USE OF LEAD ISOTOPES IN DEVELOPING CHRONOLOGIES FOR RECENT SALT-MARSH SEDIMENTS

Andrew C. Kemp1, 2*, Christopher K. Sommerfield3, Christopher H. Vane4, Benjamin P. Horton5, Simon Chenery4, Shimon Anisfeld1 and Daria Nikitina6

1 School of Forestry and Environmental Studies, Yale University, New Haven, CT 06511, USA
2 Yale Climate and Energy Institute, New Haven, CT 06511, USA
3 College of Earth, Ocean, and Environment, University of Delaware, Lewes, DE 19958, USA
4 British Geological Survey, Kingsley Dunham Center, Keyworth, Nottingham NG12 5GG, UK
5 Sea Level Research, Department of Earth and Environmental Science, University of Pennsylvania, Philadelphia, PA 19104, USA
6 Department of Geology and Astronomy, West Chester University, West Chester, PA 19380, USA

* Corresponding author. andrew.kemp@yale.edu tel: 203 436 3978
ABSTRACT

Dating of recent salt-marsh sediments is hindered by the radiocarbon plateau and the moving ~100 year window of $^{210}$Pb accumulation histories. Introduction of anthropogenic Pb to the environment is a means to date salt-marsh sediment deposited over the last 200 years by correlating downcore changes in concentration and isotopic ratios to historical production and consumption. We investigated use of Pb as a chronometer in a core of salt-marsh sediment from New Jersey, USA. Changes in Pb concentration identified horizons at AD 1875, 1925, 1935 and 1974 that correspond to features of historic U.S Pb production and consumption. Stable lead isotopes ($^{206}$Pb:$^{207}$Pb) constrained ages at AD 1827, 1857 and 1880, reflecting Pb production in the Upper Mississippi Valley with its unusual isotopic signature and at AD 1965 and 1980 from leaded gasoline. These chronostratigraphic markers of fixed dates provide precise constraints on sediment age during part of the radiocarbon plateau. Use of Pb to develop chronologies for recent salt-marsh sediment enables high resolution records of sea-level change to extend beyond the period of instrumental records and to better constrain the initiation of accelerated sea-level rise.
1 INTRODUCTION

Modern rates of sea-level rise recorded by tide gauges (Douglas, 2001; Woodworth et al., 2009; Church and White, 2011) and, more recently, satellites (Cabanes et al., 2001; Leuliette and Miller, 2009) exceed those of the last 2000 to 4000 years estimated using geological techniques (Donnelly et al., 2004; Gehrels et al., 2005; Engelhart et al., 2009). The limited duration and distribution of instrumental records hinders attempts to constrain the timing and magnitude of this apparent acceleration. High-resolution (decadal and decimeter scale) reconstructions of relative sea level (RSL) using salt-marsh sediments bridge the gap between instrumental and geological records and suggest that the increased rate of sea-level rise was initiated in the late 19th century or early 20th century (Donnelly et al., 2004; Gehrels et al., 2005; Gehrels et al., 2008; Kemp et al., 2009; Kemp et al., 2011).

Salt-marsh sediments provide detailed archives of RSL change because their spatial distribution is intimately linked to the tidal frame (Chapman, 1960). Salt marshes track moderate rates of RSL rise by accreting vertically through a combination of vegetative growth and detrital sedimentation of organic and inorganic (mineral) particles (Orson et al., 1998). The resulting sedimentary sequences can form continuous accumulations of salt-marsh peat that are well suited to producing high-resolution RSL reconstructions if accurate and precise chronologies are developed.

Abundant organic material (including plant macrofossils) in salt-marsh sediments has made radiocarbon ($^{14}$C) dating the principal means of determining the age of sea-level
indicators (Tornqvist et al., 1992; van de Plassche et al., 1998; Shennan and Horton, 2002; Tornqvist et al., 2004; Engelhart et al., 2011). Difficulties with this technique hinder its application to sediments younger than about 350 years. Between AD 1650 and 1950, a plateau in the $^{14}$C calibration curve caused by natural variability in atmospheric $^{14}$C production hampers chronological interpretation by producing multiple calendar ages for a single sample (Reimer and Reimer, 2007). Since AD 1950 introduction of anthropogenic $^{14}$C from above-ground testing of nuclear weapons has significantly altered atmospheric $^{14}$C concentration (Shotyk et al., 2003; Hua and Barbetti, 2004; McGee et al., 2004). Although new approaches to $^{14}$C dating have increased its usefulness for estimating the age of recent sediments (Marshall et al., 2007; Hua, 2009), studies seeking to provide detailed records of recent RSL changes from salt-marshes rely upon alternative techniques to achieve the desired temporal resolution for the last 350 years.

