

The freshwater marshes, Oldmans Creek (site PC-14) and Woodbury Creek (site PC-15), located down and upestuary of the heavily industrialized corridor (Fig. 1), were selected for sampling in this study. This was based in part on prior work revealing the presence of heavy metals, presumably of industrial origin, in marshes nearby to the sites in this study (Orson et al., 1992a). Hydraulically contiguous with the Delaware Estuary, these marshes possess tidal prisms that greatly exceed the volume of runoff from their watersheds. With tidal advection being the principal mechanism of inter-creek transport, dissolved and particulate constituents imported from estuarine waters are free to exchange and react within these marshes. The main sub-environments of the marshes include low-marsh vegetated by emergent macrophytes, un-vegetated intertidal mudflats, and shallow, tidal channels. The native morphology of Oldmans Creek and Woodbury Creek have been modified at their mouths, originally by dikes created by European settlers, and later by bulkheads backfilled with dredge spoils (Orson et al., 1992b; Newell et al., 1998). On the other hand, much of the vegetated marsh landward of creek mouths has not been outwardly disturbed during historical times.

2.2. Industrial and eutrophication history of the upper Delaware Estuary

The urban areas of the upper Delaware Estuary are among the most heavily industrialized waterways in the United States, experiencing a doubling of the population over the past 50 years to almost 6 million. Throughout the first half of the 20th century, there was a history of eutrophication in the upper Delaware Estuary. Here the urbanized river experienced chronic hypoxia from the discharge of untreated sewage, resulting in lack of shad fish runs and overwhelming stench of hydrosulfide. This resulted in excessive fresh and marine diatom production leading to depressed oxygen 100 to 160 km upstream from the mouth of the Delaware Bay (E.P.A., 2000).

Starting in the second half of the century, there were coordinated studies and a commission that resulted in stricter point source pollution, particularly the institution of secondary sewage treatment. These improvements in pollution and sewage control have expanded in recent decades. The result is that since approximately 1980, there has been an 86% reduction in both municipal and industrial chemical oxygen demand. Phosphorus levels have dropped by a factor of five during this same period, presumably from reduction in P detergent use, as tertiary treatment has not been implemented. Nitrogen, as nitrate, has increased substantially over this time, while ammonium-N has decreased, as better treatment of sewage has occurred (E.P.A., 2000).

Metal pollution of the urban Delaware Estuary has been a recognized problem (Orson et al., 1992a). The sources undoubtedly include local discharge from point and non-point run-off sources in the heavily urbanized and industrial surrounding areas. However, atmospheric deposition from more remote regional sources has also been recognized as equally important (Church and Scudlark, 1998; Cochran et al., 1998).

3. Analyses

3.1. Marsh coring

In August 2001, push cores were used to collect marsh deposits for radioisotope geochronology. Coring sites were selected in vegetated areas proximal to the main tidal channel, and in places where topographic maps and aerial photographs revealed the marsh to have been undisturbed in recent times. The coring apparatus consisted of a 1.5-m-long, 10-cm diameter PVC pipe (the core barrel) affixed with a piston suspended by cable from a tripod-winch assembly. As the barrel was advanced into the ground, the piston minimized short-ening of the sediment column by countering friction between the core and the inner wall of the barrel. The winch facilitated barrel extraction upon reaching the depth of refusal. Undisturbed cores 70–100 cm in length were readily recovered in this manner. The cores were then extruded vertically and sectioned into 2-cm-thick intervals for subsequent analysis.

3.2. Radioisotope measurements

To develop geochronologies for the marsh deposits, measurements of ^{210}Pb ($t_{1/2} = 22.3$ years) and ^{137}Cs ($t_{1/2} = 30.1$ years) were made in sectioned cores following methods detailed elsewhere (Cutshall et al., 1983). Activities of total ^{210}Pb and ^{137}Cs were measured nondestructively via gamma spectroscopy of the 46.5 and 661.6 keV photopeaks, respectively; excess ^{210}Pb activity was determined by subtracting the activity of its ^{214}Bi parent (at 609.3 keV) from the total activity. Dried and ground sediment samples were counted at constant geometry for 48 h on a Canberra Instruments Model 2020 low-energy Germanium detector (LEGe). Detector efficiencies were determined from counts of NIST Standard Reference Material 4357 (Inn, 2001), and a self-absorption correction for ^{210}Pb was made as described in Cutshall et al. (1983). Confidence limits reported with radioisotope data are the propagated one-sigma background, calibration, and counting errors.

3.3. Sedimentation rates and mass accumulation rates

Both linear sedimentation rates (cm/year) and mass accumulation rates (g/cm^2/year) were estimated from ^{210}Pb and ^{137}Cs activity profiles. In the case of ^{137}Cs, the basal depth of occurrence in the sediment column relative to the ca. 1954 widespread onset of atmospheric nuclear testing was used to compute a sedimentation rate averaged over the past 40−50 years. Sedimentation rates representative for the past 50−100 years were computed from ^{210}Pb data by linear regression of the excess activity-depth profile. Mass accumulation rates were computed in a similar manner but with radioisotope activity plotted, versus cumulative mass (g/cm^2) using measured dry-bulk densities for the sediments. Implicit in these dating methods is the assumption that the specific activity of ^{210}Pb deposited at the marsh surface is constant through time, and that ^{137}Cs deposition follows its atmospheric source function beginning ca. 1954. Additional assumptions are as follows: (1) biological mixing has not enhanced particle burial; (2) the radioisotopes are chemically immobile in the sediment column; and (3) the sedimentary record is

complete and not punctuated by non-depositional or erosional episodes.

3.4. Carbon, nitrogen and phosphorus contents

Sediment material was dried at 40–50 °C and ground with an agate mortar and pestle. All samples were treated in a desiccator with fuming-HCL to remove any inorganic carbon. However, some have found that treatment of organic matter (suspended solids, plants and animals) with HCl can cause a shift in the stable isotopic composition of nitrogen of approximately 0.5‰ (Bunn et al., 1995), while others have not (Lorrain et al., 2003; Bosley and Wainwright, 1999; Chanton and Lewis, 1999). This potential bias is small compared to the variations observed in the samples. Samples were re-dried and analyzed for sediment organic carbon and total nitrogen using a CE Flash 1112 Elemental Analyzer. Samples were run in duplicate or triplicate where analytical variability was generally less than 3% RSD.

Total sediment phosphorus was determined using a dry oxidation method modified from Aspila et al. (1976) and Ruttenberg (1992). Solubilized inorganic phosphorus was measured with standard phosphate procedures using an Alpkem Rapid Flow Analyzer. Standard reference material (spinach leaves) and procedural blanks were analyzed periodically during this study. All concentrations were reported on a dry weight basis.

3.5. Carbon and nitrogen stable isotopes

The stable isotopic composition of sediments was analyzed using a Finnigan Delta XL coupled to an NA2500 Elemental Analyzer (EA-IRMS). Samples were run in duplicate or triplicate with the results reported in the standard δ (‰) notation:

$$\delta X = \left(R_{\mathrm{sample}}/R_{\mathrm{standard}}\right) - 1) \times 1000$$

where X is either ^{13}C or ^{15}N and R is either $^{13}C/^{12}C$ or $^{15}N/^{14}N$.

The $\delta^{15}N$ standard was air ($\delta^{15}N = 0$), and for $\delta^{13}C$ the standard is the Vienna PeeDee Belemite (VPDB) limestone that has been assigned a value of 0.0‰. Analytical accuracy was based on the standardization of the UHP N_2 and CO_2 used for continuous flow-IRMS with IAEA N-1 and N-2 for nitrogen and IAEA sucrose for carbon, respectively. An in-house calibrated sediment standard was analyzed every 10th sample. Generally, precision based on replicate sample analysis was better than 0.2‰ for carbon and 0.6‰ for nitrogen.

3.6. Trace metal sample treatment and analysis

Samples of the dated core material were sub-sectioned from the interior of the core using clean plastic materials to minimize contamination. Sediment samples of 100 mg were digested with 6 ml of nitric acid (Instra Analysed, J.T. Baker) and 2 ml of hydrofluoric acid (Instra Analysed, J.T. Baker) using PTFE Teflon bombs in a closed microwave digestion system (Multiwave 3000, Anton Paar). The procedure first requires a 20-min temperature ramp (20–220 °C), followed by a 15-min 220 °C stage. The analysis of trace metal concentrations in these digested core samples was acquired by ICP-MS (Elan 6000, Perkin Elmer) using a CrossFlow nebulizer and Scott Spray Chamber. Method accuracy was checked for each extraction procedure with the certified reference marine sediment IAEA 405 (IAEA, Monaco).

3.7. Organo-tin analysis

3.7.1. Extraction and derivatization step

Organo-tin compounds were first extracted from 0.5 g of freeze-dried sediment using 20 ml of glacial acetic acid with mechanical stirring for 16 h. Tripropyltin (TrPT) was used as internal standard (50 µl of a 10 mg(Sn) l^{-1} solution). Ethylation was then carried out by using 500 µl of a 2% (w/v) $NaBEt_4$ in 20 ml of a sodium ethanoate-ethanoic acid buffer (pH = 4.8). Iso-octane was used as the extracting organic phase (500 µl) for the ethyl derivatives. The separation and the determination of the organo-tin compounds from 1 µl of the organic phase were performed by using an HP 6890 capillary Gas Chromatograph coupled with a G2350A Microwave-Induced Plasma-Atomic Element Detection (GC-MIP-AED) system. The analytical procedure was adapted from a procedure previously described and optimized (Bancon-Montigny et al., 1999).

3.7.2. Reagents

Mono-, di- and tri-butyl tine chloride solutions were purchased from Aldrich. Tripropyltin chloride (TPrT, 98%) was obtained from Strem Chemicals. The organo-tin stock solutions containing 1000 mg(Sn) l^{-1} were prepared in methanol. Stored at +4 °C in the dark, they were stable for 1 year (Michel and Averty, 1999). Working standards were obtained by dilution in water (10 mg(Sn) l^{-1} and 100 µg(Sn) l^{-1} solutions). They were also stored in the dark at +4 °C. Nitric and ethanoic acids were obtained from Merck, and isooctane from Fluka. The deionized water used was 18 MΩ (Millipore system). Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemicals. The solution was made daily by dis-

solving 0.02 g in 1 ml of deionized water and stored at +4 °C in the dark.

4. Results

The results for the sediment carbon, nitrogen, and phosphorus, together with the C and N stable isotopes are listed in Table 1. The results for the sedimentary metals are shown in Table 2.

4.1. Radioisotope profiles

Cores from Oldmans Creek (PC-14) and Woodbury Creek (PC-15) displayed ^{137}Cs activities that first increased up-core above the minimum detectable activity (0.02−0.03 dpm/g) and then decreased toward the core top (Fig. 2). Core PC-15 (Fig. 2b) displayed ^{137}Cs profile with an activity peak that may be concordant with ca. 1964 and an overall shape consistent with the source

Table 1
Sediment organic carbon (OC), total nitrogen (TN), phosphorus (P), their molar ratios and stable isotopic compositions (δ^{15}N, δ^{13}C) with depth in (a) PC-14 (Oldmans Creek) marsh site and in (b) PC-15 (Woodbury Creek) marsh site

