



Accumulation records of radionuclides and trace metals in two contrasting Delaware salt marshes

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Received 19 August 2003; received in revised form 18 January 2004; accepted 16 February 2004

Abstract

Single cores from two Delaware salt marshes were used to reconstruct the historical deposition of trace metals (Cu, Pb, and Zn) and radionuclide tracers (U, ²¹⁰Pb, and ¹³⁷Cs) during the 20th century. Although the sedimentation rates of both cores were similar to the local sea-level rise (~ 0.3 cm/yr), the two marshes have different depositional conditions. The Wolfe Glade salt marsh has maintained dense vegetation leading to almost complete preservation of the airborne-unsupported ²¹⁰Pb, while the Great Marsh has a large fluvial soil input leading to some loss of unsupported ²¹⁰Pb. The Wolfe Glade salt marsh accumulates more authigenic ²³⁸U from seawater but loses more ¹³⁷Cs to seawater in association with larger organic decomposition relative to the Great Marsh. The reconstructed history shows that the atmospheric deposition of Cu, Pb, and Zn was maximum during the earlier 20th century, with a secondary peak during the 1970s for Pb. The anthropogenic stable Pb isotopic signature (²⁰⁶Pb/²⁰⁷Pb=1.187) at this depth confirms that the source of Pb for this maximum is a nongasoline source, discounting postdepositional remobilization. This study suggests a possible strong regional pollution for Pb, along with Cu and Zn, in eastern Delaware during the earlier 20th century.

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Keywords: Radionuclides; Trace metals; Salt marshes; Lead; Stable lead isotopes; Delaware

1. Introduction

Salt marshes are located in intertidal areas and undergo steady accumulation of atmospheric dusts along with fluvial and oceanic sediments in accordance with the local sea-level rise rate which includes land subsidence and compaction (Church et al., 1981). Thus, the cores from salt marshes and other reservoir

sediments have been used to reconstruct changes in the atmospheric deposition of anthropogenic elements (McCaffrey, 1977; Zwolsman et al., 1993; Cochran et al., 1998; Weiss et al., 1999; Alfonso et al., 2001; Farmer et al., 2002; Thomson et al., 2002; Cundy et al., 2003). In addition, salt marshes appear to be an important sink of U due to chemical scavenging (Church et al., 1996) but a source of fallout ¹³⁷Cs due to postdepositional remobilization (Graustein and Turekian, 1986; Kim et al., 1997) in the coastal ocean.

For the reconstruction of the deposition history of trace metals from salt marshes, the exact dating of

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core sections is essential. Steady-state ^{210}Pb (half life: 22.3 years) and transient ^{137}Cs (half life: 30.2 years) tracers have been used commonly in determining the sedimentation rates of salt marshes (Delaune et al., 1978; Church et al., 1981; Sharma et al., 1987; Zwolsman et al., 1993; Kim et al., 1997). In addition to these tracers, in this study, we applied stable Pb isotopes in dating sediments based on the transient history of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios during the 20th century. For example, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in US urban air changed from about 1.14 during the 1960s to about 1.24 during the 1980s due to a shift in the major use of Pb produced from geologically old ores to much younger, abnormally radiogenic ores from Missouri (Shirahata et al., 1980; Patterson and Settle, 1987). The use of multi-independent tracers is important because the dating techniques are affected by the distribution of organic matter, sand dilution, salt content, tidal water, strong storms, and bioturbation (Church et al., 1981; Stumpf, 1983; Casey et al., 1986; Sharma et al., 1987; Bricker-Urso et al., 1989; French et al., 1994). Furthermore, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios have been useful in characterizing and distinguishing between anthropogenic and natural sources (Chow et al., 1975; Settle and Patterson, 1982; Flegal and Patterson, 1983); the ^{210}Pb has been useful for calculating the retention efficiency of aerosols in salt marshes using its inventory in the core in comparison with the steady-state atmospheric fluxes (Kim et al., 1997).

The objectives of this study were to reconstruct the historical deposition of trace metals from Delaware salt marsh sediments, to determine the historical source and postdepositional immobility of Pb in salt marsh sediments using stable Pb isotope signatures, and to determine the comparative geochemistry of U and Cs in two salt marshes which have different redox and depositional conditions.

2. Sampling and methods

2.1. Sampling

Salt marsh cores were collected carefully from the Wolfe Glade (WGIII) and the Great Marsh (GMII, at Oyster Rock Landing) salt marshes, Delaware (Fig. 1), in June 1996 by hammering in a 16 cm diameter plastic

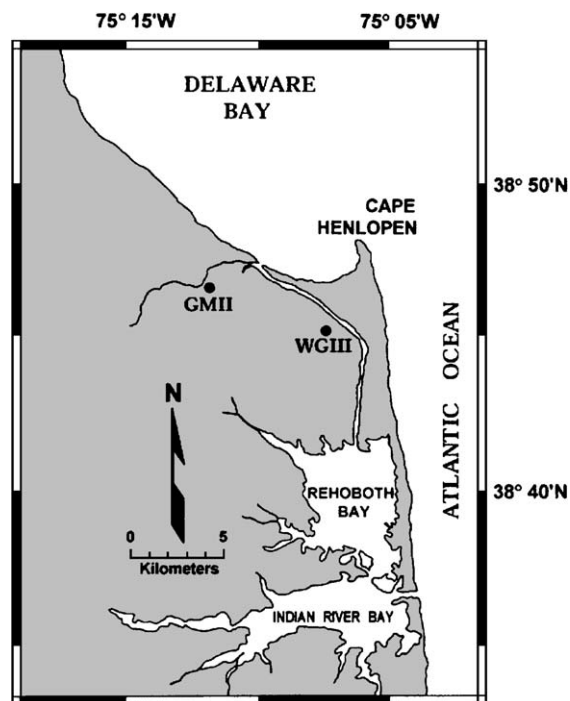


Fig. 1. Locations of two sediment coring sites of WGIII, from the Wolfe Glade salt marsh, and GMII, from the Great Marsh salt marsh, near Lewes, DE, USA.

