

A Pb isotope record of mid-Atlantic US atmospheric Pb emissions in Chesapeake Bay sediments

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Abstract

We have analyzed sediments from three sites in the mesohaline portion of Chesapeake Bay (CB) for Pb isotopes. The well-preserved and well-dated sediments provide an excellent opportunity to compare the anthropogenic Pb isotope record in CB to other Pb isotope records of US industrial atmospheric emissions. Over the past century, there is excellent temporal agreement between anthropogenic CB ²⁰⁶Pb/²⁰⁷Pb isotope ratios and those determined in a dated coral from Bermuda [Earth and Planetary Science Letters, 82 (1987) 289] almost 2000 km away. We use this correlation to argue that CB sediments contain a regional, industrial atmospheric Pb isotope signal that is representative of the mid-Atlantic region of the US. Anthropogenic Pb is found in sediments deposited as early as approximately 1800. From about 1800 to 1930, the Pb signal in the CB sediments is probably derived from the burning of coal. After this period, and up until about the 1980s, the signal is overwhelmed by the Pb derived from the combustion of gasoline. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Over the past 5000 years, anthropogenic lead has been introduced into the global environment primarily through atmospheric transport (Murozumi et al., 1969; Nriagu, 1996; Pacyna, 1986, 1987). Nriagu (1998) estimates that prior to the industrial revolution, anthro-

pogenic lead was emitted solely as a by-product of mining and smelting of lead, silver, and copper ores. By the mid-18th century, combustion of Pb-containing coal became the primary source of industrial lead emissions to the atmosphere. Since the 1920s, automobile exhaust, with Pb-containing gasoline additives, has overwhelmed all other sources of anthropogenic Pb emitted into the environment (Nriagu, 1996). Although rates of Pb emission have decreased since the mid-1970s in the western world with the banning of Pb additives in gas, those same rates in developing countries are increasing significantly (Nriagu, 1989).

The history of anthropogenic Pb emissions has been investigated by analyzing the isotope composition of Pb in sediments (e.g., Farmer et al., 1996;

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Graney et al., 1995; Hamelin et al., 1990; Ritson et al., 1994; Shirahata et al., 1980; Shotyk et al., 1998) corals (Shen and Boyle, 1987), and ice (e.g., Rosman et al., 1993, 1994a,b). Anthropogenic Pb is derived from ore bodies that have $^{206}\text{Pb}/^{207}\text{Pb}$ ratios that are distinct from those in natural sediment or soil Pb. In general, Pb in ore has lower $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios than soil or sediment Pb, which ranges from about 1.20 to 1.24 (Shirahata et al., 1980). In the US, however, Pb from Mississippi Valley ores, which has made up a significant proportion of the Pb used in industry since the late 1960s (Shirahata et al., 1980; Sturges and Barrie, 1987), is anomalous in that it has high $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (~ 1.28 – 1.33 ; Heyl et al., 1966, 1974).

Given the significant isotopic differences in US Pb emissions, researchers have been able to use historical records of anthropogenic Pb isotope variations to trace the changing sources of pollutant Pb delivered to the North Atlantic region through time (e.g., Church et al., 1990; Sturges and Barrie, 1987; Véron et al., 1992). Here, we measure Pb isotope compositions in sediment cores from Chesapeake Bay (CB), the largest estuary in the US, in an effort to document the temporal variations in anthropogenic Pb sources to the bay, and, potentially, to the North Atlantic. Using the Pb isotope record in Chesapeake Bay, we show that the anthropogenic Pb in the bay is derived from regional industrial emissions that vary through time. This regional atmospheric Pb isotope record can be used, in conjunction with other methods, to date sediments that contain Pb derived from similar sources.

2. Methodology

Sediment cores were extracted with a 3-m-long kasten corer from three sites in the mesohaline region of CB (Zimmerman and Canuel, in review). Cores RD (38° , $53.2'\text{N}$, 76° , $23.5'\text{W}$; 26.5 m water depth) and RR (38° , $52.7'\text{N}$, 76° , $26.7'\text{W}$; 9.7 m water depth) were collected in 1998 and core M3 (38° , $43.1'\text{N}$, 76° , $26.8'\text{W}$; 15.0 m water depth) in 1996 (see Fig. 1 for core locations). Due to high sedimentation rates and lack of bioturbation, the sediments are extremely well preserved. All three cores were sampled within 24 h of collection. Each sediment sample was homogen-

ized, placed into pre-combusted, acid-washed glass bottles, and stored frozen.