Depth (cm)	OC (%)	TN (%)	P (Ag/g)	C/N (molar)	N/P (molar)	C/P (molar)	δ^{15}N (‰)	δ^{13}C (‰)
a								
0–2	4.62	0.25	997	21.9	5.6	124	7.3	− 25.5
4–6	4.14	0.22	886	21.7	5.7	125	6.2	− 25.1
6–8	4.03	0.22	1066	21.4	4.7	101	6.1	− 25.3
10–12	4.27	0.20	921	25.0	4.9	123	6.3	− 25.0
14–16	3.82	0.20	867	22.2	5.3	117	6.7	− 25.1
18–20	4.22	0.18	788	27.7	5.2	143	6.2	− 25.0
20–22	3.85	0.19	846	23.7	5.1	121	6.4	− 25.2
22–24	3.63	0.18	944	23.0	4.5	103	6.2	− 24.6
24–26	3.55	0.18	884	23.3	4.6	107	6.1	− 24.1
26–28	3.33	0.14	871	27.4	3.7	102	5.9	− 28.5
28–30	1.43	0.08	351	20.3	5.4	109	5.5	− 24.6
30–32	1.47	0.06	201	26.6	7.3	194	5.1	− 27.3
32–34	0.89	0.05	142	19.9	8.4	168	5.3	− 22.5
34–36	0.69	0.02	120	39.9	3.9	154	4.1	− 24.5
36–38	0.80	0.03	114	35.3	5.3	187	4.4	− 23.5
b								
0–2	5.40	0.30	1083	21.2	6.2	133	7.51	− 27.14
4–6	4.86	0.23	1161	24.4	4.6	112	7.02	− 27.03
8–10	4.78	0.21	797	26.3	6.1	160	6.53	− 27.87
12–14	5.19	0.21	877	28.3	5.6	158	6.69	− 28.06
16–18	5.05	0.22	967	26.9	5.2	139	6.19	− 27.44
18–20	4.61	0.22	1250	24.4	4.0	98	6.33	− 26.89
22–24	5.13	0.19	1302	31.6	3.3	105	5.37	− 27.22
26–28	4.34	0.17	1351	29.3	2.9	86	4.39	− 26.87
30–32	4.32	0.17	1752	28.9	2.3	66	5.32	− 27.10
34–36	5.39	0.26	1905	24.5	3.1	75	5.04	− 25.65
38–40	4.94	0.23	1923	24.7	2.8	69	4.26	− 25.38
42–44	4.80	0.20	2169	27.4	2.2	59	3.06	− 24.85
44–46	4.03	0.20	2189	23.1	2.1	49	3.53	− 24.65
46–48	4.23	0.21	2051	23.3	2.4	55	3.39	− 24.87
48–50	5.33	0.27	2088	22.9	3.0	68	3.19	− 25.43
52–54	5.01	0.25	2261	23.8	2.5	59	3.35	− 25.27
54–56	5.58	0.27	2065	24.4	3.0	72	3.44	− 25.36
56–58	4.43	0.23	1705	22.5	3.1	69	3.68	− 24.98
58–60	4.35	0.20	1501	25.1	3.1	77	3.67	− 24.67
60–62	3.98	0.16	943	29.9	3.8	113	3.34	− 25.38
62–64	4.39	0.17	982	29.4	4.0	119	3.39	− 25.07
64–66	4.82	0.18	746	31.9	5.4	172	3.44	− 25.73
66–68	4.34	0.15	672	33.4	5.2	172	3.61	− 25.18
68–70	5.17	0.18	542	33.4	7.6	254	3.73	− 25.36
70–72	7.53	0.29	502	30.3	13.2	400	3.74	− 25.19
74–76	4.73	0.20	367	27.1	12.7	344	2.89	− 25.35
80–82	5.50	0.32	341	20.0	21.4	430	3.01	− 25.85

Table 2

(a) Sediment trace metals in PC-14 (Oldmans Creek) marsh site

Depth (cm)	Ag nmol g^{-1}	(S.D.)	As nmol g^{-1}	(S.D.)	Cd nmol g^{-1}	(S.D.)	Co nmol g^{-1}	(S.D.)	Cr μmol g^{-1}	(S.D.)	Cu μmol g^{-1}	(S.D.)
0–2	8.07	0.20	495	4	9.57	0.33	391	2	2.24	0.07	0.93	0.02
4–6	14.67	0.50	599	2	15.19	0.47	501	17	3.01	0.08	1.29	0.05
6–8	11.52	0.11	744	7	12.35	0.28	455	17	2.75	0.12	1.18	0.04
10–12	11.21	0.28	530	5	12.28	0.45	471	18	2.71	0.14	1.11	0.07
14–16	11.30	0.15	547	6	13.15	0.50	395	4	2.67	0.05	1.20	0.01
18–20	10.51	0.36	523	4	12.41	0.86	441	26	3.07	0.21	1.43	0.08
20–22	12.01	0.32	593	11	14.10	0.34	500	22	3.45	0.23	1.51	0.06
22–24	7.36	0.17	475	6	8.45	0.29	359	10	2.18	0.07	0.96	0.02
24–26	9.11	0.04	641	7	9.56	0.23	476	12	2.87	0.12	1.38	0.05
26–28	8.08	0.16	680	12	9.82	0.64	539	25	2.79	0.15	1.30	0.06
28–30	6.04	0.20	487	2	5.04	0.49	488	27	2.76	0.19	0.77	0.04
30–32	5.18	0.23	431	6	4.06	0.26	453	20	2.52	0.20	0.59	0.03
32–34	4.01	0.08	351	8	1.46	0.15	381	17	2.17	0.18	0.39	0.02
34–36	3.90	0.10	344	3	1.33	0.17	368	14	2.14	0.12	0.36	0.01
36–38	2.90	0.06	311	5	0.81	0.06	272	10	1.56	0.08	0.28	0.01

Depth (cm)	Mn μmol g^{-1}	(S.D.)	Pb nmol g^{-1}	(S.D.)	Sn nmol g^{-1}	(S.D.)	U nmol g^{-1}	(S.D.)	V μmol g^{-1}	(S.D.)	Zn μmol g^{-1}	(S.D.)
0–2	32.0	1.3	771	25	61.0	1.7	16.4	0.5	2.24	0.10	4.30	0.22
4–6	18.4	0.8	1059	32	94.5	2.3	19.2	0.5	3.00	0.08	6.04	0.31
6–8	22.1	1.1	941	35	70.6	1.4	17.1	0.6	2.76	0.10	5.04	0.17
10–12	14.5	0.8	912	37	71.4	1.5	15.2	0.6	2.75	0.11	5.15	0.51
14–16	13.0	0.4	1021	19	86.3	1.2	13.1	0.3	2.68	0.05	5.41	0.12
18–20	13.3	1.0	1318	86	76.3	3.7	20.3	1.3	2.96	0.17	5.48	0.52
20–22	15.9	1.2	1443	84	87.5	3.7	20.0	1.1	3.23	0.21	6.20	0.63
22–24	10.6	0.5	1077	30	180.6	4.1	15.4	0.4	2.14	0.06	3.80	0.12
24–26	17.1	1.0	1602	68	80.6	2.7	16.8	0.7	2.88	0.11	5.45	0.43
26–28	18.0	1.1	1762	87	103.9	3.7	18.3	0.9	3.08	0.12	5.00	0.16
28–30	13.1	1.0	752	51	91.2	3.3	17.8	1.3	3.08	0.21	3.55	0.31
30–32	11.6	0.9	430	27	41.2	2.1	19.9	1.2	2.89	0.18	3.23	0.13
32–34	9.7	0.8	194	11	27.6	1.8	16.3	0.9	2.53	0.21	2.07	0.20
34–36	9.3	0.7	168	8	23.9	1.0	17.7	0.9	2.56	0.16	2.03	0.18
36–38	6.7	0.4	131	5	23.2	0.9	14.2	0.5	1.78	0.10	1.21	0.08

(b) Sediment trace metals in PC-15 (Woodbury Creek) marsh site

Depth (cm)	Ag nmol g^{-1}	(S.D.)	As nmol g^{-1}	(S.D.)	Cd nmol g^{-1}	(S.D.)	Co nmol g^{-1}	(S.D.)	Cr μmol g^{-1}	(S.D.)	Cu μmol g^{-1}	(S.D.)	Mn μmol g^{-1}	(S.D.)
0–2	14.70	1.23	358	18	60.70	3.28	421	35	1.91	0.11	1.67	0.11	11.3	0.9
4–6	15.62	2.36	365	41	45.78	8.32	389	69	2.27	0.38	1.57	0.29	8.1	0.4
8–10	21.37	1.76	560	25	37.18	3.75	468	45	2.42	0.20	1.55	0.14	7.3	0.3
12–14	27.76	2.32	472	35	49.12	5.74	506	55	2.59	0.28	1.85	0.20	7.3	0.4
16–18	39.18	2.11	488	16	48.21	2.92	645	38	3.14	0.17	1.98	0.11	11.7	0.4
18–20	37.86	1.80	537	21	54.23	2.96	657	44	3.11	0.18	2.00	0.13	14.4	0.4
22–24	40.66	2.41	689	26	66.79	4.30	631	48	4.67	0.35	2.34	0.14	13.8	0.5
30–32	42.35	2.39	650	25	64.50	5.85	446	34	6.32	0.53	2.32	0.18	11.0	0.5
34–36	53.18	2.84	1078	57	160.43	12.66	649	51	6.49	0.51	3.50	0.24	13.2	0.5
38–40	54.70	3.43	787	50	106.01	8.54	615	48	6.99	0.53	3.18	0.25	12.8	0.5
40–42	40.07	1.93	610	30	83.63	4.03	567	25	4.84	0.22	2.69	0.12	14.6	0.6
44–46	49.29	2.77	445	20	77.53	4.97	423	24	5.27	0.31	2.87	0.16	13.9	0.6
46–48	48.88	2.28	533	22	69.58	2.80	453	18	5.95	0.29	2.92	0.13	11.3	0.6
48–50	38.85	2.87	734	39	65.23	5.24	543	46	5.33	0.48	2.60	0.19	10.6	0.3
52–54	38.93	3.24	767	47	71.65	7.04	456	46	5.55	0.57	2.70	0.26	9.3	0.3
56–58	20.05	0.83	598	18	49.17	3.38	335	19	3.52	0.19	2.03	0.11	7.5	0.5

Table 2 (continued)

(b) Sediment trace metals in PC-15 (Woodbury Creek) marsh site

Depth	Ag		As		Cd		Co		Cr		Cu		Mn	
(cm)	nmol g^{-1}	(S.D.)	nmol g^{-1}	(S.D.)	nmol g^{-1}	(S.D.)	nmol g^{-1}	(S.D.)	μmol g^{-1}	(S.D.)	μmol g^{-1}	(S.D.)	μmol g^{-1}	(S.D.)
58–60	29.06	3.83	872	95	55.16	8.14	464	76	4.63	0.77	2.66	0.39	6.1	0.2
60–62	15.10	0.83	615	27	29.22	1.57	432	29	2.50	0.18	1.33	0.08	7.7	0.4
62–64	15.03	1.45	828	79	32.88	5.06	531	77	3.11	0.44	1.61	0.21	6.9	0.3
64–66	10.39	1.03	722	58	23.95	2.77	473	59	2.24	0.29	1.21	0.14	7.5	0.3
66–68	8.43	0.59	678	48	20.02	1.84	497	56	2.57	0.28	1.29	0.12	10.2	0.2
68–70	7.85	0.41	715	21	14.17	0.55	470	8	2.48	0.06	1.17	0.02	6.5	0.2
70–72	6.02	0.28	1304	18	21.51	0.80	590	12	1.93	0.04	1.34	0.02	12.5	0.3
74–76	4.84	0.22	670	23	13.32	0.66	327	12	1.80	0.07	0.81	0.02	8.4	0.3
80–82	3.66	0.11	360	13	8.26	0.38	302	7	1.54	0.05	0.63	0.01	8.2	0.2

Depth	Ni		Pb		Sb		Sn		U		V		Zn	
(cm)	nmol g^{-1}	(S.D.)	nmol g^{-1}	(S.D.)	nmol g^{-1}	(S.D.)	nmol g^{-1}	(S.D.)	nmol g^{-1}	(S.D.)	μmol g^{-1}	(S.D.)	μmol g^{-1}	(S.D.)
0–2	941	67	720	39	30.3	1.9	97.4	6.9	20.6	1.2	2.21	0.08	12.39	0.73
4–6	905	150	686	117	26.4	3.5	107.3	12.5	19.2	3.4	2.54	0.33	9.41	1.62
8–10	952	92	745	65	33.5	2.4	117.5	5.6	18.7	1.8	2.78	0.19	9.75	0.89
12–14	1004	109	872	97	49.8	4.6	142.3	10.6	19.4	2.1	2.92	0.26	11.10	1.21
16–18	1133	58	892	43	54.6	2.1	157.2	6.3	19.3	1.2	3.06	0.12	10.42	0.51
18–20	1362	91	788	51	57.6	2.8	158.6	7.6	14.3	1.3	3.32	0.16	12.43	0.84
22–24	1453	107	1024	68	65.5	3.6	201.1	9.6	19.2	1.3	4.09	0.25	14.48	1.04
30–32	1255	83	1016	88	86.4	4.1	225.4	7.3	17.4	2.2	7.18	0.52	11.36	1.02
34–36	1795	140	1477	98	144.3	7.8	288.4	16.5	16.1	1.1	9.39	0.67	24.58	1.64
38–40	1650	124	1343	54	157.4	10.3	284.8	14.2	12.7	1.2	7.67	0.57	18.86	1.43
40–42	1392	72	1382	73	86.3	3.6	223.1	10.4	14.0	0.7	4.79	0.18	16.94	0.68
44–46	1170	57	1293	37	73.1	3.5	239.5	12.9	10.6	1.0	3.65	0.19	15.18	0.83
46–48	1422	52	1442	65	80.8	3.5	229.3	9.8	13.6	0.5	4.33	0.17	14.91	0.68
48–50	1489	118	1180	42	86.0	4.9	197.7	12.5	12.2	1.7	5.02	0.36	13.78	1.29
52–54	1311	113	1247	119	83.1	6.7	202.2	15.7	13.0	1.6	5.88	0.55	13.97	1.38
56–58	857	56	942	44	58.9	2.8	113.8	3.5	11.0	0.4	4.25	0.18	9.25	0.40
58–60	1155	179	1215	139	73.2	7.9	156.4	17.5	14.4	2.4	5.49	0.76	10.31	1.69
60–62	806	52	723	40	37.6	1.8	100.7	3.7	8.5	0.9	2.76	0.18	6.92	0.44
62–64	840	117	1053	140	78.0	7.5	138.1	11.3	11.7	1.9	2.85	0.36	9.50	1.30
64–66	842	105	984	70	36.5	3.2	247.9	21.1	9.0	1.4	2.36	0.26	7.31	0.88
66–68	716	75	709	66	24.1	1.4	124.6	9.2	10.2	1.6	2.37	0.22	5.78	0.66
68–70	706	19	681	19	18.7	0.8	122.5	3.9	10.9	0.7	2.01	0.04	5.95	0.11
70–72	875	15	669	14	23.0	0.5	104.5	2.5	10.8	0.3	1.68	0.03	6.48	0.13
74–76	601	19	381	18	12.0	0.3	70.4	1.8	9.7	1.1	1.55	0.04	4.63	0.24
80–82	558	18	284	7	8.9	0.3	55.5	0.8	8.5	0.8	1.54	0.04	3.56	0.10

function for the Mid-Atlantic region (Olsen et al., 1981). Linear sedimentation rates (and mass accumulation rates) based on the basal depth of ^{137}Cs activity were 0.6 cm/year (0.4 g/cm^2/year) and 1.4 cm/year (0.5 g/cm^2/year) for PC-14 and PC-15, respectively.