coring device (18 cm length). The vertical compaction during coring was within 1%. The Wolfe Glade site was dominated by the grass of low marsh species, *Spartina alterniflora*, and the Great Marsh site by a mixture of *S. alterniflora* and *Spartina patens* (Carey, 1996). Soon after collection, the cores were sectioned into 2-cm intervals from the bottom and stored in clean plastic bags for laboratory analyses.

2.2. Determination of radionuclides

In the laboratory, the sediment core samples were weighed and dried at 60 °C for 3 days. Moisture content was determined by weight loss after drying. Dried samples were ashed at 420 °C for about 5 h in order to determine the organic components of the sediments (loss on ignition, LOI). Samples for gamma counting were homogenized and carefully transferred into 100 cm³ aluminum cans. The cans were sealed to prevent loss of ingrown ^{222}Rn because its short-lived daughter nuclides, ^{214}Pb and ^{214}Bi , were used for gamma counting. Samples were stored for more than

3 weeks to establish equilibrium between ^{226}Ra and ^{222}Rn (^{214}Pb).

Samples were counted using a $2100\text{ mm}^2 \times 49\text{ mm}$ thick intrinsic germanium coaxial detector with a Be window. Detector resolution was 654 eV at 4.4 keV and 763 eV at 122 keV, with a 4 μs amplifier shaping time. The high detector resolution allows one to identify and separate the gamma interference from other nuclides, for example, ^{238}Pu (43 keV) interference, in the region of ^{210}Pb (46.5 keV; Hussain et al., 1996). Individual samples were counted for 2 to 6 days. Background photo-peak areas, determined with empty cans, were subtracted from the spectra of the standard. Self-absorption corrections were made following the procedure of Hussain et al. (1996).

2.3. Determination of stable Pb isotopes and trace elements

The stable Pb isotopic composition analyses for sediments were carried out in an ultraclean laboratory to avoid any interference from unknown blank isotopic composition. Approximately 0.1 g of dry-sediment samples were digested over night with a mixture of $\text{HNO}_3/\text{HCl}/\text{HF}$ (double-distilled acids), and the sample was purified twice using an anionic resin extraction procedure (AG1X8; Shen and Boyle, 1987). The extraction blank was reproducible at $116 \pm 56\text{ pg}$ of

Pb (18 replicates) and considered negligible. Lead isotopic ratios were obtained by thermal ionization mass spectrometry at the CEREGE laboratory (France) employing the multicollector Thermal Ionization Mass Spectrometers, Finigan MAT 262 producing a precision better than 0.05% for two standard deviations of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio. The mass fractionation corrections were calibrated against the repeated analyses of a common lead standard reference material SRM 981 from the National Institute of Standards and Technology (NIST).

For trace element analyses, about 1 g of ashed sediments was digested with a mixture of $\text{HNO}_3/\text{HCl}/\text{HF}$. The solution was diluted to an appropriate concentration for ICP analyses, employing JY70Plus Spectroanalyzer, at the CMS, Lewes, DE. The accuracy of the analytical procedure was confirmed by analyzing laboratory standards.

3. Results and discussion

3.1. Organic contents

The loss on ignition (LOI) content, which is directly related to the density of stems and roots of marsh grass, varied from 50–80% and 20–60% in WGIII and GMII cores, respectively (Fig. 2). The LOI

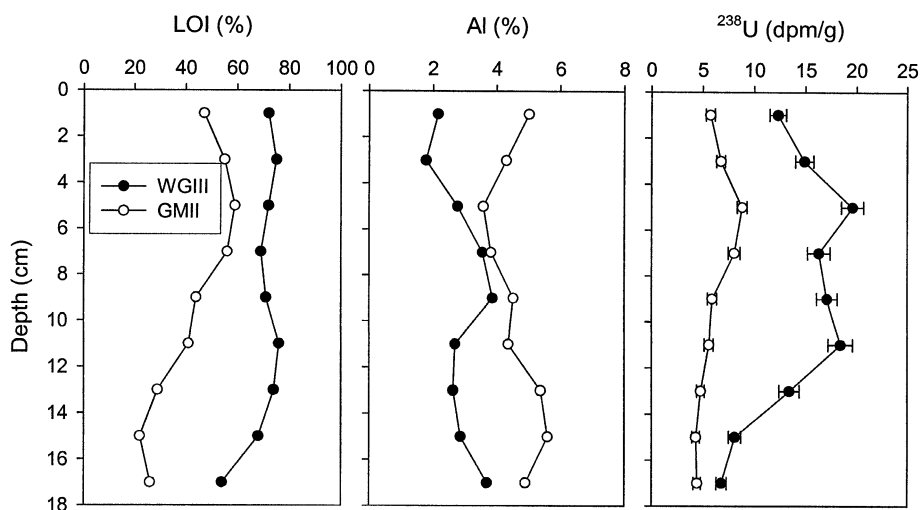


Fig. 2. Depth profiles of LOI (loss on ignition), Al, and ^{238}U at the WGIII and GMII sites. The error bars for ^{238}U are based on the counting uncertainties.