Sediments analyzed for Pb were processed under Class 100 cleanroom conditions. Approximately 50 mg of sediment were weighed into clean Savillex beakers and digested overnight using a hot (95°C) concentrated 4:1 mixture of ultrapure HF and HNO_3 (Seastar reagents). After evaporating to dryness, ultrapure aqua regia (Seastar reagents) was added to the samples. If organic residue was still present after digestion, the aqua regia step was repeated. After drying a final time, the samples were dissolved in ultrapure 1% HNO_3 .

Solutions were analyzed for Pb isotopes on a Finnigan Element 2 double focusing magnetic sector inductively coupled mass spectrometer (ICP-MS) at Tulane University. All analyses were performed in low-resolution e-Scan mode. The nebulizer employed was a Micromist low-flow nebulizer ($100\ \mu\text{l}/\text{min}$) from Glass Expansion. Typical gas flows for all runs were $14.0\ \text{l}\ \text{min}^{-1}$ Ar (plasma), $1\ \text{l}\ \text{min}^{-1}$ Ar (auxiliary), and $1\ \text{l}\ \text{min}^{-1}$ Ar (sample). Since samples were previously analyzed by atomic absorption spectroscopy for Pb concentrations (Zimmerman and Canuel, in review), all solutions could be diluted accurately to 1 ppb for Pb isotope analysis. Sensitivity for this concentration of Pb on the ICP-MS ranged between 1×10^6 and 1.5×10^6 counts s^{-1} during the course of this study.

To correct for mass bias, several NIST 981 standards were run. These standard runs bracketed sample runs in a ratio of 1:2. In other words, each sequence had the following pattern: standard, sample, sample, standard, sample, sample, standard, etc. The reproducibility of mass bias was, thus, measured and determined to be no higher than 1.5 ‰/amu. A linear correction over the full mass range was applied to each isotope ratio. Although the mass bias value did not change over the course of 1 day, there was variability on a day-to-day basis. Overall, the long-term external reproducibility of the Pb isotope ratios of the NIST 981 standard was approximately 0.7 ‰ to 1.0 ‰. This reproducibility represents the uncertainty in the mass bias correction, and is, by far, the maximum uncertainty in the isotope analysis. Procedural Pb blanks were less than 0.010 ppb (usually <0.005 ppb) and had Pb isotope compositions within the range of those measured in the samples, so that blank corrections were not necessary.