Excess ^{210}Pb profiles for both cores exhibited a monotonic decrease in the log of the activity downcore, indicative of steady-state sediment accumulation and radioactive decay (Fig. 2). Linear sedimentation rates derived from these profiles were 0.6 cm/year (0.3 g/cm^2/year) and 0.9 cm/year (0.3 g/cm^2/year) for PC-14 and PC-15, respectively. The fact there is uniform porosity with depth in both cores with depth (0.6–0.7 for PC-14; 0.7–0.8 for PC-15) supports the notion

that these marshes have accumulated with a steady import of fine-grained sediment over the past 50 years without evidence of episodic input.

At site PC-15, the ^{137}Cs-derived rate was higher than that based on ^{210}Pb by nearly a factor of 2. In part, this difference can be attributed to the dissimilar time spans over which these radiotracers average sedimentation rates, 40–50 years for ^{137}Cs, and 50–100 years in the case of ^{210}Pb. Because ^{210}Pb geochronology averages over a wider range of sedimentary conditions, including short periods of non-deposition, it may yield rates that are somewhat lower than those based on ^{137}Cs. An alternative explanation for the disparity is that the rate of sedimentation has increased over the past several
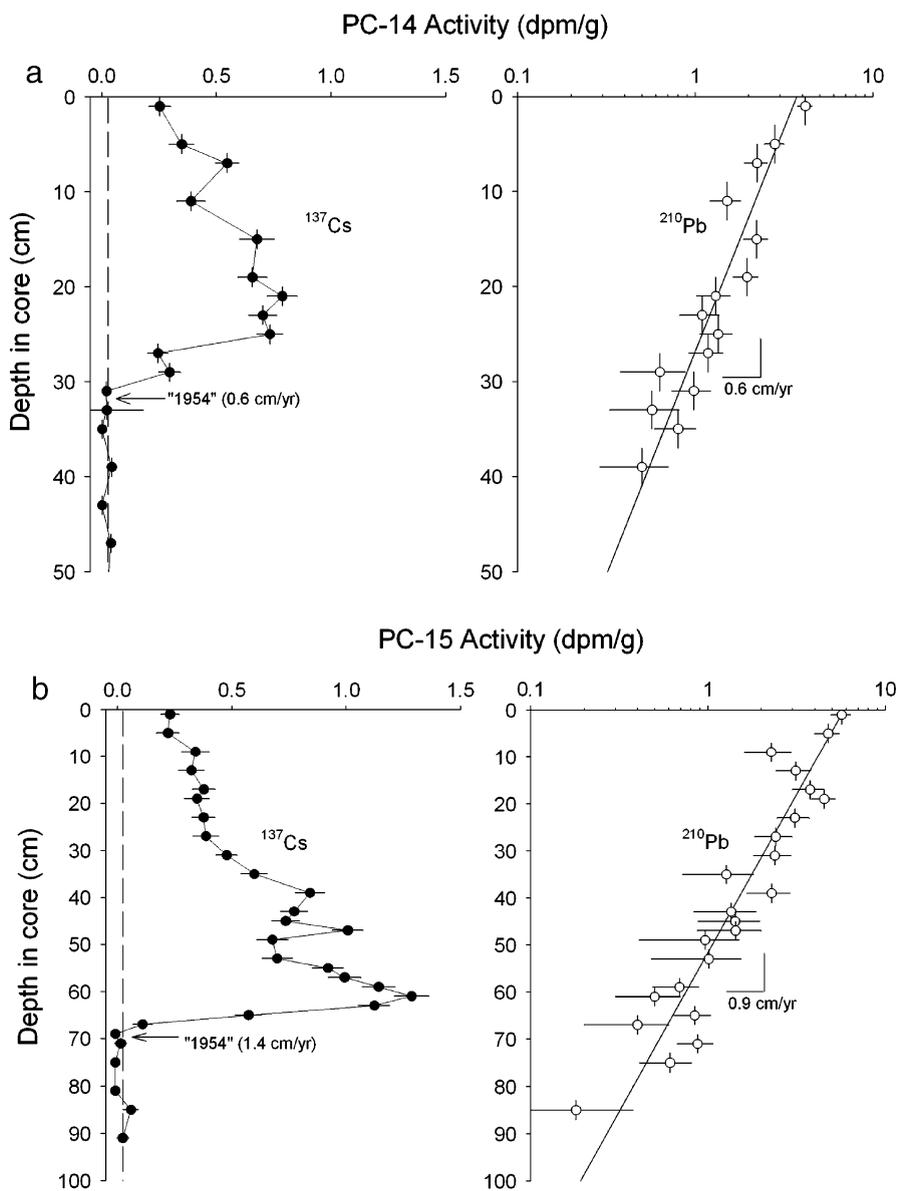
Fig. 2. Geochronology for the two marsh sediment cores (a) Oldmans Creek and (b) Woodbury Creek using both the transient fallout ^{137}Cs and steady-state natural ^{210}Pb radionuclides. Both nuclides give concordant sedimentation rates of 6 and 12 mm/year (average) at these two sites.

decades, perhaps due to accelerated fine-grained sediment delivery to the marshes, yet a change in sedimentation rate is not apparent from the log-linear slope of the ^{210}Pb activity profiles. The computed sedimentation rate for PC-15 based on ^{137}Cs chronology is markedly higher at 1.6 cm/year, assuming the activity peak is representative for ca. 1964. However, the separation assigned to the dates of 1954 and 1964, the background and peak of atmospheric weapons testing, do not support this high rate of sedimentation. Thus, as a compromise, we have assigned the upstream Woodbury Creek site (PC-15) a

sedimentation rate of 1.2 cm/year, the average of that determined by [137]Cs (1.4 cm/year) and [210]Pb (0.9 cm/year) geochronology. However, the rate assigned to the downstream Oldmans Creek site (PC-15) is the lower concordant rate of 0.6 cm/year. These two rates are used to plot the corresponding dated depths in the figures.

4.2. Carbon, nitrogen and phosphorus contents

All concentrations for C, N and P are plotted on a dry weight basis (Fig. 3).
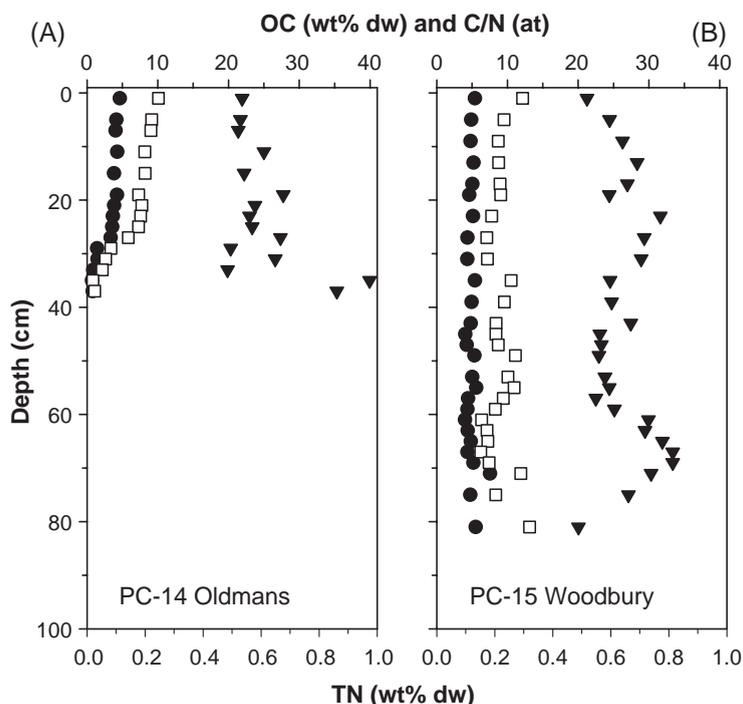
Fig. 3. Distribution of organic carbon (●), total nitrogen (□) and the molar ratio of C to N (▼) in (A) Oldmans Creek and (B) Woodbury marshes from the upper Delaware estuary.

Sediment organic carbon (OC) and total nitrogen (TN) exhibited slight differences between locations and with depth. Surface OC and TN concentrations decreased slightly from up-estuary (5.4% and 0.3%) to down-estuary (4.6% and 0.25%), which resulted in similar C to N molar ratios (C/N) between sites (21.2 and 21.9). The distribution of OC and TN followed slightly different trends with depth. In Oldmans Creek (core PC-14), OC and TN decreased by approximately 85% from the surface concentration to 37 cm (Fig. 3A), whereas in Woodbury Creek (PC-15), OC and TN remained fairly constant with depth (Fig. 3B). The C to N ratio (molar) with depth was similar between locations (Fig. 3A, B). In the upper 40 cm, there was a slight increase with depth in both cores, excluding the two lower depths in PC-14 due to very low TN concentrations. In the deeper sections of PC-15, the C to N ratio showed another maximum TN concentration located between 66 and 70 cm.

Total sediment P (TSP) and the C to P molar ratios (C/P) revealed large variations in PC-15, with only small changes in PC-14 (Fig. 4). The surface sections in both cores had similar TSP concentrations and C to P ratios of approximately 1000 μg P/g dw and 125, respectively. In PC-14, TSP concentrations generally decreased slightly from the surface to approximately 27 cm, then decreased to between 113 and 120 μg P/g dw near the bottom (Fig. 4A). The C/P ratio was nearly

constant to 27 cm, but then increased to approximately 190 near the bottom. In PC-15, TSP increased to 2261 μg P/g dw at 53 cm then decreasing to 351 μg P/g dw at 81 cm near the bottom of the core (Fig. 4B). C/P values decreased slightly to a minimum (with higher TSP concentrations) at similar depths in both cores, and increased to >300 as TSP decreased.