content was relatively higher in the upper layer due to some nondecayed stems. Kim et al. (1997) suggested that the Wolfe Glade salt marsh has a higher density of vegetation relative to other areas of the eastern USA salt marshes due to lower loading of fluvial sediments. Although the organic content was lower, the inventories of Al were much higher in the GMII core (120 mg cm^{-2}) relative to the WGIII core (25 mg cm^{-2}) in the upper 18 cm (Fig. 2). This indicates that the inventory of the earth's crust is a factor of five higher in the GMII site. Therefore, we suggest that the vegetation and fluvial soil inputs play an important role in keeping the Wolfe Glade and Great Marsh salt marshes, respectively, from submergence because the rate of regional sea-level rise should be identical at both marshes.

3.2. Preservation of aerosols in salt marshes

The retention efficiency of aerosols in salt marshes can be calculated based on a steady-state model for the airborne excess ^{210}Pb in sediments in comparison with the annual depositional fluxes of ^{210}Pb in this region. The excess ^{210}Pb is calculated by subtracting ^{226}Ra activities from the ^{210}Pb activities in sediments (Tables 1 and 2). The inventories of excess ^{210}Pb , corrected for the porosity and organic content, are calculated to be 22 and 16 dpm cm^{-2} in the WGIII and GMII cores, respectively. These excess ^{210}Pb inventories may include both direct fallout from the atmosphere and indirect inputs from seawater or fluvial soils. Nevertheless, the excess ^{210}Pb inventory at the WGIII site is comparable to that (25 dpm cm^{-2}) expected from the atmospheric depositional fluxes

directly measured at Lewes, DE (Hartman, 1987), divided by the decay constant of ^{210}Pb (0.0311 yr^{-1}). Although there are large uncertainties (more than 5%) in this direct comparison, we assume that about 90% and 65% of the atmospheric aerosols are retained in the Wolfe Glade and Great Marsh salt marshes, respectively. The higher retention efficiency in the Wolfe Glade salt marsh might be due to denser vegetation, limiting the washout during seawater inundation. As such, the atmospheric–anthropogenic sources for Zn, Pb, and Cu should be efficiently trapped in the Wolfe Glade salt marsh. Although the specific concentrations of these elements were lower as a result of dilution to fluvial soils at the GMII site, the total inventories of these species were higher due to higher fluvial soil components.

3.3. Accumulation of authigenic uranium

The specific activity of ^{238}U is a factor of two higher at the WGIII core relative to that at the GMII core (Fig. 2). As reasons for the net accumulation of dissolved uranium in salt marshes, Church et al. (1996) hypothesized that either (1) uranium scavenging occurs during the process of tidal mixing and attendant flocculation of humic acids and iron oxides—favoring this process is the presence of sulfonate complexes in salt marsh humic substances, and iron coprecipitation during its extensive redox cycling in the salt marsh—or (2) uranium extraction occurs at the marsh surface during extensive flooding of the salt marsh surface sediments—favoring this process is the increase in sulfuric acidity at the summer salt marsh surface that could destabilize the tetracarbonate species of U(VI).

Table 1

Activities of radionuclides and the concentrations of trace metals in ignited sediments, stable Pb isotope ratios, water content (WC), and loss on ignition (LOI) of the WGIII core from the Wolfe Glade Delaware salt marsh

Depth (cm)	^{210}Pb (dpm/g)	^{226}Ra (dpm/g)	^{238}U (dpm/g)	^{137}Cs (dpm/g)	$^{206/207}\text{Pb}$	Al (%)	Zn (ppm)	Pb (ppm)	Cu (ppm)	WC (%)	LOI (%)
0–2	45.6 ± 1.3	0.49 ± 0.14	12.3 ± 0.8	0.34 ± 0.04	1.2010	2.15	62	35	20	87	72
2–4	35.0 ± 1.0	0.23 ± 0.17	14.9 ± 0.9	0.34 ± 0.04	1.2046	1.78	61	22	15	87	75
4–6	38.3 ± 1.0	0.74 ± 0.12	19.6 ± 1.1	1.66 ± 0.08	1.2107	2.77	78	99	22	84	72
6–8	32.1 ± 1.0	0.74 ± 0.18	16.3 ± 1.1	6.24 ± 0.16	1.1966	3.55	84	189	30	82	69
8–10	26.2 ± 1.0	0.83 ± 0.25	17.1 ± 1.0	14.5 ± 0.28	1.1843	3.87	91	180	33	82	71
10–12	30.6 ± 1.5	0.31 ± 0.35	18.4 ± 1.2	7.06 ± 0.23	1.1865	2.69	100	215	55	84	76
12–14	28.0 ± 1.3	0.81 ± 0.26	13.4 ± 1.0	3.96 ± 0.16	1.1873	2.63	84	212	130	85	74
14–16	16.4 ± 0.6	0.82 ± 0.13	8.1 ± 0.6	3.06 ± 0.09	1.1898	2.86	67	132	22	85	68
16–18	10.5 ± 0.5	0.83 ± 0.14	10.2 ± 0.8	1.08 ± 0.05	1.1962	3.69	51	90	13	84	54

In either case, U enrichment should be more favorable at the Wolfe Glade salt marsh due to a higher organic content and subsequent decomposition, relative to the Great Marsh.