The most widely used radionuclide for estimating the accumulation rate and relative age of recent salt-marsh sediments is $^{210}$Pb (Gehrels et al., 2005; Kemp et al., 2009). Use of $^{210}$Pb as a sediment chronometer involves assumptions regarding how $^{210}$Pb is delivered from the atmosphere to sediments (Robbins, 1978; Appleby and Oldfield, 1992; Appleby, 2001). The relative amount of atmospheric rainout versus tide-water sources of $^{210}$Pb to salt marshes cannot be determined with certainty, therefore $^{210}$Pb-based sediments age estimates are corroborated by independent means. Radiocesium ($^{137}$Cs) is most frequently used in this capacity as it provides an absolute time marker for peak fallout in AD 1963-64 (Ritchie and McHenry, 2000). A limitation of $^{210}$Pb geochronology is that it
is restricted to the last 100 to 120 years, and this range moves forward each year leaving a
growing “chronological vacuum” (Gale, 2009).

Stable Pb isotopes can extend sediment chronologies developed using $^{210}$Pb and $^{137}$Cs,
and narrow the crucial gap (approximately AD 1650 to 1900) between time scales
covered by these radionuclides and $^{14}$C geochronology. The age and geological history
of mineral deposits results in Pb ores having differing isotopic compositions (Russell and
Farquhar, 1960; Chow and Earl, 1972). During industrial processes (including
production and consumption of leaded gasoline), there is minimal fractionation of Pb
isotopes and emissions preserve the Pb isotopic signature of the ore from which they
were derived (Ault et al., 1970; Doe, 1970). Prior to AD 1979 as much as 19.6 x 10^9 kg
of Pb was added to the atmosphere from global anthropogenic emissions (Nriagu, 1979),
primarily high-temperature industrial activities and combustion of leaded gasoline (Kelly
et al., 2009). The atmospheric residence time of Pb aerosols permits their dispersal and
subsequent deposition over continental-scale distances by prevailing winds (Sturges and
Barrie, 1987; Wu and Boyle, 1997; Bollhöfer and Rosman, 2000, 2001), as shown by
measurements at sites distal to source regions, such as Greenland (Rosman et al., 1993;
Hong et al., 1994), Bermuda (Shen and Boyle, 1987; Kelly et al., 2009), and deep ocean
basins (Schaule and Patterson, 1981; Shen and Boyle, 1987; Hamelin et al., 1997; Wu et
al., 2010). There is close agreement between the timing of emissions and deposition
(Graney et al., 1995). As the precision of analytical measurements is smaller than the
variability of source material (Shen and Boyle, 1987; Chillrud et al., 2003), ratios of
stable Pb isotopes preserved in sedimentary archives can distinguish among different
sources of anthropogenic Pb (Shotyk et al., 1998; Kamenov et al., 2009). Most investigations of historical Pb deposition used independent chronological control or correlation with dated sedimentary records (Lima et al., 2005b) to describe the timing of Pb contamination and to apportion sources of pollution (Edgington and Robbins, 1976; Graney et al., 1995; Cochran et al., 1998; Marcantonio et al., 2002; Lima et al., 2005b; Kamenov et al., 2009). Alternatively, changing concentrations and ratios of Pb isotopes measured in sediments can be ascribed to historical variations in Pb production and consumption with well-established ages (Shen and Boyle, 1987; Graney et al., 1995; Farmer et al., 2001; Marcantonio et al., 2002; Chillrud et al., 2004; Lima et al., 2005b; Gehrels et al., 2008; Kelly et al., 2009; Vane et al., 2011). Anthropogenic Pb emissions are thus a potentially valuable source of chronological control on salt-marsh accretion history over the last 200 years in the northeastern U.S.