4.3. Carbon and nitrogen stable isotopes

The isotopic compositions of OC and N exhibited large changes within each core (Fig. 5). In Oldmans Creek (PC-14), the $\delta^{13}C$ increased slightly with depth, from $-25.5‰$ to $-24.1‰$ at 22 cm, then became extremely variable to the bottom of the core, ranging from $-28.5‰$ to $-22.5‰$ (Fig. 5A). In Woodbury Creek (PC-15), the $\delta^{13}C$ value was $-27.1‰$ at the surface and decreased slightly to $-28.1‰$ at 10 cm, after which the sediments became more enriched in ^{13}C with a $\delta^{13}C$ of $-24.7‰$ at 45 cm (Fig. 5B). Below this depth, the $\delta^{13}C$ decreased to approximately $-26‰$ near the bottom. The nitrogen isotopic compositions were similar between cores with highest $\delta^{15}N$ at the surface ($\sim7.3‰$), decreasing with depth to approximately $4.1‰$ at the bottom of PC-14 (similar to PC-15). In PC-15, sediments below 40 cm had similar N isotopic compositions, averaging (±1S.D.) $3.4\pm0.3‰$ ($n=16$).
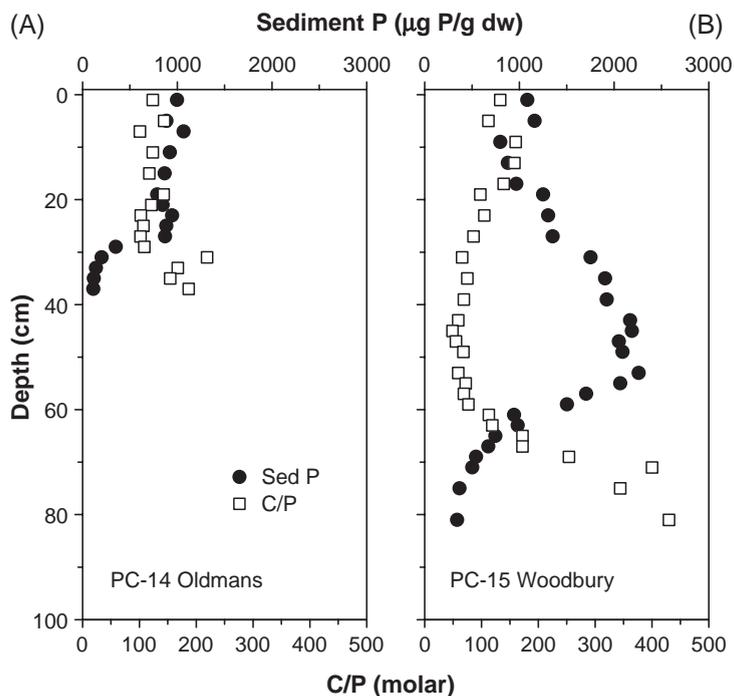
Fig. 4. Distribution of total sedimentary P (●) and C to P molar ratio (□) in (A) Oldmans and (B) Woodbury Creek marshes from the upper Delaware estuary.
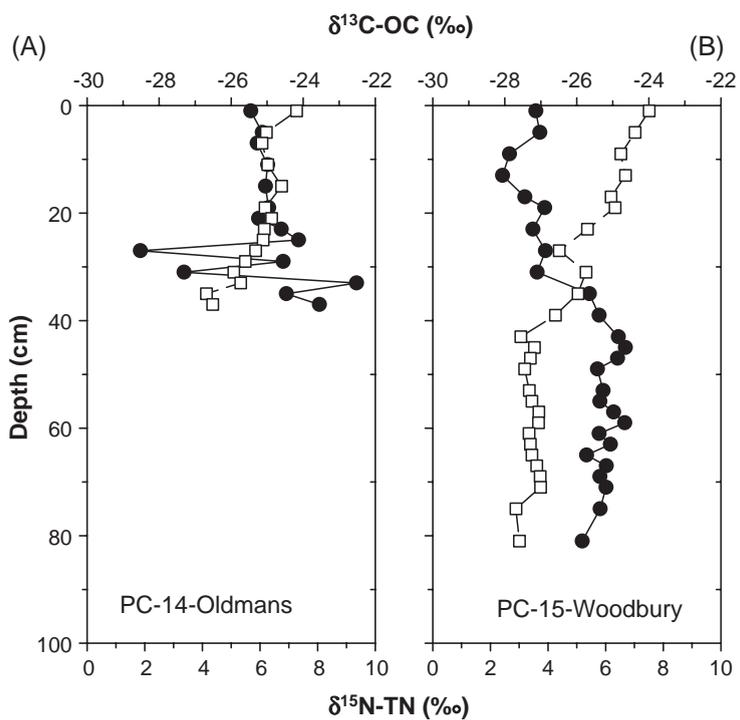

Fig. 5. Carbon (●) and nitrogen (□) isotopic composition with depth in (A) Oldmans and (B) Woodbury Creek marshes from the upper Delaware estuary.

4.4. Trace metals

The concentration of metals in the core on a dry weight basis is plotted in Fig. 6.

In the Oldmans Creek site (PC-14), two groups of metals can be identified:

1) Ag, Cd, Cu, Cr, and Co displayed a 2- to 5-fold increase after 1950 up to 1963–1965, after which steady inventories over the past 20–30 years are observed.
2) Pb and Sn displayed a 10-fold increase after 1950. Steady inventories over the last 30 years are then observed for Sn, whereas decreasing levels are evident for Pb.

In comparing the absolute concentration back from 1950, similar concentrations are seen for As, Cd, Co, Cr, and V, whereas Cu, Ag and Sn displayed 3- to 4-fold higher levels. A marked anthro-

pogenic influence is suspected for Pb, in that it actually displayed a 6-fold higher level, peaking in 1960–1970.

In the Woodbury Creek core (PC-15), three groups of metals can be identified. Starting from before 1940s to 1969, a marked increase of metal concentrations is manifested. Three groups of metals can be identified:

1) Cr, Sn, V, Ni, Co and Cu that displayed a 2- to 5-fold increase;
2) Pb, Zn, Sb and Ag that displayed a 7- to 12-fold increase; and
3) Cd that displayed a 20-fold increase.

Comparing the concentrations before 1950 suggest similar levels for As, Co, Cr and V, whereas Ni, Cu, Zn, Ag, Sn and Pb displayed 1.5- to 3-fold higher levels. A marked anthropogenic influence is suspected for Cd in that it actually displayed a 7-fold higher concentration
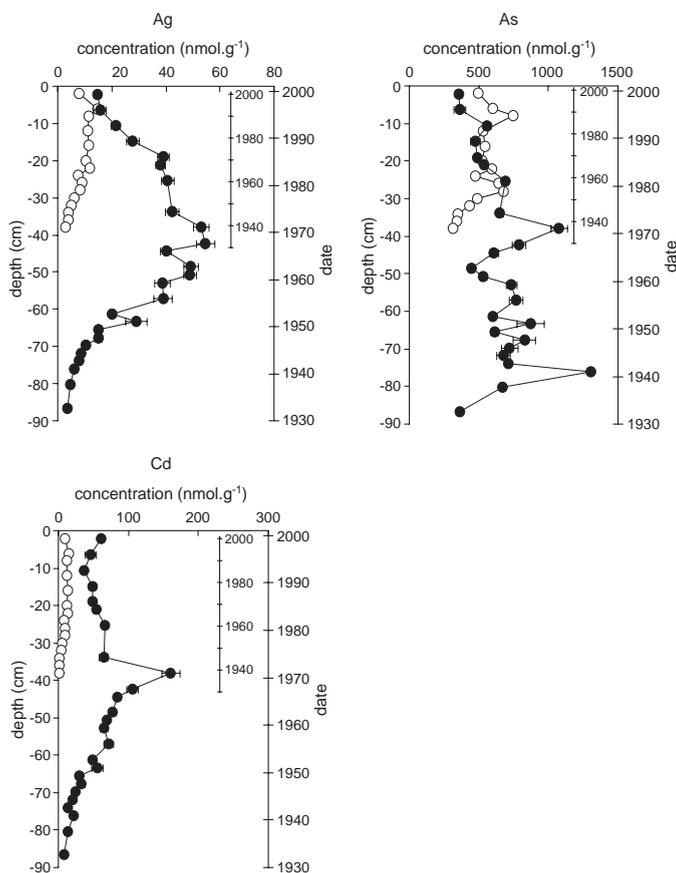
Fig. 6. Metal (Ag, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Sn, V and Zn) concentration profiles in the Oldmans Creek (PC-14) marsh (○) and Woodbury Creek (PC-15) marsh (●) sites in the upper Delaware estuary.
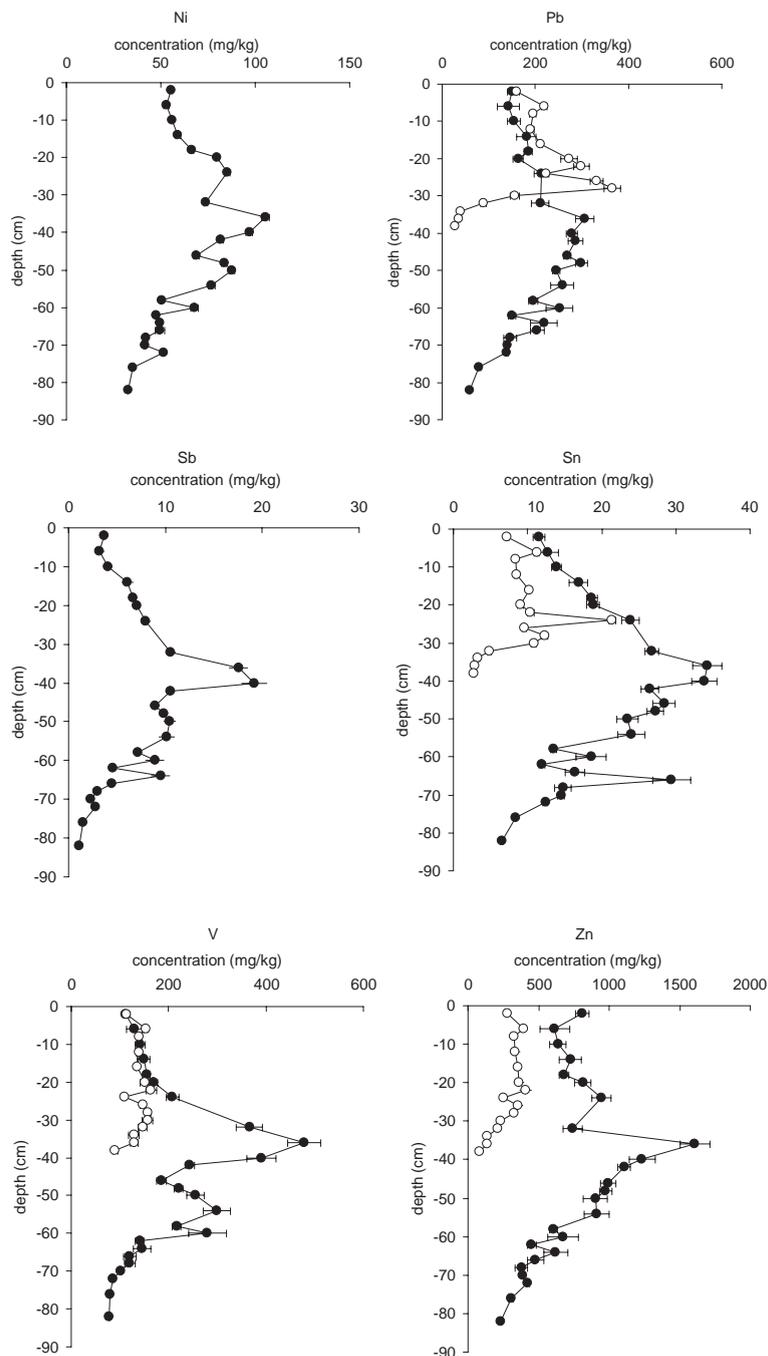
Fig. 6 (*continued*).

overall. When the comparison of concentrations is made from 1972 to present, one group of metals (V, Cr, V, Sn, and Ag) displayed gradually decreasing levels, whereas another group (Pb, Cu, Zn, Cd and Co) displayed a more rapid decrease starting about 1976, before showing steady inventories up to the present.