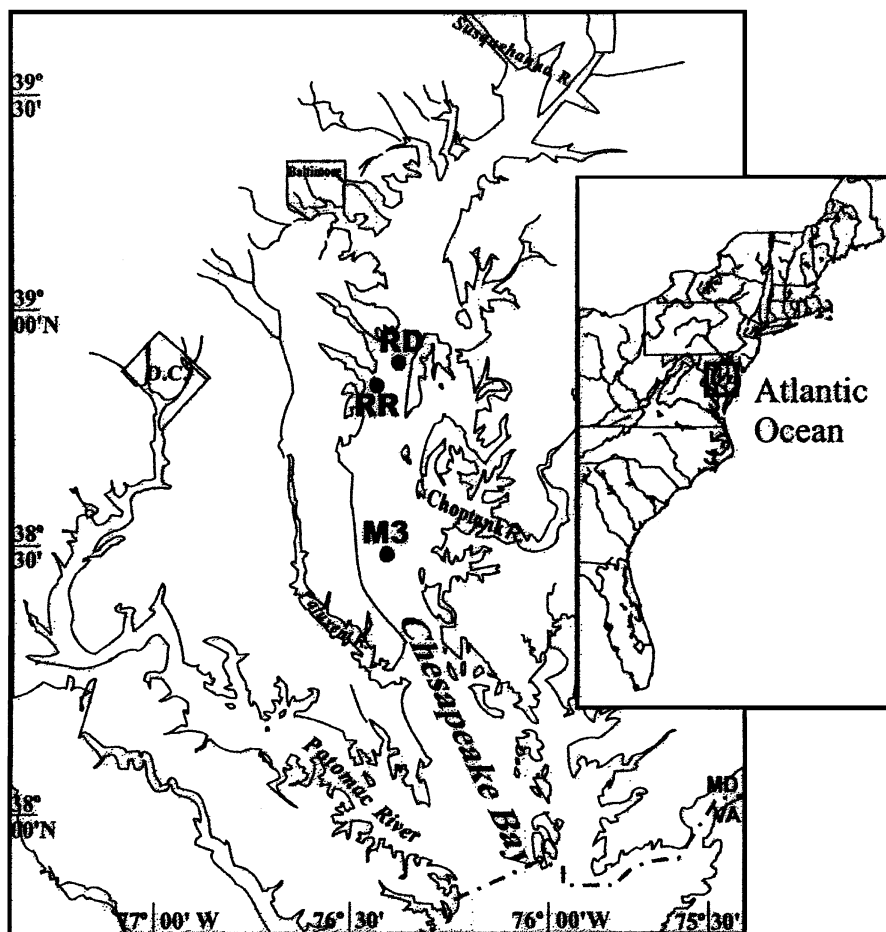


Fig. 1. Map of northern Chesapeake Bay showing locations of core collection (from Zimmerman, 2000).

The sediment cores were dated using a combination of techniques including ^{210}Pb (constant initial concentration method) and ^{137}Cs radioisotopes, and pollen indicators. The full age models for both cores are described in detail elsewhere (Zimmerman and Canuel, in review). In addition, the age model data sets can be accessed at http://www.geosc.psu.edu/~azimmer/supplemental_data.htm. Distinct laminations revealed by x-radiographs along with the logarithmically decreasing ^{210}Pb activities support the notion that little, if any, sediment disturbance has taken place (i.e., no bioturbation or resuspension). ^{210}Pb -derived sediment mass accumulation rates are constant and equal to 0.47 and $1.21 \text{ g cm}^{-2} \text{ year}^{-1}$

in the upper portion of cores M3 and RD, respectively (Zimmerman and Canuel, in review). Sediment accumulation rates, for these same cores, calculated using ^{137}Cs activity maxima and penetration depths are similar to those calculated using ^{210}Pb activities (Zimmerman and Canuel, in review). Accumulation rates for the lower portions of cores M3 ($< 100 \text{ cm}$) and RD ($< 180 \text{ cm}$) are estimated using ragweed pollen data (Zimmerman and Canuel, in review). The average accumulation rate derived for core RR using ^{210}Pb data is $0.138 \text{ g cm}^{-2} \text{ year}^{-1}$ (Zimmerman and Canuel, in review). Unlike the other two cores, the sediments in this core are not laminated. In addition, ^{137}Cs activities were a factor of 2–3 lower than those

Table 1
Stable Pb isotope data for Chesapeake Bay sediment

	Mid-depth (cm)	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{208}\text{Pb}$	Pb (ppm) ^a	$^{206}\text{Pb}/^{207}\text{Pb}$ anthropogenic model ^b	Age model ^c
Core M3	0.25	1.2024	0.4861	30.4	1.201	1996
	6	1.2018	0.4857	34.3	1.200	1993
	26	1.2041	0.4865	37.5	1.204	1983
	31	1.2041	0.4870	40.8	1.204	1981
	41	1.2027	0.4870	45.7	1.202	1975
	51	1.1970	0.4855	48.0	1.195	1967
	61	1.1927	0.4838	47.1	1.189	1956
	71	1.1941	0.4837	42.0	1.191	1943
	86	1.1951	0.4835	38.1	1.192	1922
	91	1.1983	0.4849	28.2	1.195	1915
	101	1.2067	0.4868	17.9	1.209	1898
	111	1.2121	0.4881	21.3	1.218	1879
	121	1.2126	0.4880	12.7	1.241	1861
	131	1.2132	0.4885	18.7	1.223	1841
	151	1.2103	0.4874	16.3	1.219	1797
	160.5	1.2058	0.4863	8.8		1771
	171	1.2040	0.4856	13.2		1743
	181	1.2071	0.4861	10.1		1715
	191	1.2050	0.4867	8.8		1687
Core RD	1	1.2056	0.4871	34.0	1.206	1998
	21	1.2034	0.4874	43.0	1.203	1994
	41	1.2041	0.4877	55.1	1.204	1989
	49	1.2010	0.4873	54.2	1.200	1986
	55	1.2004	0.4873	60.5	1.200	1981
	59	1.2008	0.4872	58.1	1.200	1979
	72.5	1.1976	0.4858	47.4	1.196	1971
	82.5	1.1969	0.4853	54.8	1.195	1964
	107.5	1.1954	0.4846	54.7	1.193	1948
	122.5	1.1947	0.4841	49.1	1.192	1938
	132.5	1.1936	0.4845	50.0	1.191	1932
	142.5	1.1966	0.4847	43.8	1.194	1925
	157.5	1.2004	0.4859	44.5	1.199	1915
	177.5	1.2030	0.4862	39.5	1.202	1902
	192.5	1.2058	0.4862	22.4	1.206	1890
	227.5	1.2141	0.4877	24.1	1.221	1863
	257.5	1.2213	0.4902	22.1	1.235	1838
	282.5	1.2164	0.4886	16.4	1.234	1815
	297.5	1.2117	0.4873	16.6	1.222	1800
	325	1.2106	0.4870	13.3	1.228	1767
345	1.2111	0.4867	13.6	1.228	1746	
365	1.2093	0.4873	13.0	1.223	1726	
Core RR	1	1.1987	0.4866	32.8	1.196	
	3	1.1973	0.4859	35.1	1.194	
	5	1.1983	0.4855	36.4	1.196	
	7	1.2004	0.4861	37.0	1.199	
	9	1.2004	0.4860	37.1	1.199	
	11	1.2018	0.4859	31.5	1.200	
	13	1.2034	0.4867	26.9	1.202	
	15	1.2047	0.4866	23.7	1.204	
	17	1.2047	0.4866	20.3	1.204	
	19	1.2050	0.4862	18.0	1.205	