In this paper we investigate Pb concentrations and isotopes ($^{210}$Pb with $^{137}$Cs and $^{206}$Pb:$^{207}$Pb) as a chronometer of recent salt-marsh sediments using a sediment core from a U.S. Mid-Atlantic salt marsh. We discuss the application of anthropogenic Pb chronostratigraphic markers for future studies seeking to develop high-resolution RSL reconstructions from salt marshes in this region.

**2 Regional Setting**

Sediment core BB1 was obtained from a salt marsh in northern Barnegat Bay (New Jersey), an archetype back-barrier coastal lagoon in the U.S. Mid-Atlantic region (Figure 1). The 280 km$^2$ bay, which is fringed by *Spartina alterniflora* salt marsh, has a mean...
depth of 1.5 m and a mean tidal range that decreases from 1.4 m at the inlet to 0.3 m at its northern and southern limits. Although the bay and its extensive marshes have a history of human impacts, including grid ditching (Kennish, 2001) and eutrophication (Kennish et al., 2007), much of the marsh accretes vertically unobstructed by human influences. Barnegat Bay lacks a large source of river sediment, therefore supply of allochthonous mineral sediment to the marsh platform is low compared to Mid-Atlantic river-estuarine marshes. Consequently, salt-marsh accretion rates determined by $^{210}$Pb and $^{137}$Cs measurements at sites throughout the bay are low (0.2–0.3 cm/yr) compared to minerogenic marshes in the region (Velinsky et al., 2011). Importantly, supply of $^{210}$Pb to Barnegat Bay salt marshes is derived mostly (if not exclusively) from direct atmospheric deposition, an ideal condition for developing chronologies of anthropogenic Pb isotopes. Core BB1 was selected because it exhibited concordant $^{210}$Pb and $^{137}$Cs chronologies, and was sufficiently long (94 cm) to capture the full post-industrial record of anthropogenic Pb fallout.

3 METHODS

Sediment cores from Barnegat Bay salt marshes were collected in 2009 as part of an unrelated study of historical sediment and nutrient loading (Velinsky et al., 2011). Using a push-piston core (10 cm diameter) system designed to minimize compaction, BB1 was collected in a high-marsh floral zone (short-form Spartina alterniflora), 25 m landward of Reedy Creek, at a surveyed elevation of 0.10 m NAVD 88 (Figure 1). Duplicate cores of BB1 were recovered, one for radionuclide and chemical analysis and another for
stratigraphic description and archiving. Cores were capped in the field and transported to the laboratory for processing.

3.1 Sample preparation

The core for radionuclide and chemical analysis was sectioned in 2 cm thick intervals. Samples were weighed wet, dried at 110°C for 24 hours in a convection oven, and weighed again dry to determine gravimetric water content, porosity, and dry-bulk density (Bennett and Lambert, 1971). Approximately 20–60 g of dried sediment was ground to a homogeneous powder, and a 4 g aliquot was combusted in a muffle furnace to determine loss on ignition (LOI) following methods described in (Heiri et al., 2001). LOI quantified the relative proportion of organic (combustible) and mineral (residual ash) materials in the sediments. Gravimetric and LOI data were used to interpret the downcore radionuclide and stable Pb profiles. Each sample between depths of 0 and 94 cm (n=47) was analyzed for Pb concentrations and stable Pb isotopes, whilst only samples from 0 to 36 cm (n=18) were analyzed for ²¹⁰Pb and ¹³⁷Cs activity.

3.2 Radionuclide Measurement

Powder samples were sealed in a 60 ml plastic jar, stored for at least 30 days to ensure equilibrium between ²²⁶Ra and ²¹⁴Bi, and then counted for 24 hours on Canberra Model 2020 low-energy Germanium detectors. Measurements of ²¹⁰Pb (t₁/₂=22.3 years) and ¹³⁷Cs (t₁/₂=30.1 years) activity were made by gamma spectroscopy of the 46.5 and 661.6 keV photopeaks, respectively (reviewed by (Cutshall et al., 1983; Wallbrink et al., 2002). The full-energy peak efficiency of these detectors is 4% at 46.5 keV and 1% at 661.6.
keV, and the minimum detectable activity for photopeaks of $^{210}$Pb and $^{137}$Cs is approximately 2–3 Bq/kg. Excess $^{210}$Pb activity was determined by subtracting the activity of its parent nuclide ($^{214}$Bi at 609.3 keV) from the total activity ($^{210}$Pb$_{ex}$=$^{210}$Pb$_{tot}$–$^{214}$Bi). Detector efficiencies were determined using the NIST Ocean Sediment Standard Reference Material 4357 (Inn et al., 2001). The standard (a sediment powder) and core material were counted in an identical geometry, thus negating a self-absorption correction for $^{210}$Pb. Confidence limits for radionuclide data are computed as the propagated one-sigma background, calibration, and counting errors.