4.5. Organo-tins

In the Oldmans Creek (PC-14) core downstream, the cumulated butyl tin species displayed a gradual increase up to a well defined by 1981, followed by some decreasing concentrations in recent times (Fig. 7). This
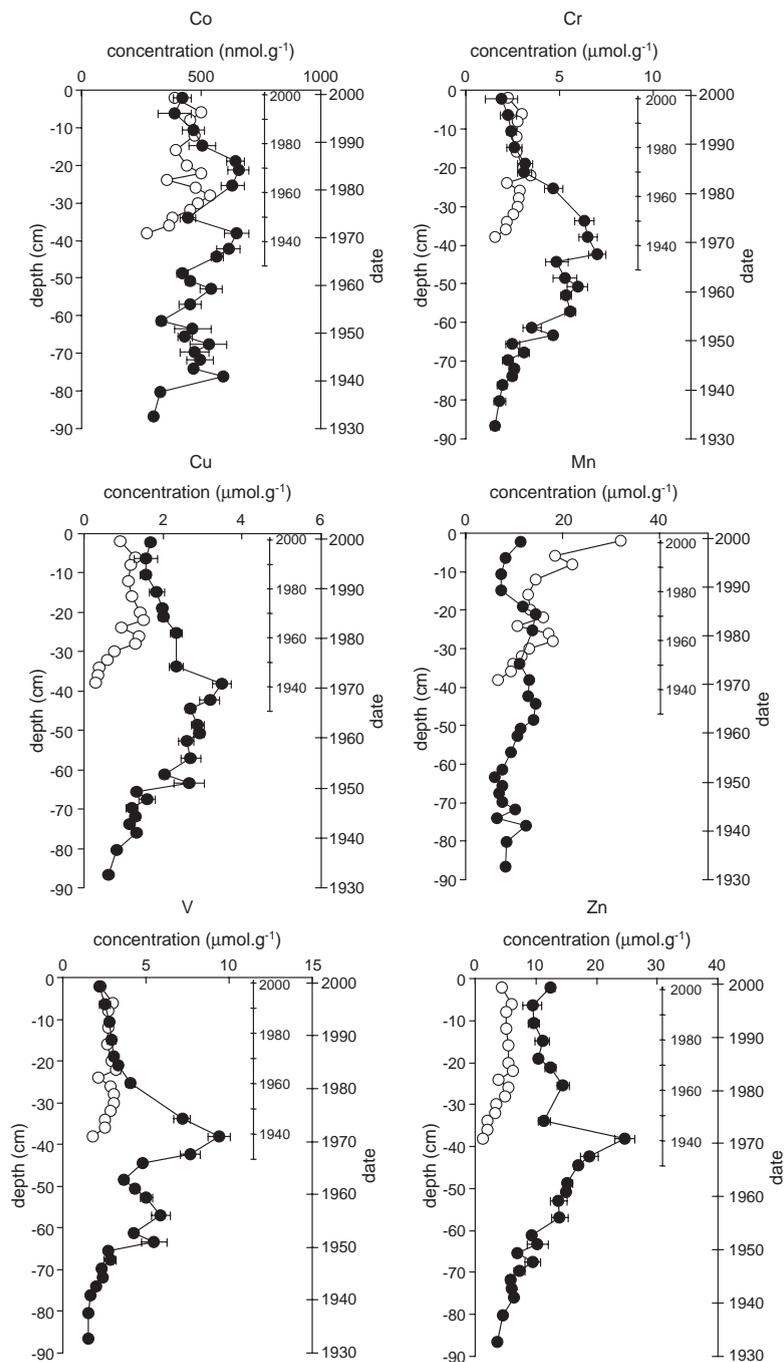
Fig. 6 (*continued*).

peak corresponds to a maximum input for each species (MBT, DBT and TBT) between 1981 and 1986.

In the Woodbury Creek (PC-15) core profile upstream, there is a broad peak peaking by the mid-late 1970s (Fig. 7) for all cumulated butyl species. These concentrations appear to decrease only somewhat in more modern times.

5. Discussion

5.1. Marsh sedimentation rates in perspective

The influence of biological mixing on particle burial in an accreting sediment column cannot generally be deduced from the shape of a radioisotope profile. Thus,
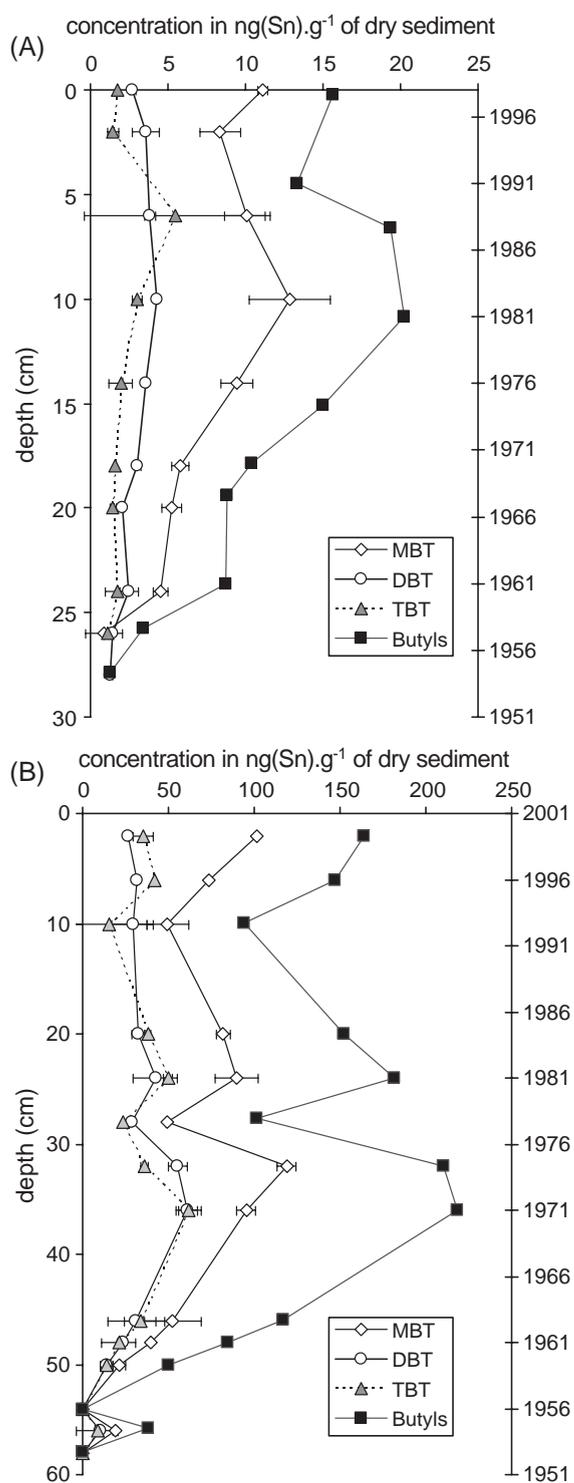
Fig. 7. Concentration profiles for organo-tin butyl compounds in the (A) Oldmans and (B) Woodbury Creek marshes in the upper Delaware estuary. The date scale reported on the right axis for the two cores is based on the sedimentation rate of 0.6 cm/year and 1.2 cm/year for PC-14 and PC-15, respectively.

mixing effects on sedimentation rates are commonly estimated through iterative numerical modeling of paired ^{210}Pb and ^{137}Cs (or ^{239,240}Pu) profiles (Benninger et al., 1979; Olsen et al., 1981; Sharma et al., 1987). The results of such mixing models revealed that bioturbation can increase the apparent sedimentation rate by as much as a factor 2−3 over the true rate, depending on mixing intensity, mixing depth, and sedimentation rate. Biological mixing was not apparent in PC-14 and PC-15, as X-radiographs of these cores revealed well-preserved bedding surfaces and no burrow traces. Nonetheless, because the potential effects of biological mixing cannot be ruled out, the rates reported herein should be taken as maximum estimates of the actual values.

Linear sedimentation rates determined in this study are comparable to those reported previously for the freshwater and brackish intertidal marshes of the Delaware Estuary (Orson et al., 1992a; Sommerfield and Madsen, 2004; Scileppi, 2004). Collectively, these rates are up to an order of magnitude higher than the local rate of relative sea level rise (2−3 mm/year) as documented by local National Ocean Service tide-gauge records. Though it is widely assumed that the rate of marsh accretion is limited by the rate of sea-level rise (Sharma et al., 1987), on decadal-to-centennial time scales, intertidal deposits of marshes, lagoons and estuaries in fact accrete at rates in excess of sea level rise (Nichols, 1989). Here it is important to distinguish among marsh sub-environments and note that the sites sampled in this study were within the low marsh (subjected to daily tidal inundation) and proximal to the main tidal channel. Because the channel-to-marsh flux of suspended sediment is controlled by ambient sediment concentrations and the frequency of tidal inundation, the so-called hydroperiod, sediment trapping and marsh accretion rates tend to be highest near the source channel (Friedrichs and Perry, 2001). For this reason, the low marsh is able to accrete relative to the high marsh, whose tidal inundation is on the order of 10 days to a fortnight. This relatively long hydroperiod limits high-marsh accretion to a rate approximating that of local sea-level rise. Accordingly, the low-marsh sedimentation rates reported herein are likely to be maximal values for the greater marshes of Woodbury Creek and Oldmans Creek. Fringing marshes of the Delaware Estuary are clearly capable of trapping large amounts of tidally imported suspended sediment, much of which is sequestered in the low marsh.

It is worth noting that ^{137}Cs activity is present in sediments of the marsh sites at appreciable levels, despite the fact that atmospheric fallout has been negligible since about 1980. Recalling that post-depo-

sitional biological mixing at the coring sites is unlikely, this implies a non-atmospheric source for ^{137}Cs such as wash-in from upland soils and (or) redistribution of recent sediments previously buried in the estuary. An advective source for ^{137}Cs is corroborated by inventories of excess ^{210}Pb at Woodbury Creek (78 dpm/cm^{2}) and Oldmans Creek (55 dpm/cm^{2}), which greatly exceed that which could be supported by the steady-state atmospheric flux for the Mid-Atlantic region of $23-26$ dpm/cm^{2} (Graustein and Turekian, 1986). Regional radioisotope distributions and patterns of historical bathymetric change revealed that the Delaware Estuary is presently non-depositional or erosional throughout much of its subaqueous extent (Scileppi, 2004; Walsh, 2004), and that the fringing marsh on the whole is apparently a terminal sink for eroded fine-grained material. The estimated erosional sediment yield is significant at $2-3 \times 10^9$ kg/year averaged over the past 50 years, which exceeds the annual load of fine-grained sediment delivered to the estuary (Walsh, 2004). This erosional sediment source may explain the high inventories of ^{137}Cs measured in the sediments of Woodbury and Oldmans Creeks.

5.2. Eutrophication history as recorded by P and C content

Changes in TSP concentrations with depth occurred over a 60-year time frame at the Woodbury Creek site (Fig. 8) and are supported by water quality monitoring data for total phosphorus in the upper Delaware Estuary (J. Sharp and E. Santoro, unpublished data; E.P.A., 2000). Although consistent TP monitoring information is only available from the late 1960s, a similar trend was observed between TP water concentrations (i.e., high concentrations in the early 1970s) and the distribution of TSP over time. These apparent trends indicate substantial change in TSP concentrations in the Woodbury core and most likely reflect the changes in net usage and load of P from the Delaware watershed (Fig. 8). In the late 1940s, inputs were lower and increased dramatically over the next 30 years. Peak loads appear to have occurred in the early 1970s, after which loads and resultant concentrations decreased.

The anthropogenic input of P is a result of both point (i.e., waste water discharges) and non-point sources (i.e., farmland runoff, atmospheric deposition). The most likely factors resulting in the changes in loads of P are from fertilizer use and P-detergent use. Fertilizer use would be a main component of non-point or diffuse sources of P, while P use in detergents would be a main contributor to point sewage sources. Similar water quality trends in various water bodies within the United States showed that the reduction of P in detergents, starting in the early 1970s, quickly reduced the concentrations and loadings of P to many systems including the Delaware estuary (Roman et al., 2000; E.P.A., 2000). As such, sewage point source discharge of P was most likely the dominant source of P to many river systems, and although fertilizer inputs are variable, they can be large in some cases
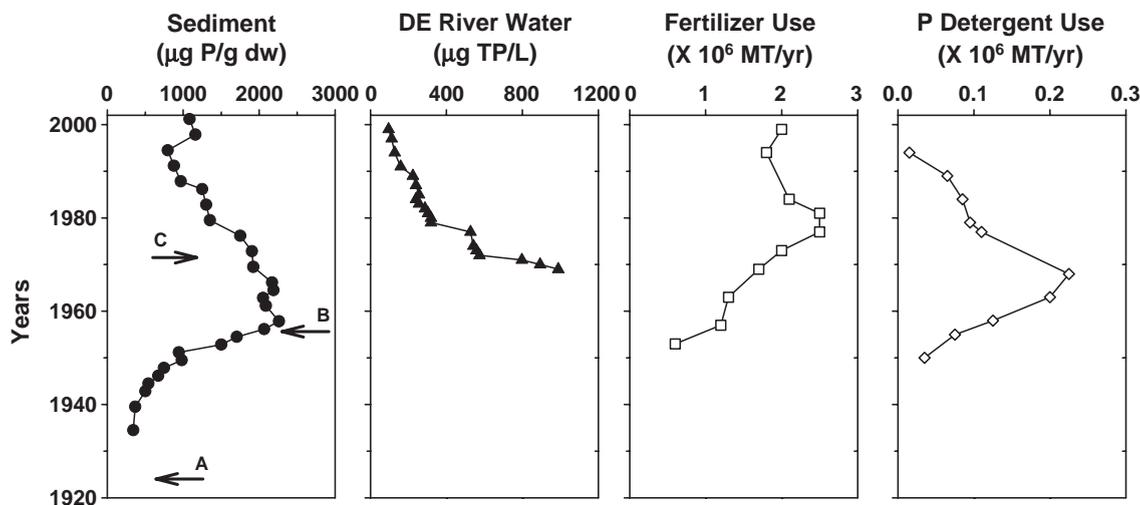

Fig. 8. Total sediment P (TSP) in Woodbury Creek (PC-15) and total P (TP) in bottom portion of the tidal freshwater Delaware River (RM 78). TP (4-year running average) for the Delaware River is from Santoro, 1998 (E.P.A., 2000) and Sharp (unpublished data). The fertilizer and the detergent P are national data taken from Litke (1999). Dates for sediment P are based on 1.2 cm/year. (A) First WWTP in Philadelphia started operations in approximately 1923. (B) Three WWTP facilities operating with primary treatment (1957). (C) 1972 Clean Water Act, all three plants went online with secondary treatment (biological treatment and chlorination) by 1974 (Grusheski, Phila. Water Dept; personal communication).