Table 1 (continued)

	Mid-depth (cm)	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{208}\text{Pb}$	Pb (ppm) ^a	$^{206}\text{Pb}/^{207}\text{Pb}$ anthropogenic model ^b	Age model ^c
Core RR	21	1.2054	0.4864	18.6	1.206	
	23	1.2063	0.4867	19.9	1.208	
	25	1.2059	0.4872	19.3	1.207	
	27	1.2074	0.4860	19.7	1.210	
	31	1.2052	0.4873	19.9	1.205	
	33	1.2099	0.4861	19.9	1.215	

^a Pb concentration data from Zimmerman and Canuel (in review).

^b Model isotope composition of anthropogenic Pb component within sediment. Average of bottom four sediment samples from core M3 was used as non-anthropogenic Pb component in model.

^c Age model from Zimmerman and Canuel (in review).

in the other cores, so that determining maxima and penetration depths was more difficult.

3. Results and discussion

3.1. CB sediment isotope variations

Profiles of Pb isotope ratios and Pb concentrations versus depth/age (Table 1, Fig. 2) show the same pattern in cores M3 and RD. The bottom of all three cores is characterized by sediment with $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios in the range of 1.204 to 1.211. From bottom to top in cores M3 and RD, the isotope ratios increase to about 1.220, steeply decrease to about 1.195, and then increase again to about 1.205. The highest $^{206}\text{Pb}/^{207}\text{Pb}$ ratios occur at about 130 cm in M3 and 260 cm in RD. The lowest $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are observed at about 60 cm in M3 and 130 cm in RD. Core RR can be distinguished from the other cores in that its Pb isotope profile consists of constantly decreasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios from the bottom (~ 1.215 at 33 cm) to the top (1.198 at 1 cm).

In cores M3 and RD, the peaks in Pb concentration (Zimmerman and Canuel, in review) do not coincide with maxima or minima in Pb isotope ratio values. This is not unusual, and even to be expected, given that the isotope ratios track changes in the source of Pb, while the concentrations do not. Although the Pb isotope ratios and Pb concentrations have similar changing patterns in both cores (Fig. 2), these patterns occur across depths that are different by a factor of 2, an indication that the sedimentation rate recorded by core RD is twice that of core M3. The age models

(Zimmerman and Canuel, in review), which are independent of the Pb isotopic trends, concur with this assessment.

The anthropogenic Pb isotope signal can be derived from the total Pb isotope signal by assuming that the total Pb is composed only of two components, natural and anthropogenic Pb. Furthermore, the assumption is made that natural Pb throughout the sediment column at both sites is equal to the average Pb in the oldest sediment at the bottom of core M3, which probably spans the greatest length of time. Four sediment samples from the lowest section of this core have the lowest Pb concentrations measured (i.e., ~ 10 ppm) and $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios that converge to a relatively constant value of about 1.205 (Fig. 2a). This sediment was deposited prior to the industrial revolution in the early 18th century and late 17th century (Zimmerman and Canuel, in review), the earliest time represented in any of the cores. Therefore, this section of core presumably represents sediment that is the least affected by human activities. By subtracting this pre-anthropogenic natural component of Pb from the total Pb, the isotopic signature of the anthropogenic Pb component can be obtained (Table 1). The equation used is as follows:

$$\begin{aligned}
 &^{206}\text{Pb}/^{207}\text{Pb}_{\text{anthropogenic}} \\
 &= [({}^{206}\text{Pb}/^{207}\text{Pb}_{\text{total}})(\text{ppm Pb}_{\text{total}}) \\
 &\quad - ({}^{206}\text{Pb}/^{207}\text{Pb}_{\text{natural}})(\text{ppm Pb}_{\text{natural}})] \\
 &\quad / [\text{ppm Pb}_{\text{total}} - \text{ppm Pb}_{\text{natural}}] \quad (1)
 \end{aligned}$$