3.4. Postdepositional loss of Cs from salt marshes

As has been previously observed in other studies of salt marsh cores (Graustein and Turekian, 1986; Fuller and Hammond, 1983; Cochran et al., 1998), the inventories of ^{137}Cs in our two cores show that ^{137}Cs is mobilized and lost from the marshes. Whereas the US lowland average is 16.6 dpm cm^{-2} (correct to 1996; Graustein and Turekian, 1986), our cores had inventories of only 4.0 and 5.4 dpm cm^{-2} for WGIII and GMII, respectively. The lower inventory in the WGIII core as compared to that in GMII is probably related to more active decay of organic matter in the Wolfe Glade marsh, which has been shown elsewhere, promoting exchange and loss of univalent ions, such as Cs^+ (Casey et al., 1986; Comans et al., 1989). Thus, it is suggested that about 73% and 50% of the fallout ^{137}Cs was lost from the Wolfe Glade and Great Marsh salt marshes, respectively (relative to the 90% and 65% retention efficiencies, respectively, based on the ^{210}Pb inventory).

3.5. Sedimentation rates

The excess ^{210}Pb profiles for the WGIII and GMII cores suggest that the actual sedimentation rate may have varied (Fig. 3). Factors like compaction and abrupt environmental disturbance, such as strong storms or water current in salt marshes, can also produce such changes (Bricker-Urso et al., 1989). If the fallout flux of ^{210}Pb has remained constant, the effect of compaction can be corrected through a constant flux model (McCaffrey, 1977; Appleby et al., 1986; Kim et al., 1997), which allows the age (t) of a core section to be determined using cumulative ^{210}Pb activity as described by Eq. (1):

$$t = -\frac{1}{\lambda} \ln \left(1 - \frac{\sum A_z}{\sum A} \right) \quad (1)$$

where $\sum A_z$ is the integrated unsupported ^{210}Pb activity from the surface to a depth z , $\sum A$ is the total integrated unsupported ^{210}Pb activity of the core, and λ is the decay constant of ^{210}Pb . The calculated ages for the WGII and GMII core sections show an exponential increase with depth (Fig. 4), probably due to compaction effect as shown from the progressive decrease of water content and organic content in both cores

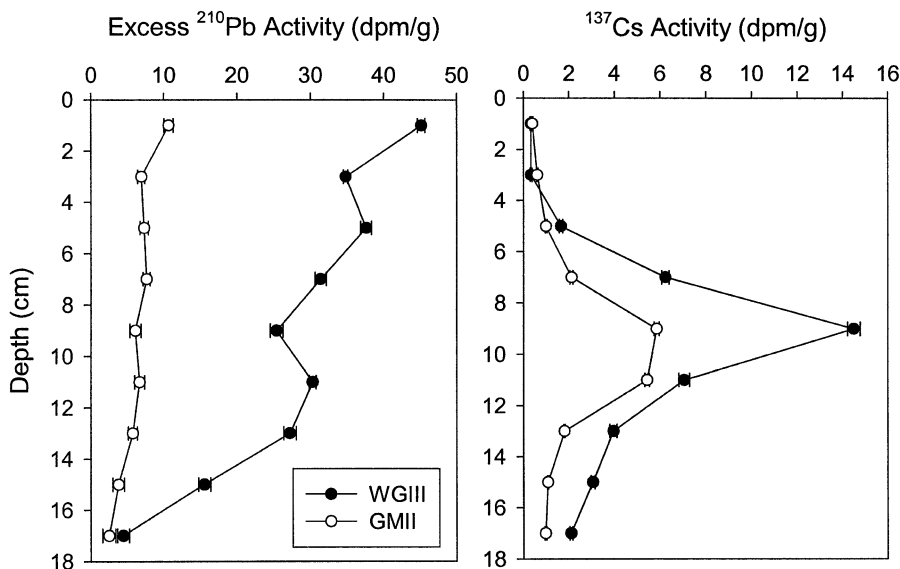


Fig. 3. Depth profiles of excess ^{210}Pb and ^{137}Cs at the WGIII and GMII sites. The error bars are based on the counting uncertainties.

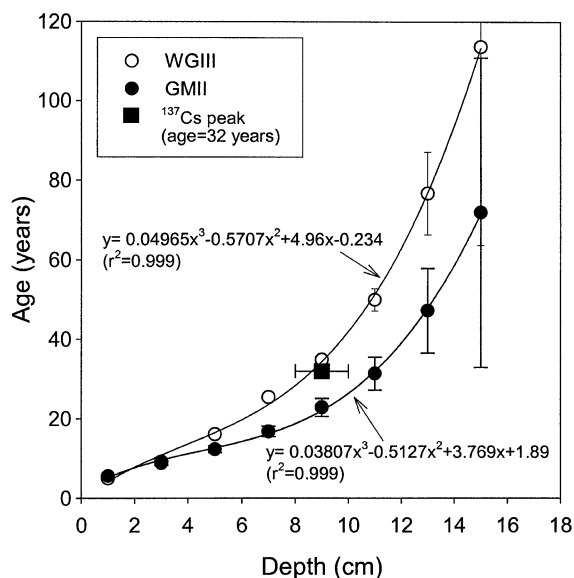


Fig. 4. The ^{210}Pb and ^{137}Cs dates for the WGIII and GMII cores. The constant rate of supply was assumed for modeling excess ^{210}Pb .