(Carco, 1995). Approximately 60% of the P loads to the Delaware Estuary between 1988 and 1994 have been estimated to be derived from wastewater treatment facilities, with the remainder from agriculture (31%) and other sources (<10%) such as atmospheric deposition (Roman et al., 2000). In the Philadelphia area, wastewater (currently at 470 mgd) is treated mainly by 3 major facilities (Fig. 8). Between the late 1950s and early 1970s, treatment was primary (including screening and sludge removal), until secondary biological treatment started in 1974 that removed a substantial amount of organic matter and oxygen demand.

Phosphorus used for detergent manufacturing started in the 1940s when synthetic detergent compounds (up to 15% P by weight) were first introduced. By the mid-1960s, detergent production consumed approximately 2.2×10^5 metric tons of P per year (Litke, 1999) (Fig. 8). Starting in the early 1970s, the P content, and its use in detergents, was reduced to <1% P, and over the next 20 years P detergent bans were enacted in many states. Since the Woodbury Creek site (PC-15) is located in the more urban core of the Delaware River watershed, point sources of P are probably more dominant in the local area. Therefore, it is probable that distribution of TSP is related to some combination of fertilizer and detergent use. However, the decrease starting in the mid-1960s is more reflective of detergent use P reductions and the variable changes in fertilizer use starting in the late 1970s (Litke, 1999).

5.3. Eutrophication history as recorded by C and N isotopes

Changes in P concentrations and loads to the tidal freshwater Delaware River may have also affected the level of primary productivity in the system. Stable isotopes of C in organic matter have been shown to follow productivity and eutrophication processes in lakes (Schelske and Hodell, 1991, 1995). In aquatic plants, carbon isotopes (^{12}C and ^{13}C) are fractionated during photosynthesis because the enzyme ribulose 1,5-bisphosphate (RuBP) preferentially removes the lighter isotope (^{12}C-CO$_2$) from the dissolved inorganic carbon pool (Vogel, 1980; Estep, 1984; Raven et al., 1994). The variability and enrichment of ^{12}C in algae are influenced by a number of factors including temperature, species composition, inorganic C composition and concentrations, productivity and the δ^{13}C of the inorganic C pools (Sackett et al., 1964; Rau et al., 1989; Fogel et al., 1992). For example, as productivity increases, there would be less discrimination between the two isotopes, resulting in more ^{13}C enriched algal/plant cells and organic matter. In addition, there can be a change in the source of inorganic carbon (dissolved CO$_2$ versus HCO$_3^{2-}$) taken up, due the availability of dissolved CO$_2$ at higher growth rates (Fogel et al., 1992; Goericke et al., 1994).

In the sediments sampled at Woodbury Creek (PC-15), changes in the δ^{13}C-OM are related to TSP concentrations, suggesting changes in overall production with time (Fig. 9). However, there were two significant relationships between sedimentary P and the δ^{13}C of organic matter, both of which show higher δ^{13}C with increasing TSP. The first relationship ($r^2 = 0.505$, $p < 0.01$) is for the time period when P levels increased sharply from the 1940s to 1960s, whereas the second relationship starts from the peak in TSP concentrations in the mid-1970s to lower concentrations in 2000 ($r^2 = 0.894$; $p < 0.01$). During the increasing first phase, as TSP and P loadings increased, there is a small change in δ^{13}C with increasing TSP. When loadings and TSP begin to decrease, there is a
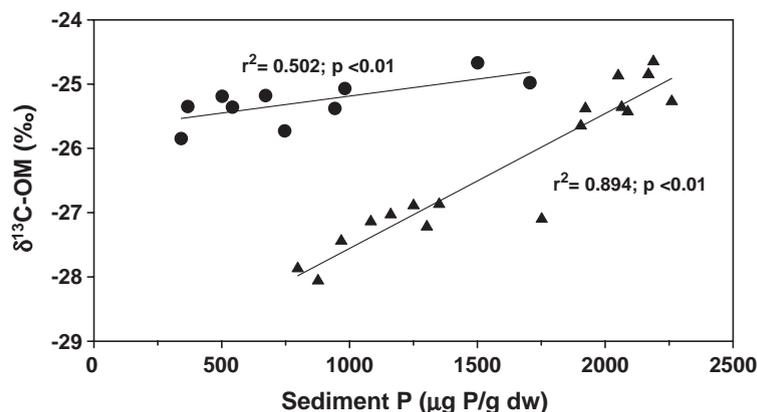

Fig. 9. The relationship between total sediment P (TSP) and the carbon isotopic composition of organic matter (δ^{13}C-OM) in Woodbury Creek marsh (PC-15) is shown. The (●) points are from late the 1940s to mid-1960s, just below the maximum TSP while (▲) are points from the maximum in the 1970s to the present when TSP decreased substantially.

substantial decrease in $\delta^{13}C$ with decreasing TSP. It is unclear why there are two distinct relationships over time, but it may be due to the response time between TSP and algal/plant production, or possibly interactions with other chemicals introduced to the river between the 1940s and 1960s. Accordingly, the correlations observed between carbon isotopes of organic matter and TSP can be an indication in the variations of primary production in the tidal freshwater portion of the Delaware Estuary. This has been observed in various lake environments using either sediment organic matter (Schelske and Hodell, 1991, 1995), or scales from fish collected over time (Perga and Gerdeaux, 2003). In laboratory experiments, Gervais and Riebesell (2001) demonstrated that P limitation decreased the growth rate of a marine diatom (*Skeletonema costatum*) and increased the C isotope fractionation. During a yearlong field study, there was a positive linear relationship between $\delta^{13}C$-suspended particulate material in the Delaware Estuary and areal productivity rates (Cifuentes et al., 1989). While decreased light levels in this estuary due to high turbidities are a primary controlling factor for algal production in the winter, P can limit production, especially in the spring (Pennock and Sharp, 1994). The carbon isotope data from marsh sedimentary records suggests that system productivity levels in the tidal freshwater portion of the river may be controlled by P levels. Thus, by controlling P concentrations in the river via the P-detergent ban, overall water quality has improved (E.P.A., 2000).

In the tidal freshwater portion of the Delaware River, sources of organic matter range from in situ production (marsh and planktonic), river runoff, and sewage. While there was no significant relationship between $\delta^{13}C$ and TSP ($r^2 = 0.275$) in the Oldmans Creek core, it is interesting to note that the $\delta^{13}C$-OM in the core from Oldmans Creek was approximately 1.6‰ higher than the values measured in the Woodbury Creek core. For example, the upper 6 cm at Oldmans averaged -25.1‰ while Woodbury averaged -27.2‰. Additionally, the $\delta^{13}C$-OM for a site in the Salem River, which is further downstream than Oldmans and Woodbury Creeks, was substantially more positive (-20.5 ‰). The more positive $\delta^{13}C$-OM may reflect a slightly greater contribution of sewage or phytoplankton-derived carbon. Cifuentes et al. (1989) and Fogel et al. (1992) showed a general downstream shift in $\delta^{13}C$-OM to more positive values related to more coastal and marsh sources.

Nitrogen isotopes ($^{15}N/^{14}N$) showed a systematic increase in $\delta^{15}N$ of the total sedimentary N (TN) since the mid-1970s, according to the sediment chronologies. The profile of the $\delta^{15}N$-TN in the sediments of Woodbury Creek marsh was nearly constant (3.4 ± 0.3‰, $n = 16$) from the late 1940s to early 1970s (Fig. 5), after which the $\delta^{15}N$-TN linearly increased from approximately 3‰ to 7.5‰. A similar trend was observed in the core from Oldmans Creek marsh, which had a core top $\delta^{15}N$-TN value of 7.3‰. This increase does not appear to be related to changes in organic matter sources (terrestrial versus marine or aquatic; as per C/N) but probably more to processes within the water column and long-term changes in the isotopic composition of the dissolved N (Cifuentes et al., 1989; Teranes and Bernasconi, 2000; Bratton et al., 2003).

Over time, inputs from wastewater treatment plants and agricultural run-off can vary, each having a distinct isotopic signature (Kendall, 1998). In addition to varying sources (and N isotopic compositions), processes within the water column and sediments can modify the N isotopic composition before deposition. Off-setting processes include: (1) algal uptake of heavy residual nitrate or ammonium formed from the sequential uptake and fractionation of N by algae (Wada, 1980; Pennock et al., 1996), (2) reduction of nitrate via de-nitrification and subsequent algal uptake (Cline and Kaplan, 1975), and (3) the breakdown of particulate organic N by bacteria that may preferentially release ^{14}N organic and inorganic N, leaving behind more enriched particulate material (Wada, 1980; Sachs and Repta, 1999; Lehmann et al., 2002). The latter process, however, can further change the $\delta^{15}N$ of TN by the re-incorporation of N via bacterial growth.

This change in $\delta^{15}N$-TN corresponded to the increase in dissolved nitrate (and decrease in dissolved ammonium) in the Delaware River near Philadelphia over this time period (Jaworski and Hetling, 1996; E.P.A., 2000). Concentrations of dissolved nitrate were fairly stable from the 1920s to late 1960s (ca. 37–40 μM N), increasing to approximately 100 μM N by the mid-1990s. These changes are likely to be due to population increases and agricultural use. In addition, changes in the processing of wastewater (e.g., solids removal, chlorination, and nitrification) in the Philadelphia-Camden areas during the late 1960s to mid-1970s (D. McCarty, Philadelphia Water Department, personal communication) could impact the load and isotopic composition of nitrogen to the river.

Along with these changes, dissolved oxygen concentrations have increased since the mid-1960s (from < 1 mg/L to > 5 mg/L; E.P.A., 2000). Low dissolved oxygen concentrations sporadically observed from the 1940s to 1960s indicate that de-nitrification could have occurred either in the water column or sediments (Seitzinger, 1988). This process can enrich the dissolved nitrate pool in ^{15}N, with further enrichment via algal uptake

and particulate N formation (Fogel and Cifuentes, 1993). Interestingly, the N isotopic composition of suspended particulate material collected in this reach of the river between 1988 and 1989 (Velinsky et al., 1990) averaged 6.4 ± 3.7 ($n = 15$). This is similar to the isotopic composition in the Woodbury Creek marsh at a corresponding depth/time (5.4–6.3‰). However, during the 1940s to 1960s (80 to 50 cm) there was no apparent increase in $\delta^{15}N$ in the sediment core (Fig. 5), but an increase in $\delta^{15}N$-TN was noted during the period when dissolved oxygen concentrations had been improving (>1970).

Therefore, it is suggested that increases in $\delta^{15}N$-TN in the sediment cores are attributed to changes in the source and isotopic composition of N to the river since the mid-1970s and algal uptake of the N in the water column. Similar conclusions were made for Lake Baldeggersee in Switzerland (Teranes and Bernasconi, 2000). In this study, the largest increase in $\delta^{15}N$-TN was observed after increases in dissolved oxygen and dissolved nitrate concentrations. It was concluded that variations in N sources (e.g., wastewater versus agricultural inputs) were the primary cause for this change. However, given that the increase in $\delta^{15}N$-TN started at the same time as changes in the treatment of wastewater due to the Federal Water Pollution Control Act Amendments of 1972 and amendments in 1977 (Clean Water Act), changes in the N isotopic signature of discharged wastewater could be important.

5.4. Metal comparisons

A comparison of the metal concentrations agree very well in both profile shapes, magnitude, and timing with those reported earlier at the same marsh sites (Orson et al., 1992a). In this study, a comparison to the 1954 levels in the two cores suggests similar levels for V, Cr, Ag, Co and Pb. However Woodbury Creek (PC-15) display 1.5–3 higher levels for Cu, Zn, Cd, As and Sn, suggesting specific enrichment at this upstream marsh site closer to the urban Philadelphia area. The maximum historical metal levels in Oldmans Creek site (PC-14) is assigned to 1963–1964 (-25 cm), whereas for PC-15 is it appears to be somewhat later in 1969 (-38 cm). This suggests that in this watershed, or at this location in the river, the industrial activities have been more extensively developed since about 1950 (-60 cm). Nevertheless, the peak maximum recorded in the PC-15 core in 1969 (-38 cm), displays significantly higher levels compare to PC-14 at 1963 (-25 cm). Here they range between 1.5 and 4.6 fold for Sn, V, Cr, Cu, Zn, As, and Ag, whereas it can go up to 16-fold for Cd. For the two other elements (Co and

Pb), similar concentrations are reported. Thus, for most elements, the PC-15 higher levels can be explained by its closer proximity to Philadelphia compared to PC-14. Normalization of the metal concentrations to organic carbon at both sites exhibits similar depth profiles of metal loads, except for the deeper part of PC-14 core (28–38 cm) that is characterized by a modification of the C and P contents (Figs. 3 and 4).