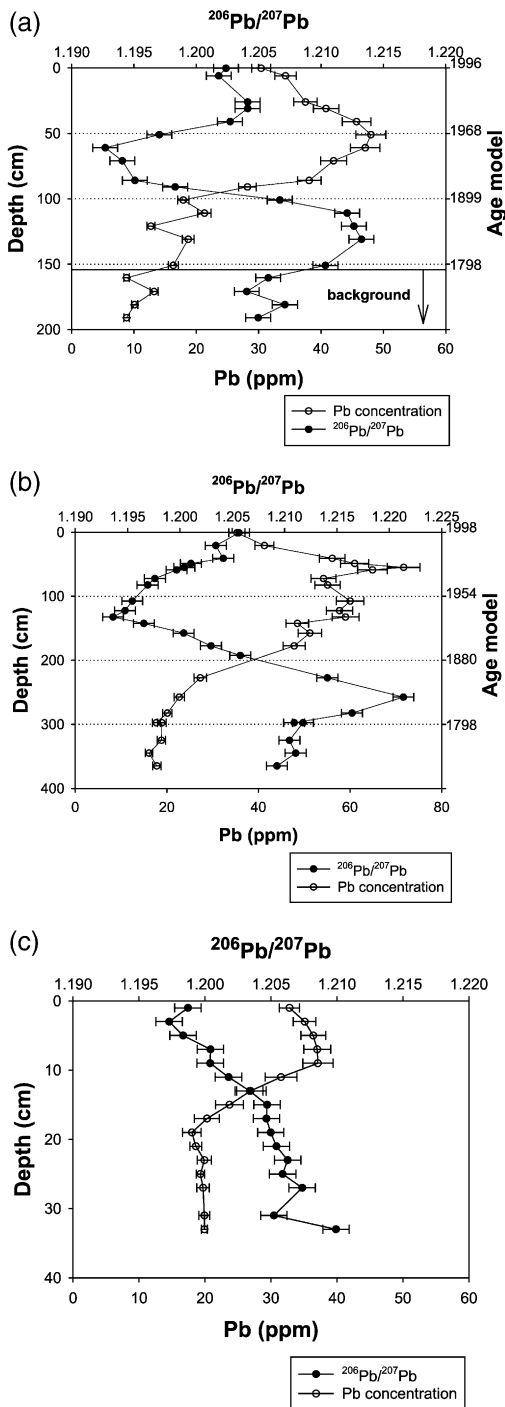


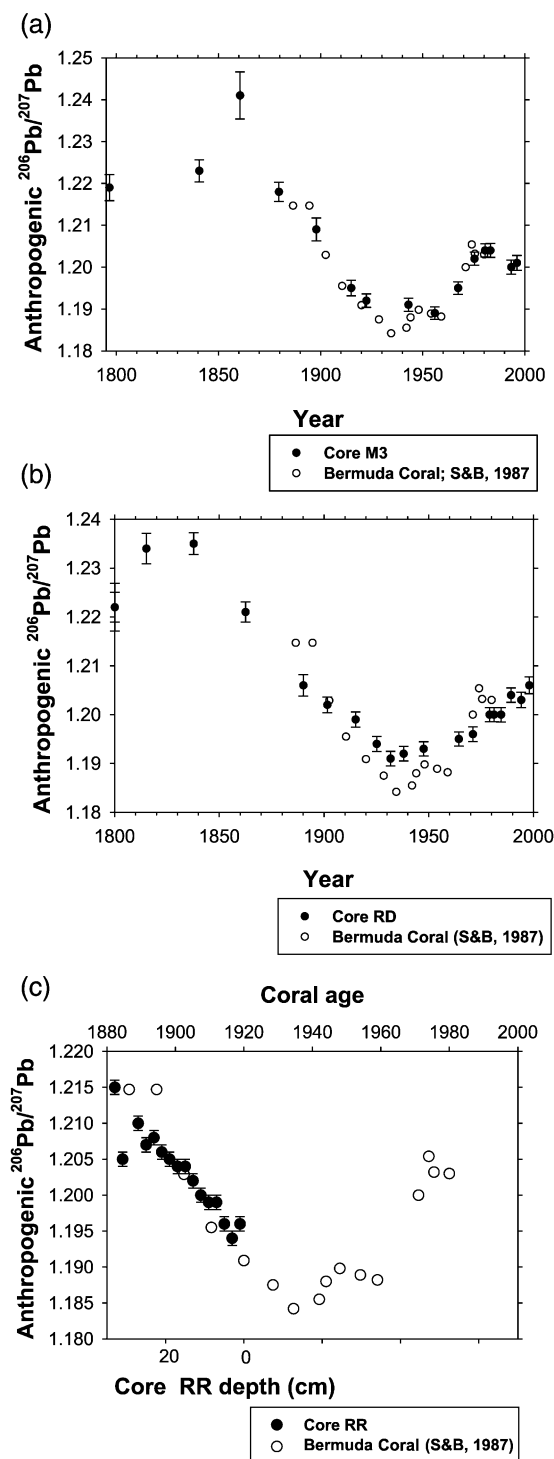
Fig. 2. $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios and Pb concentrations versus depth for sediment from CB cores M3 (a), RD (b), and RR (c). The right-hand y-axis is an approximation of the age model presented in Zimmerman and Canuel (in review).