(Tables 1 and 2). Based on this method, the average sedimentation rates are estimated to be about 0.26 ± 0.02 and 0.39 ± 0.06 cm yr^{-1} at the WGIII and GMII sites, respectively, in the upper 10 cm. Because the age dating results below 10 cm have large uncertainties (Fig. 4), we accept the ^{210}Pb model only down to 10 cm in this study.

Because the peak of atmospheric ^{137}Cs fallout occurred in 1963, this event has been used as a geochronological index in rapidly accumulating sediments (Sharma et al., 1987; Zwolsman et al., 1993;

French et al., 1994). The ^{137}Cs -based independent estimate yields sedimentation rates of 0.27 ± 0.06 cm yr^{-1} at both sites in the upper 10 cm (Fig. 3). Within the uncertainties in the assumptions of both dating methods, the sedimentation rates at both sites in the upper 10 cm are similar to the local sea-level rise rate at Lewes, DE, based on the NOAA tidal record of about 0.3 cm yr^{-1} since 1919 (Stumpf, 1983).

Because the ^{210}Pb method has large uncertainties and ^{137}Cs is not applicable to the deeper sediment (below 10 cm), we used the stable Pb isotopic signature as a geochronological index for the deeper depths. The natural components of Pb in the WGIII core should be negligible if the natural Pb concentration is assumed to be 10 ppm as found in the Chesapeake Bay sediments located nearby (Marcantonio et al., 2002). As such, fluvial contributions of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios to the WGIII core were negligible based on a mass-balance calculation using the same equation and the natural endmembers (for Pb concentrations and isotopic ratios) as for the Chesapeake Bay sediments (Marcantonio et al., 2002). The evolution trend of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the upper 10 cm of the WGIII core agrees with that of Bermuda coral (Shen and Boyle, 1987) and Chesapeake Bay sediments (Marcantonio et al., 2002; Fig. 5). When the ratio evolution curve of WGIII below 10 cm is fitted to that of Bermuda coral, the sedimentation is calculated to be about 0.16 cm yr^{-1} (Fig. 5). This rate is about the same as that for the depth between 8–10 cm using the ^{210}Pb dating method (Fig. 4). Therefore, use of this $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for determining sedimentation rates is very advantageous in a changing sedimentary environment.

Table 2

Activities of radionuclides and the concentrations of trace metals in ignited sediments, stable Pb isotope ratios, water content (WC), and loss on ignition (LOI) of the GMII core from the Great Marsh at Oyster Rock Landing in Delaware

Depth (cm)	^{210}Pb (dpm/g)	^{226}Ra (dpm/g)	^{238}U (dpm/g)	^{137}Cs (dpm/g)	$^{206}/^{207}\text{Pb}$	Al (%)	Zn (ppm)	Pb (ppm)	Cu (ppm)	WC (%)	LOI (%)
0–2	11.3 ± 0.5	0.61 ± 0.09	5.73 ± 0.45	0.40 ± 0.03	1.1930	5.01	82	31	23	77	47
2–4	7.4 ± 0.4	0.49 ± 0.09	6.75 ± 0.42	0.61 ± 0.03	1.1972	4.30	69	19	25	79	55
4–6	7.9 ± 0.4	0.56 ± 0.09	8.83 ± 0.47	1.00 ± 0.04	1.1970	3.58	44	23	26	79	59
6–8	8.1 ± 0.5	0.45 ± 0.14	8.05 ± 0.57	2.12 ± 0.07	1.1980	3.82	42	28	31	78	56
8–10	6.9 ± 0.4	0.76 ± 0.12	5.91 ± 0.45	5.86 ± 0.11	1.1962	4.52	47	38	34	75	44
10–12	7.4 ± 0.5	0.68 ± 0.13	5.58 ± 0.44	5.44 ± 0.10	1.1963	4.36	49	41	38	76	41
12–14	6.4 ± 0.3	0.61 ± 0.09	4.80 ± 0.38	1.81 ± 0.03	1.1919	5.38	83	55	32	71	29
14–16	4.6 ± 0.3	0.79 ± 0.08	4.32 ± 0.38	1.08 ± 0.03	1.1912	5.59	89	48	28	66	22
16–18	3.4 ± 0.4	0.89 ± 0.10	4.43 ± 0.35	0.98 ± 0.04	1.1909	4.90	68	42	29	70	26