As most metal inputs appear to be clearly related to industrial activities, the influence of sewage water treatment plants might also be considered as a non-negligible source. In fact, the vicinity of the coring sites to the urban area of Philadelphia appears to reveal the potential impact of sewage treatments plants. The higher Ag levels recorded in PC-15 compared to PC-14 (Fig. 6) are assumed to trace the specific pollution gradient originating from sewage treatment plants located in the upstream part of the Delaware estuary (i.e. Philadelphia urban area). The metal Ag has been established as a specific tracer of the watershed inputs from wastewater treatment plants (Sanudo-Wilhelmy and Flegal, 1992; Shafer et al., 1998; Gobeil et al., 2005; Point, 2004). This specificity of Ag towards wastewater inputs is confirmed when Ag concentrations in the two cores are compared with those of total phosphorous. Although total phosphorous is not completely linked to sewage inputs, having other sources (e.g. fertilizers), significant correlations are obtained between the two parameters exhibiting regression coefficients R^2 of 0.62 ($p < 0.001$) and 0.41 ($p < 0.002$) for PC-14 and PC-15, respectively.

5.5. Organo-tin records

Organo-tin compounds are dominated by industrial butyl tins that are a result of production from use in plasticizers and biocides. A common compound has been tri-butyl tin (TBT) that was widely used as an anti-fouling paint applied to ship bottoms. However, this usage has been banned in the US as it proved to contain powerful contaminants, causing large-scale mortality in coastal marine organisms (Donard et al., 2001). The Delaware Estuary has been historically dominated by shipping, construction and maintenance of ships, and serving as a major port that hosted the large Philadelphia Navy Yard. Thus, the organo-tin profiles at both the marsh sites should reveal both specific and similar industrial inputs, including organo-tin compounds, such as TBT anti-fouling additives. If so, a recent decrease might correspond to the adoption in recent decades of legislation that has banished the use of TBT in anti-fouling paints first on civilian and more recently, military ships.

5.5.1. Changes in butyl-tin inputs

The highest levels of TBT are observed at the same maximum in cumulative butyl compounds in the two cores (Fig. 7). The levels of TBT recorded in Oldmans Creek (PC-14) core (Fig. 7A) are low (6 ng(Sn) g^{-1}) and similar to contamination background levels observed in other coastal environments (Donard et al., 2001). However, 10-fold higher concentrations are observed (Fig. 7B) at the Woodbury Creek (PC-15) site (60 ng(Sn) g^{-1}). Here, the core site is located upstream in an area more highly influenced by urban and industrial activities. In particular, it is situated closer to the Philadelphia Navy Yard, potentially a specific point source. This indicates that the two sites are and have been impacted by a single organo-tin source, linked to TBT release from leaching anti-fouling paints and shipyard activities in the upper Delaware estuary. It can be presumed that the main source of butyl-tin compounds is provided by TBT inputs, and that the TBT degradation in both water and sediment is occurring on average at a steady state. If so, the total butyl tin measured in the sediment profile should then correlate with the total TBT record over the sedimentation period.

Also, independent of the degradation stage of TBT when buried in sediments, total butyl-tin concentrations should be directly related to the level of exposure at the two sites investigated to this specific pollutant. Even though TBT concentrations remain relatively low in the Oldmans Creek (PC-14) core profile (i.e. close to the detection limits), the level of accumulated butyl tin species in both core profiles indicates that the maximum input corresponds to the early 1980s (Fig. 7).

Downstream in the Oldmans Creek (PC-14) core profile, a more modern peak is well defined as recently as 1988, whereas the maximum input for the cumulative species (MBT, DBT and TBT) corresponds to the middle of 1980s. As the sediment structure is undisturbed, a historical recording of TBT input as recently as 1988 appears possible.

In the Woodbury Creek (PC-15) core profile, the relatively high concentrations of TBT recorded along the core show two well-defined peaks, both starting at 1968 and again at 1981. Thus, the maximum of input of organo-tins occurred here in the 1970s. This date is totally in agreement with the historical use of TBT-based paint in marine industries. The first record of organo-tin contamination in the PC-15 core (1955) is almost identical to that in the PC-14 (1954) and defines this date as the first use of TBT in the Delaware River. The decreased concentrations at the sur-

face may be explained by the more restrictive regulation concerning the use of TBT-based paint, including the closure of the Philadelphia Navy Yard. It is interesting to note that in both cores there is evidence of sustained modern concentrations and perhaps continued mobilization. Specifically there are sustained levels of TBT in the past decades at both the PC-14 and PC-15 sites, presumably from a common source remobilized along this section of the industrial river. Since this observation is not in accord with the international policy concerning the restricted use of TBT-based paint, it can only be presumed to be a relict source. For example, it may indicate the period of transition between closure of the Philadelphia Navy Yard and its conversion to commercial ship construction. Such anomalies observed in more recent times, particularly in the past decade at PC-15 (Fig. 7B), can probably be related to the proximity of the Philadelphia Navy Yard with associated maintenance or decommissioning activities.

5.5.2. Source and fate of butyl-tin contaminants

In order to investigate both organo-tin source and fate at the coring sites, TBT concentrations can be compared to MBT and DBT levels. Direct relationships between TBT and its potential degradation products support assumptions on the specific sources of organo-tins and the relative degradation of butyl-tin compounds. The linear correlation (through zero) of MBT and DBT (TBT degradation products) with TBT, evidences specifically the degradation of TBT (Fig. 10). This trend is particularly evident in PC-15 with the higher loading of TBT with a better concentration resolution compared to PC-14. The slope ratio between MBT and DBT versus TBT also provides information on degradation kinetics that assumes a steady state.

In the Oldmans Creek (PC-14), the DBT/TBT ratio is close to 1.7 whereas it is more than twice that for MBT/TBT with a constant ratio of 4. This indicates that TBT and DBT have close degradation kinetics, whereas the MBT degradation rate is, on average, two times slower than TBT. In Woodbury Creek (PC-15), the DBT/TBT ratio is close to 1, approaching 2 for MBT/DBT. Previous investigation in many coastal environments have highlighted the higher persistence of MBT compared to TBT and DBT (Donard et al., 2001). These results also indicate that TBT degradation to DBT and MBT is relatively higher in PC-14 compared to PC-15. Several studies have demonstrated that the degradation rate of TBT is faster in waters (hours–days) compared to sediments (month–years) (Donard et al., 2001). The highest degradation of TBT in PC-14 (25 km), compared to PC-15 (4
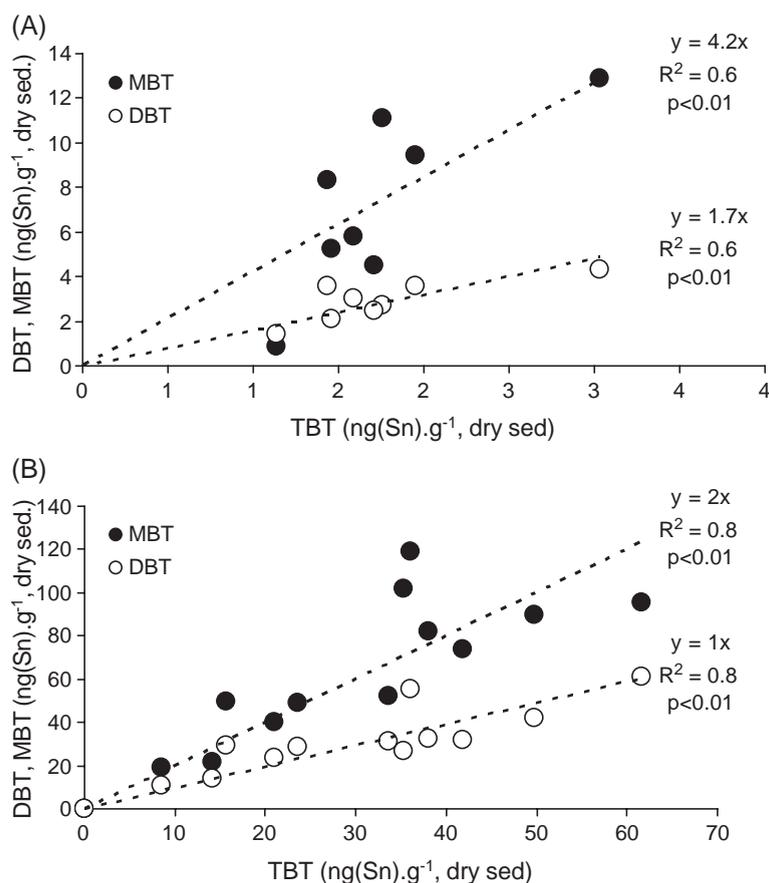
Fig. 10. Linear correlation between TBT and its degradation products (MBT and DBT) in (A) Oldmans Creek and (B) Woodbury Creek marshes in the upper Delaware estuary. This strongly suggests tri-butyl tin (TBT) as the primary source undergoing subsequent degradation before and after deposition.

km) downstream of the Philadelphia Navy Yard, is probably linked to the higher residence time of TBT in the tidal waters of the Delaware estuary before being trapped in the marsh sedimentation areas.

6. Conclusions

The results of this study indicate that fresh water marsh deposits in highly dynamic and polluted regions of urban estuaries can provide concordant and reliable sediment geochronologies. This supports the concept of their role as repositories of fine sediment reflecting associated historical records of anthropogenic activities and pollution loading in industrial tidal areas. From the two sedimentary records obtained from the industrialized zone of the upper Delaware Estuary, the following conclusions can be reached:

1) Sedimentation rates (0.6–1.2 cm/year) at low-marsh sites within the Woodbury and Oldmans creeks are

steady and significantly higher than the regional rate of sea level rise (0.2−0.3 cm/year). This confirms that low fresh water marshes are preferential depocenters of fine-grained sediments in the greater part of this urban estuarine system. However, additional work is needed to identify how suspended sediments tidally advected into the marshes are permanently sequestered. In any case, the sedimentary record is complete and not punctuated by either non-depositional or erosional episodes.

2) Changes in C, N, P and C–N stable isotopes in the marsh sediments record historical activities associated with population growth, detergent and fertilizer use, or potentially sewage treatment and discharge. Carbon isotopes may also reflect changes in overall algal productivity in the upper tidal river and suggest tight controls by phosphorus levels.

3) The historical records associated with metals record the urban and industrial metal activities over the past 50 years, which peaked about 30 years ago. How-

ever, such input continues to some extent even today from secondary relict sources such as urban runoff, as there is no evidence in the constant geochronology and porosity of episodic sedimentary sources.

4) The use of organo-(butyl) tin pollutants in the upper Delaware Estuary appears to originate from the widespread use since 1955 of TBT anti-fouling bottom paints associated with the dominant ship construction, maintenance, and transit activities. In spite of the ban on further use of TBT several decades ago, the marsh sediments continue to record modern input presumably from relict sources, such that even after burial, TBT degradation products continue to enter the urban Delaware Estuary.

Acknowledgements

References

Aspila, K.I., Aspila, H., Agemian, A., Chau, S.Y., 1976. A semi-automated method for the determination of inorganic and total phosphate in sediments. Analyst 101, 187–197.

Bancon-Montigny, C., Lespes, G., Potin-Gautier, M., 1999. Optimisation using experimental designs of the sample pretreatment: application to the control of the-tins in sewage sludge by GC-FPD. Analyst 124, 1265–1270.

Benninger, L.K.A., Cochran, R.C., Truekian, K.K., 1979. Effects of biological sediment mixing on the Pb-210 chronology and trace-metal distribution in a Long Island sound sediment core. Earth and Planetary Science Letters 43, 241–259.

Bosley, K.L., Wainwright, S.C., 1999. Effects of preservatives and acidifications on the stable isotope ratios (15N:14N, 13C:12C) of

two species of marine animals. Canadian Journal of Fisheries and Aquatic Sciences 56, 2181–2185.

Bratton, J.F., Coleman, S.M., Seal, R.R. II, 2003. Eutrophication and carbon sources in Chesapeake Bay over the last 2700 yr.: human impacts in context. Geochimica et Cosmochimica Acta 67, 3385–3402.