where ($^{206}\text{Pb}/^{207}\text{Pb}_{\text{total}}$) and (ppm Pb_{total}) are the measured $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and Pb concentration of the sample, respectively, and ($^{206}\text{Pb}/^{207}\text{Pb}_{\text{natural}}$) and (ppm $\text{Pb}_{\text{natural}}$) are the estimated $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and Pb concentration of the natural component of the sediment, respectively. In the highly contaminated sediments near the core tops, the model $^{206}\text{Pb}/^{207}\text{Pb}_{\text{anthropogenic}}$ ratios are not sensitive to the concentration of natural Pb in Eq. (1), even if the natural Pb concentration is 20 ppm (i.e., a factor of two higher than the presumed 10 ppm). The least contaminated sediments at the bottom of the cores are the most sensitive to any model calculation. However, the similar patterns of temporal variability in $^{206}\text{Pb}/^{207}\text{Pb}_{\text{anthropogenic}}$ ratios from independently dated cores (M3 and RD) provide evidence for the validity of our model calculations.

3.2. Regional atmospheric Pb emissions and stable Pb isotopes as a chronologic tool

The range in calculated anthropogenic Pb isotope signatures (Table 1) for all three cores is similar to that found in a 100-year-old Bermuda coral by Shen and Boyle (1987) (i.e., ~ 1.19 to 1.21 ; Fig. 3). The Bermuda coral Pb-isotope record represents a history of atmospheric Pb fallout into western North Atlantic waters. Tropospheric westerlies carry the atmospheric Pb from the eastern US to the surface waters of the Sargasso Sea. Upon fallout, the Pb dissolves and is subsequently incorporated into the coral skeleton. By counting the distinct annual bands within the coral and analyzing several samples for Pb isotope ratios, Shen and Boyle (1987) determined the timing of shifts in the sources of atmospheric Pb from the eastern US.

Since the turn of the 20th century, almost all of the Pb within the coral has been anthropogenically derived (i.e., there is little natural Pb within the Bermuda coral). The evidence for this supposition is as follows. Assuming a maximum background Pb/Ca ratio of $3.5 \text{ nmol mol}^{-1}$ in the coral, Shen and Boyle (1987) have shown that not more than 15% of the Pb is derived from natural sources. In this case, any “corrected” Pb isotope ratio would be only slightly lower than that measured. However, this Pb/Ca ratio is estimated from the oldest part of the coral (~ 1880 – 1890 ; Shen and Boyle, 1987). During this time period, it is likely that the coral has been significantly con-



taminated with anthropogenic Pb from coal combustion (this study; Brabander et al., in review), so that the natural coral Pb/Ca ratio is potentially much lower than $3.5 \text{ nmol mol}^{-1}$. Hence, it is probable that the Bermuda coral anthropogenic Pb isotope compositions are virtually the same as those measured.