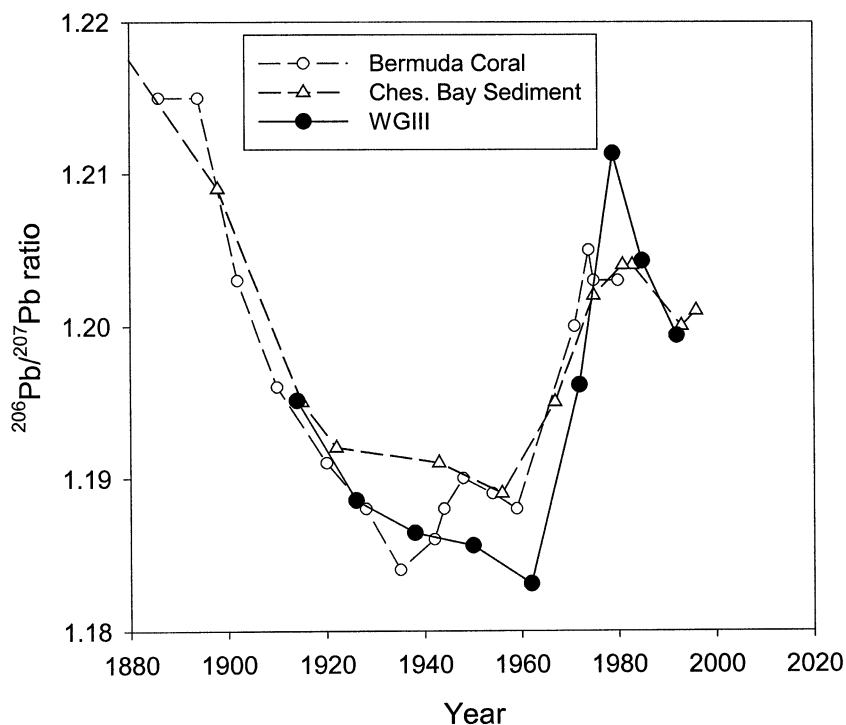


Fig. 5. Variations of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the WGIII core, in comparison with that reconstructed from a Bermuda coral (Shen and Boyle, 1987) and a Chesapeake Bay sediment core (Marcantonio et al., 2002). Like the coral, both the Chesapeake and Delaware salt marsh cores appear to have recorded the historical sources of atmospheric Pb in the western Atlantic Ocean, which originated mainly from the eastern US. The minimum values in the earlier part of the 20th century reflect regional fossil fuel/coal combustion, while the maximum values in the later part reflect leaded gasoline emissions.

In the GMII core, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios were in the range 1.1909–1.1980, which are close to the natural signature of 1.205 (Marcantonio et al., 2002). This may be associated with large dilution of anthropogenic sources to natural fluvial sediments, as discussed earlier. Thus, isotopic signals in the GMII core do not provide good information on sedimentation rates. Because there was some loss of atmospheric ^{210}Pb in the GMII core, ages calculated from the transient tracer, ^{137}Cs , may be more accurate than those from the steady-state ^{210}Pb model. This is also shown in Fig. 4 from the offset between the two methods in GMII.

3.6. Pollution history of trace metals

The inventories of anthropogenic metals in salt marsh cores can be used to reconstruct quantitative depositional histories from the atmosphere (i.e.,

Cochran et al., 1998). However, in this study, we concentrate on the identification of the source of anthropogenic metals occurring in salt marsh sediments because the cores were very short to include the entire anthropogenic inventories. For the interpretation of data, the vertical profiles of trace metals were normalized on Al to correct for differences in grain-size composition with depth (Finney and Huh, 1989).

In the GMII core, the vertical variations of trace metal (Zn, Pb, and Cu) to Al ratios were small (Fig. 6). This may be related to dilution of the anthropogenic fraction by the dominant natural soil components. In contrast, trace metal to Al ratios varied dramatically in the WGIII core, peaking altogether in the earlier 20th century. In comparison with the GMII data and natural compositions of the Earth's crust (Turekian and Wedepohl, 1961), most components for the WGIII core appear to be anthropogenic,

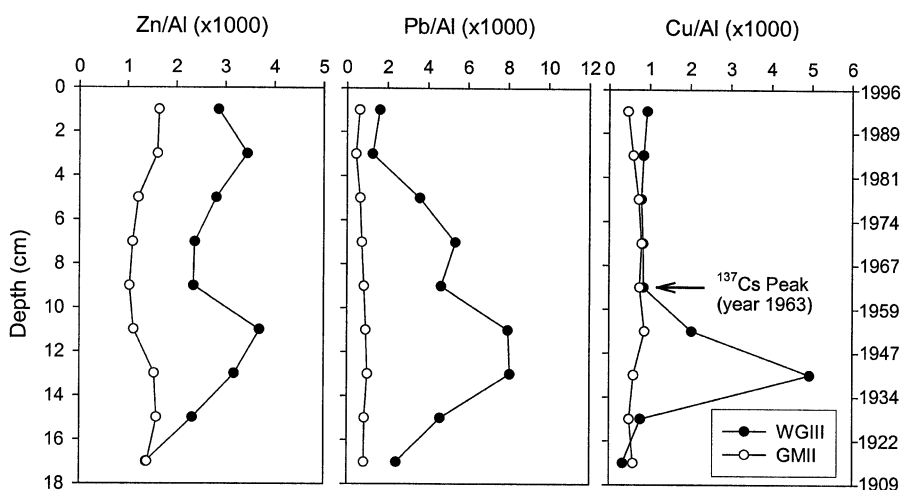


Fig. 6. Variations of trace metal to Al ratios at the WGIII and GMII cores. The ages shown are based on the ^{137}Cs method (0–10 cm) and the curve fitting of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio evolution (10–18 cm) for the WGIII core.