Bunn, S.E., Loneragan, N.R., Kempster, M.A., 1995. Effects of acid washing on stable isotope ratios of C and N in penaeid shrimp and seagrass: implications for food-web studies using multiple stable isotopes. Limnology and Oceanography 40, 622–625.

Carco, N.F., 1995. Influence of human populations on P transfers to aquatic systems: a regional scale study using large rivers, International Council of Scientific Unions Scientific Committee, United Nations Environment Programme (SCOPE45). Phosphorus in the Global Environment Transfers, Cycling and Management.

Chanton, J.P., Lewis, F.G., 1999. Plankton and dissolved inorganic carbon isotopic composition in a river-dominated estuary: Apalachicola Bay, Florida. Estuaries 22, 575–583.

Church, T.M., 1991. Biogeochemical processes in model estuaries. EOS 74 (53), 595–598.

Church, T.M., Scudlark, J.R., 1998. Trace metals in estuaries: a Delaware Bay synthesis. Metal Speciation and Contamination of Surface Water, vol. 1. Ann Arbor Press Inc., pp. 1–20.

Church, T.M., Lord, C.J., Somayajulu, B.L.K., 1981. Uranium, thorium, and lead nuclides in a Delaware salt marsh sediment. Estuarine, Coastal and Shelf Science 13, 267–275.

Cifuentes, L.A., Sharp, J.H., Fogel, M.L., 1989. Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. Limnology and Oceanography 33, 1102–1115.

Cline, J.D., Kaplan, I.R., 1975. Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical North Pacific Ocean. Marine Chemistry 38, 453–477.

Cochran, J.K., Hirschber, D.J., Want, J., Dere, C., 1998. Atmospheric Deposition of Metals to Coastal Waters (Long Island Sound, New York, USA): Evidence from Salt Marsh Deposits. Estuarine Coastal Shelf Science.

Cook, T.L., 2004. Observations of sediment transport in the Delaware Estuary during spring runoff conditions. Unpublished MS thesis, University of Delaware, 64 pp.

Cutshall, N.H., Larsen, I.L., Olsen, C.R., 1983. Direct analysis of Pb-210 in sediment samples: self-absorption corrections. Nuclear Instruments and Methods 206, 309–312.

Donard, O.F.X., Lespes, G., Amouroux, D., Morabito, R., 2001. Organo-tin compounds in the environment: still a most critical issue. In: Cornelis , R., Ebdon, L., Donard, O.F.X., Quevauviller, P. (Eds.), Speciation 21—Preparing for the 21st Century. Royal Society of Chemistry, pp. 142–175.

E.P.A., 2000. Progress in Water Quality: An Evaluation of National Investment in Municipal Wastewater Treatment, EPA-832-R-00-008. Office of Water, Washington, D.C.

Estep, M.L.F., 1984. Carbon and hydrogen isotopic compositions of algae and bacteria from hydrothermal environments. Geochimica et Cosmochimica Acta 48, 591–599.

Fogel, M.L., Cifuentes, L.A., 1993. Isotope fractionation during primary production. In: Engel, M.H., Macko, S.A. (Eds.), Organic Geochemistry. Plenum, New York, pp. 73–98.

Fogel, M.L., Cifuentes, L.A., Velinsky, D.J., Sharp, J.H., 1992. Carbon limitation during photosynthesis by estuarine phytoplankton. Marine Ecology. Progress Series 82, 291–300.

Friedrichs, C.T., Perry, J.E., 2001. Tidal salt marsh morphodynamics: a synthesis. Journal of Coastal Research 27, 7–37.

Goericke, R., Montoya, J.P., Fry, B., 1994. Physiology of isotopic fractionation in algae and cyanobacteria. In: Lajtha, K., Michener, R.H. (Eds.), Methods in Ecology: Stable Isotopes in Ecology and Environmental Science. Blackwell Scientific Publications, Boston (Chapter 9).

Gervais, F., Riebesell, U., 2001. Effect of phosphorus limitation on elemental composition and stable carbon isotope fractionation in a marine diatom growing under different CO_2 concentrations. Limnology and Oceanography 46, 497–504.

Gobeil, C., Rondeau, B., Beaudin, L., 2005. Contribution of municipal effluents to metal fluxes in the St. Lawrence River. Environmental Science and Technology 39, 456–464.

Graustein, W.C., Turekian, K.K., 1986. Pb-210 and Cs-137 in air and soils measure the rate and vertical profile of aerosol scavenging. Journal of Geophysical Research 91, 14355–14366.

Inn, K.G.W., 2001. The NIST natural-matrix radionuclide standard reference material program for ocean studies. Journal of Radioanalytical and Nuclear Chemistry 248, 227–231.

Jaworski, N., Hetling, L., 1996. Water quality trends of the Mid-Atlantic and Northeast watersheds over the past 100 years. Proceedings Watershed '96: A National Conference on Watershed Management, June 8–12, 1996, Baltimore, MD. Water Environment Federation, Alexandria, VA, pp. 980–983.

Kendall, C., 1998. Tracing nitrogen sources and cycling in catchments. In: Kendall, C., McDonnell, J.J. (Eds.), Isotope Tracers in Catchment Hydrology. Elsevier, Amsterdam, The Netherlands (Chapter 16).

Kim, G., Alleman, L.Y., Church, T.M., 2004. Records of the accumulation of radionuclides and trace metals in two Delaware salt marshes with contrasting accumulation conditions. Marine Chemistry 87, 87–96.

Lehmann, M.F., Bernasconi, S.M., Barbieri, A., McKenzie, J.A., 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. Geochimica et Cosmochimica Acta 66, 3573–3584.

Litke, D.W., 1999. Review of phosphorus control measures in the United States and their effects on water quality. U.S. Geological Survey, Water Sources Investigations Report 99-4007National Water Quality Assessment Program, Denver, CO.

Lorrain, A., Savoye, N., Chauvaud, L., Paulet, Y.-M., Naulet, N., 2003. Decarbonation and preservation method for the analysis of organic C and N contents and stable isotope ratios of low-carbonated suspended particulate material. Analytica Chimica Acta 491, 125–133.

Mansue, L.J., Commings, A.B., 1974. Sediment Transport by Streams Draining into the Delaware Estuary. U.S. Geological Survey Water-Supply Paper 1532-H.

Michel, P., Averty, B., 1999. Distribution and fate of tributyltin in surface and deep waters of the Northwestern Mediterranean. Environmental Science & Technology (33), 2524–2528.

Newell, W.L., Powars, D.S., Owens, J.P., Stanford S.D. and Stone, B.D., 1998. Surficial Geologic Map of Central and Southern New Jersey. U.S. Geological Survey Miscellaneous Investigations Series, Map I-2540-D.

Nichols, M.M., 1989. Sediment accumulation rates and relative sea-level rise in lagoons. Marine Geology 88, 201–219.

Olsen, C.R., Simpson, H.J., Peng, T.H., Bopp, R.F., Trier, R.M., 1981. Sediment mixing and accumulation effects on radionuclide depth profiles in Hudson estuary sediments. Journal of Geophysical Research 86, 11020–11028.

Orson, R.A., Simpson, R.L., Good, R.E., 1992a. A mechanism for the accumulation and retention of heavy metals in tidal freshwater marshes of the upper Delaware River estuary, Estuarine. Coastal and Shelf Science 34, 171–186.

Orson, R.A., Simpson, R.L., Good, R.E., 1992b. The paleoecological development of a late Holocene, tidal freshwater marsh of the upper Delaware River Estuary. Estuaries 15, 130–146.

Pennock, J.R., Sharp, J.H., 1994. Temporal alternations between light and nutrient limitation of phytoplankton production in a coastal plain estuary. Marine Ecology. Progress Series 111, 275–288.

Pennock, J.R., Velinsky, D.J., Ludlam, J.L., Sharp, J.H., Fogel, M.L., 1996. Isotopic fractionation of nitrogen during the uptake of ammonium and nitrate by *Skeletonema costatum*. Limnology and Oceanography 41, 451–459.

Perga, M.E., Gerdeaux, D., 2003. Using the d13C and d15 N of whitefish scales for retrospective ecological studies: changes in isotope signatures during restoration of Lake Geneva, 1980–2001. Journal of Fish Biology 63, 1197–1207.

Point, D., 2004. Speciation and biogeochemistry of trace metals in the Adour estuary, PhD Thesis, Nov 2004. Université de Pau et des pays de l'Adour, France. 340 pp.

Rau, G.H., Takahashi, T., DeMarais, D.J., 1989. Latitudinal variations in plankton d13C: implications for CO_2 and productivity in past oceans. Nature 341, 516–518.

Rven, J.A., Johnston, A.M., Newman, J.R., Scrimgeour, C.M., 1994. Inorganic carbon acquisition by aquatic photolithotrophs of Dighty Burn, Angus, UK: uses and limitations of natural abundance measurements of carbon isotopes. New Phsycologist 127, 271–286.

Roman, C.T., Jawaroski, N., Short, F.T., Findlay, S., Warren, R.S., 2000. Estuaries of the Northeastern United States: habitat and land use signatures. Estuaries 23, 743–764.

Ruttenberg, K.C., 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnology and Oceanography 37, 1460–1482.

Sachs, J.P., Repta, D.J., 1999. Oligotrophy and nitrogen fixation during eastern Mediterranean sapropel events. Science 286, 2485–2488.

Sackett, W.M., Echelmann, W.R., Bender, M.L., Be, A.W.H., 1964. Temperature dependence of carbon isotope composition in marine plankton and sediments. Science 148, 235–237.

Sanudo-Wilhelmy, S.A., Flegal, A.R., 1992. Anthropogenic silver in the Southern California Bight: a new tracer of sewage in coastal waters. Environmental Science and Technology 33, 2147–2151.

Shafer, M.M., Overdier, J.T., Armstrong, D.E., 1998. Removal, partitioning, and fate of silver and other metals in wastewater treatment plants and effluent-receiving streams. Environmental Toxicology and Chemistry 17, 630–641.

Schelske, C.L., Hodell, D.A., 1991. Recent changes in productivity and climate of Lake Ontario detected by isotopic analysis of sediments. Limnology and Oceanography 36, 961–975.

Schelske, C.L., Hodell, D.A., 1995. Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. Limnology and Oceanography 40, 918–929.

Scileppi, E.M., 2004. Patterns of fine-grained sedimentation in the Delaware Estuary from Pb-210 and Cs-137 distributions, Unpublished M.S. thesis, University of Delaware. 80 pp.

Seitzinger, S.P., 1988. Benthic nutrient cycling and oxygen consumption in the Delaware Estuary. In: Majumdar, S.K., Miller, E.W.,

Saruhaski, K. (Eds.), Ecology and Restoration of the Delaware River Basin. The Pennsylvania Academy of Science, Easton, PA.

Sharma, P.G., Gardner, L.R., Moore, W.S., Bollinger, M.S., 1987. Sedimentation and bioturbation in a salt marsh as revealed by Pb-210, Cs-137 and Be-7 studies. Limnology and Oceanography 32, 313–326.

Sommerfield, C.K., Madsen, J.A., 2004. Sedimentological and Geophysical Survey of the Upper Delaware Estuary. Final Report to the Delaware River Basin Commission Delaware Sea Grant Publication DEL-SG-04-04, 124 pp.

Teranes, J.L., Bernasconi, S.M., 2000. The record of nitrate utilization and productivity limitation provided by 815N values in lake organic matter—a study of sediment trap and core sediments from Baldeggersee, Switzerland. Limnology and Oceanography 45, 801–813.

Velde, B., Church, T.M., Bauer, A., 2003. Contrasting trace element geochemistry in two American and French salt marshes. Marine Chemistry 83 (304), 131–144.

Velinsky, D.J., Fogel, M.L., Pennock, J.R., Sharp, J.H., 1990. Biogeochemistry of nitrogen isotopes in the Delaware Estuary and coastal salt marshes. 199th American Chemical Society National Meeting. Division of Geochemistry, Boston, MA.

Vogel, J.C., 1980. Fractionation of carbon isotopes during photosynthesis. Stizungsber. Heidelb. Akad. Wiss. Math.-Nathurwiss., K1, vol. 3, pp. 11–135.

Wada, E., 1980. In: Goldberg, E., Horibe, Y., Saruhaski, K. (Eds.), Nitrogen Isotope Fractionation and its Significance in Biogeochemical Processes Occurring in Marine Environments. Uchida Rokakuho, Isotope Marine Chemistry, Japan, pp. 375–398.

Walsh, D.R., 2004. Anthropogenic influences on the morphology of the tidal Delaware River and Estuary: 1877–1987. Unpublished M.S. thesis, University of Delaware 90 pp.