The anthropogenic Pb isotope signatures in cores M3 and RD follow a synchronized and distinct temporal pattern that is similar to that displayed in the Bermuda coral anthropogenic Pb isotope record (Fig. 3a and b). The agreement between the M3 and RD sediment and Bermuda coral records provides strong support for the Zimmerman and Canuel (in review) age models. The same temporal pattern in Pb isotope ratios is not observed in the sediment from core RR (this will be further discussed below). There are three distinct sections contained within the Bermuda coral and CB sediment (M3 and RD) isotope records (Fig. 3a and b). From 1890 to 1930, the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios decreased rapidly, and linearly, from about 1.215 to 1.185. During the mid-20th century, from 1930 to 1960, there was a slight increase in this isotope ratio from about 1.185 to 1.190. In the latest part of the record from 1960 to 1980, there seems to have been a rapid and linear increase in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios from about 1.190 to 1.205. That there is little difference between records separated by 1750 km is astounding and supports the notion that the CB Pb isotope signal is derived from a regional atmospheric source of Pb that is similar to that archived in the Bermuda coral.

Atmospheric anthropogenic Pb from the mid-Atlantic region of the US, recorded in the sediments of CB, must have, over the last century, made its way into the Sargasso Sea. That there is no lag between the records is in keeping with the short 2-week residence time of atmospheric Pb (e.g., Véron et al., 1992). One

Fig. 3. (a) Anthropogenic $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios versus age for CB cores M3 (a), RD (b), and RR (c). Age model from Zimmerman and Canuel (in review). Bermuda coral $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio data from Shen and Boyle (1987). Errors are propagated assuming no variation in the natural endmember. In (c), we superimpose our RR Pb isotope data set over that part of the coral record data set with which it best agrees. In this way, an age model can be estimated for the sediments in core RR. The interval of sediment between 33 and 0 cm appears to represent deposition between 1880 and 1920.

can infer from the clear correspondence between the isotope signatures (Fig. 3a and b) that local point-source contributions of Pb were the same as or had no effect on CB sediment Pb isotope ratios. There is further evidence that Pb in CB sediments is characteristic of a regional atmospheric Pb signal. Measurements of the Pb isotope composition of aerosols within the US temperate westerlies range from 1.20 to 1.21 (Church et al., 1990; Rosman et al., 1994a,b; Véron et al., 1992, 1993, 1998), in complete agreement with the anthropogenic Pb isotope ratios of CB sediment deposited between 1980 and 1998 (Fig. 3a and b).

The temporal pattern of anthropogenic Pb isotope ratios in sediment from core RR is unlike that in the other two cores. From the oldest to the youngest sediments, all that is observed is a nearly linear decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio. By superimposing and compressing the RR Pb isotope data set over that part of the coral record (and CB sediment) data set with which it best agrees, one can estimate an age model for the sediments in core RR. In this way, it would seem that the interval of sediment between 33 and 0 cm represents deposition between 1880 and 1920 (Fig. 3c). Hence, one can infer that the topmost stratigraphy of core RR, representing approximately 80 years of sediment accumulation, has been removed (Fig. 3c). Additional evidence for missing sediment comes from the existing ^{210}Pb inventory, which is 50% lower than that expected from atmospheric input (Zimmerman and Canuel, in review), and from the ^{137}Cs and elemental Pb inventories, which are both much lower than those in the other cores studied here (Zimmerman and Canuel, in review). Possible explanations for the disappearance of sediment at the core top are that this part of the sediment column was: (a) not collected by the kasten corer, (b) removed by anthropogenic sediment dredging, or (c) eroded during natural sediment focusing processes. None of these possibilities can effectively be ruled out and, therefore, further investigation is necessary. The important point, however, is the fact that sediment is missing from the record. This conclusion could not have been reached without a careful evaluation of the stable Pb isotope data. Indeed, without this data, an age model based solely on average ^{210}Pb -derived accumulation rates would be in error.

3.3. Sources of atmospheric Pb emissions

The potential sources of anthropogenic Pb emissions include combustion of fossil fuels (mainly coal and oil), mining and smelting of Pb and other metal ores (e.g., Cu, Ni), and the combustion of Pb-containing gasoline additives (Nriagu, 1998). Anthropogenic Pb has made up a significant portion of the total Pb within the CB record for more than just the past 100 years. Indeed, anthropogenic Pb can be detected in CB prior to 1880 (start of the coral record), beginning in the early 19th century (Fig. 3). For sediment in both cores deposited prior to 1800 it is difficult to predict with certainty the Pb isotopic composition of the anthropogenic component since the Pb concentration is so low (< 14 ppm) and close to the natural component. The source of the pollutant atmospheric Pb from the earliest part of the CB records (~ 1800) until about 1930, is probably derived from the burning of coal mined in nearby Pennsylvania, Virginia, West Virginia, and Kentucky. The Pb isotope composition of coal derived from these states ranges from about 1.19 to 1.25 (Chow and Earl, 1972), within the range of the anthropogenic ratios measured in CB sediments. Among these sources, the most radiogenic (i.e., highest $^{206}\text{Pb}/^{207}\text{Pb}$) ratios are obtained in coal from West Virginia and Kentucky (Chow and Earl, 1972), suggesting that early in the 19th century, combustion of these coals was the main source of Pb emitted into the atmosphere over the eastern US. On the other hand, from the mid-19th century to about 1930, combustion of coal from Pennsylvania (least radiogenic Pb values; Chow and Earl, 1972) played an increasingly dominant role in supplying Pb to the atmosphere over the eastern US.