especially for Pb. Although there are some uncertainties in age determination, the pollution of Cu, Pb, and Zn peaked before the 1960s (Fig. 6), with a secondary peak for Pb during the 1970s and for Zn during the 1980s. In general, these metals are believed to have peaked during the 1970s before the Clean Air Act in US, especially for Pb due to a large source from tetra-alkyl leaded gasoline. Thus, we suspected possible downward remobilization of these elements by forming insoluble species (such as PbS) in the redox boundary depths (8–10 cm; Velde and Church, 1999; Velde et al., 2003) when the actual peaks were above the depth, and the subsequent sedimentation until 1996. However, the gasoline signature of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (about 1.20) was confined within the upper 8 cm (Fig. 4). As has been shown in studies of sediment and peat cores (Weiss et al., 1999; Farmer et al., 2002), our analysis of stable Pb isotopes indicates no postdepositional migration of Pb. This also proves that the dating of sediments using the ^{210}Pb and stable Pb isotopes are accurate for the Wolfe Glade site. Therefore, it is certain that a significant nongasoline source of Pb, along with Cu and Zn, was deposited onto a Delaware salt marsh from the atmosphere or coastal waters in the earlier 20th century. Although we do not know the source of those anthropogenic metals at this stage, the contamination of seawater in Delaware Bay around World War II is suspected. For example, there was extensive upwind

steel production in both the Chesapeake and Delaware watersheds that involved the coking of coal that contains characteristically lower stable lead isotopic ratios ($206/207 = 1.18\text{--}1.19$).

4. Conclusions

The sedimentation rates of two Delaware salt marshes, Wolfe Glade and Great Marsh, based on the ^{210}Pb and ^{137}Cs dating techniques were shown to be similar to the known local sea-level rise rate. However, they showed very different sedimentological features: the Wolfe Glade salt marsh has retained nearly all atmospheric deposition due to dense vegetation and more intense diagenesis, while the Great Marsh salt marsh showed some wash-out of the atmospheric and contaminant sources due to a large natural–fluvial soil input. The reconstructed pollution history of Cu, Pb, and Zn in the Wolfe Glade revealed that these elements had been significantly polluted in the earlier 20th century, exceeding the pollution peak of the 1970s. The immobility of Pb in sediments was confirmed with stable Pb isotopic signatures on the Wolfe Glade site. It is suggested that the stable Pb isotopic signature is a powerful tracer in coastal sediment studies on the determination of changing sedimentation rates, postdepositional mobilization, and historical Pb sources.

Acknowledgements

We thank Dr. W.L. Carey (University of Delaware) for core sampling assistance, and Dr. A.J. Véron (CEREGE, France) for stable Pb isotope analyses. This research was supported by a Sea Grant Project (No. NA16RG0162) administered for the NOAA, US Department of Commerce, by the College of Marine Studies at the University of Delaware. The preparation of this manuscript was supported by the BK21 project through the School of Earth and Environmental Sciences, Seoul National University, Korea.

References

- Alfonso, S., Grousset, F., Masse, L., Tastet, J.-P., 2001. A European lead isotope signal recorded from 6000 to 300 years BP in coastal marshes (SW France). *Atmos. Environ.* 35, 3595–3605.
- Appleby, P.G., Nolan, P.J., Gifford, D.W., Godfrey, M.J., Oldfield, F., Anderson, N.J., Battarbee, R.W., 1986. ^{210}Pb dating by low background gamma counting. *Hydrobiologia* 143, 21–27.
- Bricker-Urso, S., Nixon, S.W., Cochran, J.K., Hirschberg, D.J., Hunt, B., 1989. Accretion rates and sediment accumulation in Rhode Island salt marshes. *Estuaries* 12, 300–317.
- Carey, W.L., 1996. Transgression of Delaware's fringing tidal salt marshes: surficial morphology, subsurface stratigraphy, vertical accretion rates, and geometry of adjacent and antecedent surfaces. PhD thesis, Univ. Delaware.
- Casey, W.H., Guber, A., Bursey, C., Olsen, C.R., 1986. Chemical controls on ecology in a coastal wetland. *Eos* 67 (45), 1310–1311.
- Chow, T.J., Snyder, C.D., Earl, J.L., 1975. Isotope ratios of lead as pollutant source indicators. Proceeding of IAEA-SM-191/4 International Atomic Energy Commission, Vienna, Austria, pp. 95–108.
- Church, T.M., Lord, C.J., Somayajula, B.L.K., 1981. Uranium, thorium, and lead nuclides in a Delaware salt marsh sediment. *Estuar., Coast. Shelf Sci.* 13, 267–275.
- Church, T.M., Sarin, M.M., Fleisher, M.Q., Ferdeman, T.G., 1996. Salt marshes: an important coastal sink for dissolved uranium. *Geochim. Cosmochim. Acta* 60, 3879–3887.
- Cochran, J.K., Hirschberg, D.J., Wang, J., Dere, C., 1998. Atmospheric deposition of metals to coastal waters (Long Island Sound, New York U.S.A.): evidence from salt marsh deposits. *Estuar., Coast. Shelf Sci.* 46, 503–522.
- Comans, R.N.J., Middelburg, J.J., Zonderhuis, J., Woittiez, J.R., de Lange, G.J., Das, H.A., van der Weijden, C.H., 1989. Mobilization of radiocaesium in pore water of lake sediments. *Nature* 339, 367–369.
- Cundy, A.B., Croudace, I.W., Cearreta, A., Irabien, M.J., 2003. Reconstructing historical trends in metal input in heavily-disturbed, contaminated estuaries: studies from Bilbao, Southampton Water and Sicily. *Appl. Geochem.* 18, 311–325.
- Delaune, R.D., Patrick, W.H., Buresh, R.J., 1978. Sedimentation rates determined by ^{137}Cs dating in a rapidly accreting salt marsh. *Nature* 275, 532–533.
- Farmer, J.G., Eades, L.J., Atkins, H., Chamberlin, D.F., 2002. Historical trends in the lead isotopic composition of archival Sphagnum mosses from Scotland (1838–2000). *Environ. Sci. Technol.* 36, 152–157.
- Finney, B.P., Huh, C.A., 1989. History of metal pollution in the southern California Bight: an update. *Environ. Sci. Technol.* 23, 294–303.
- Flegal, A.R., Patterson, C.C., 1983. Vertical concentration profiles of Pb in the Central Pacific at 15 N and 20 S. *Earth Planet. Sci. Lett.* 64, 19–32.
- French, P.W., Allen, J.R.L., Appleby, P.G., 1994. ^{210}Pb dating of a modern period salt marsh deposit from the Severn Estuary (southwest Britain), and its implications. *Mar. Geol.* 118, 327–334.
- Fuller, C., Hammond, D.E., 1983. The fallout rate of Pb-210 on the western coast of the United States. *Geophys. Res. Lett.* 10, 1164–1167.
- Graustein, W.C., Turekian, K.K., 1986. ^{210}Pb and ^{137}Cs in air and soils measure the rate and vertical profile of aerosol scavenging. *J. Geophys. Res.* 91, 14355–14366.
- Hartman, M.C., 1987. The total deposition of Pb, Cd, Zn, and ^{210}Pb and atmospheric transport to the western Atlantic using ^{222}Rn and air mass trajectory analysis. MS thesis, Univ. Delaware.
- Hussain, N., Kim, G., Church, T.M., Carey, W., 1996. A simplified technique for gamma spectrometric analysis of ^{210}Pb in sediment samples. *Appl. Radiat. Isotopes* 47, 473–477.
- Kim, G., Hussain, N., Church, T.M., Carey, W.L., 1997. The fallout isotope ^{207}Bi in a Delaware salt marsh: a comparison with ^{210}Pb and ^{137}Cs as a geochronological tool. *Sci. Total Environ.* 196, 31–41.
- Marcantonio, F., Zimmerman, A., Xu, Y., Canuel, E., 2002. A Pb isotope record of mid-Atlantic US atmospheric Pb emissions in Chesapeake Bay sediments. *Mar. Chem.* 77, 123–132.
- McCaffrey, R.J., 1977. A record of the accumulation of sediment and trace metals in a Connecticut, USA, salt marsh. PhD thesis, Yale University.
- Patterson, C.C., Settle, D.M., 1987. Review of data on eolian fluxes of industrial and natural lead to the land and seas in remote regions on a global scale. *Mar. Chem.* 22, 137–162.
- Settle, D.M., Patterson, C.C., 1982. Magnitudes and sources of precipitation and dry deposition fluxes of industrial and natural Pb to the North Pacific at Enewetak. *J. Geophys. Res.* 87, 8857–8869.
- Sharma, P., Gardner, L.R., Moore, W.S., Bollinger, M.S., 1987. Sedimentation and bioturbation in a salt marsh as revealed by ^{210}Pb , ^{137}Cs , and ^7Be studies. *Limnol. Oceanogr.* 32, 313–326.
- Shen, G.T., Boyle, E.A., 1987. Lead in corals: reconstruction of historical industrial fluxes to the surface ocean. *Earth Planet. Sci. Lett.* 82, 289–304.
- Shirahata, H., Elias, R.W., Patterson, C.C., Koide, M., 1980. Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond. *Geochim. Cosmochim. Acta* 44, 149–162.

- Stumpf, R.P., 1983. The processes of sedimentation on the surface of a salt marsh. *Estuar., Coast. Shelf Sci.* 17, 495–508.
- Thomson, J., Dyer, F.M., Croudace, I.W., 2002. Records of radionuclide deposition in two salt marshes in the United Kingdom with contrasting redox and accumulation conditions. *Geochim. Cosmochim. Acta* 66, 1011–1023.
- Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of the earth's crust. *Geol. Soc. Amer. Bull.* 72, 175–192.
- Velde, B., Church, T., 1999. Rapid clay transformations in Delaware salt marshes. *Appl. Geochem.* 14, 559–568.
- Velde, B., Church, T., Bauer, A., 2003. Contrasting trace element geochemistry in two American and French salt marshes. *Mar. Chem.* 83, 131–144.
- Weiss, D., Shotyk, W., Appleby, P.G., Kramers, I.D., Cheburkin, A.K., 1999. Atmospheric Pb deposition since the industrial revolution recorded by five Swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources. *Environ. Sci. Technol.* 33, 1340–1352.
- Zwolsman, J.J.G., Berger, G.W., van Eck, G.T.M., 1993. Sediment accumulation rates, historical input, postdepositional mobility and retention of major elements and trace metals in salt marsh sediments of the Scheldt estuary, SW Netherlands. *Mar. Chem.* 44, 73–94.