Across the US, beginning in about the mid-1920s and until the mid-1970s, Pb-containing industrial aerosols were derived predominantly from gasoline combustion (Nriagu, 1989). It is during this time that the Pb concentration profile of Chesapeake Bay sediments mimics the profile of US consumption rates of leaded gasoline (Shen and Boyle, 1987; Wu and Boyle, 1997). This is similar to other Pb concentration records from sediment throughout North America and the world (Nriagu, 1996). On the other hand, the Pb isotopic composition of aerosols produced during the same time period has values that vary spatially and temporally across the globe (e.g., Farmer et al., 1996;

Gobeil et al., 1995; Graney et al., 1995; Moor et al., 1996; Ritson et al., 1994; Shirahata et al., 1980; Shotyk et al., 1998; Sturges and Barrie, 1987), presumably because of differing sources of Pb ore used in the production of leaded gasoline. In the US, although the temporal variability of the Pb isotope composition of gasoline emissions has been recognized (i.e., increasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the 1960s and 1970s due to the increasing role of Missouri ores in Pb-additive manufacturing; Shirahata et al., 1980; Sturges and Barrie, 1987), at any given time depending on the specific location within the US, the exact $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic signature of atmospheric Pb differs. For example, in California, data from pond sediments and urban air filters indicate that $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of atmospheric emissions increased from 1.13 in the 1950s to about 1.24 by the mid-1970s (Erel and Patterson, 1994; Patterson and Settle, 1987; Shirahata et al., 1980). During the same time period (i.e., 1950 to 1975), there is no evidence for ratios as low as 1.13 or as high as 1.24 in regions far from the west coast. For example, sediment from the Great Lakes region (Graney et al., 1995; Ritson et al., 1994) that is assumed to contain US atmospheric Pb contains relatively high anthropogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of about 1.20 in the 1950s. These ratios decrease to about 1.18 by the 1960s, and then increase throughout the 1970s until they reach 1.20 by 1980. Although the range in anthropogenic Pb isotope ratios from the Great Lakes region is similar to that found in CB, there are distinct differences in the temporal patterns of the ratios.

A compilation of published $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for US lead measured in aerosols and gasoline reveals much scatter in the Pb isotope signature from 1960 to 1990 (Fig. 3 in Rosman et al., 1994a). It is clear that regional differences in atmospheric Pb isotope ratios are the norm, and exist because of variable sources of Pb in a single industry or in variable industries. However, if a temporal regional atmospheric signal can be determined, as has been here in the CB sediments, then the opportunity exists to use the pattern of variability in Pb isotope ratios as an aid in dating sediments that are as old as 120 years old. More work is needed to deduce the exact spatial extent of the mid-Atlantic US atmospheric Pb signal like that found in the CB sediments. But, given that the same integrated signal is found in regions separated by almost 2000

km, it is likely that this signal permeates a relatively large portion of the mid-Atlantic US.

4. Conclusion

Sediments from three sites in the mesohaline portion of Chesapeake Bay (CB) have anthropogenic Pb isotope ratios that are within the same range as those measured in a Bermuda coral (Shen and Boyle, 1987). The Pb isotope profiles determined on well-dated sediments from two of the sites (M3 and RD) are in excellent temporal agreement with the Pb isotope profile established for a dated coral from Bermuda (Shen and Boyle, 1987) almost 2000 km away. This correlation suggests that CB sediments contain a regional atmospheric Pb isotope signal that is representative of the mid-Atlantic region of the US. This signal, at least up until 1980 (the extent of the coral record), was the dominant Pb signal to reach the waters of the Sargasso Sea within which the coral formed. The distinct changing pattern of this particular regional stable Pb isotope signal through time can be used, in conjunction with ^{210}Pb , to date sediments that contain similar sources of Pb. In addition, the CB Pb isotope record provides clues as to the changing sources of Pb industrial emissions over the past 200 years in this highly urbanized region of the US.

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