3.3 Radionuclide chronology

Two models were used to develop $^{210}$Pb chronologies for core BB1. Detailed descriptions of both approaches are available in the literature (Robbins, 1978; Appleby and Oldfield, 1992; Appleby, 2001). The Constant Initial Concentration (CIC) model assumes that the specific activity (dpm/g) of excess $^{210}$Pb deposited on a marsh surface remained constant through time and that variations in the rate of sediment deposition do not influence the initial activity of excess $^{210}$Pb. The Constant Rate of Supply (CRS) $^{210}$Pb model relates sediment age and depth by assuming that the depositional flux of $^{210}$Pb (Bq/cm$^2$/yr) to a marsh surface was constant. Peak $^{137}$Cs at AD 1963-64 provided an independent means to corroborate $^{210}$Pb accumulation histories.

3.4 Determination of Pb and Sb concentrations and ratios of stable Pb isotopes

In preparation for determining concentrations of stable Pb isotopes and Sb, 0.25 g of powdered sediment was dissolved by a HF/HClO$_4$/HNO$_3$ mixed concentrated acid attack
in Savillex™ PFA vials. Samples were reconstituted in dilute nitric acid and diluted to:

(i) within the calibration range of Pb and Sb chemical standards for concentration measurements; and (ii) within the pulse counting range (< 1Mcps) of the ICP-MS for isotope ratio measurements.

Concentration and isotope ratio determinations were made using a quadrupole ICP-MS instrument (Agilent 7500c) with a conventional glass concentric nebuliser. The long term 2σ precision for the BCR-2 reference material used for quality control, which has a total Pb concentration of 11 mg/kg was $^{207/206}\text{Pb} = 0.0008$, $^{208/206}\text{Pb} = 0.0020$, based on $n=32$ replicates over 29 months and a mean accuracy, relative to the published values of (Baker et al., 2004), within that error. Data (raw isotope intensity count rates) were processed off-line using Microsoft Excel spreadsheets. Processing consisted of: (i) removal of background; (ii) calculation of isotope ratios; (iii) determination of mass bias correction factor from defined isotope ratios of SRM981; (iv) application of mass bias factors derived from SRM981 using external standard-sample-standard bracketing; and (v) optional further correction for linearity of ratio with signal strength.

### 3.5 Identifying Pb chronostratigraphic markers

We identified nine historical features of U.S. Pb production and consumption that could be used as chronostratigraphic markers to estimate sediment age in core BB1 (Table 1; Figure 2). Four were recognized in Pb concentration and five in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. Changes in production and consumption are assumed to have caused a corresponding change in Pb emissions that were transported through the atmosphere and deposited on
the salt-marsh surface within a few years (Graney et al., 1995) and without isotopic fractionation (Ault et al., 1970). As emissions per unit of production or consumption are likely to have changed over time, trends rather than absolute values are the basis for recognizing these features in core BB1. The stratigraphic context of core BB1, and the ordering of samples, provides an appropriate sedimentary constraint for interpreting downcore changes in Pb concentration and $^{206}\text{Pb}:{}^{207}\text{Pb}$ as being reliably correlated to the nine historical features. We used downcore concentration of Sb to distinguish between changes before and after the widespread introduction of automobiles around AD 1920 because it has low abundance in pristine environments, similar environmental behavior to Pb (Shotyk et al., 2005) and is a high-contrast marker for aerial deposition from road traffic (Gomez et al., 2005; Amarasiriwardena and Wu, 2011; Fujiwara et al., 2011). Its association with automotive emissions makes it useful for confirming interpretations of Pb data as being related (or unrelated) to leaded gasoline.

4 RESULTS

4.1 $^{210}\text{Pb}$ and $^{137}\text{Cs}$ activities and chronology

Radionuclides were measured in the upper 36 cm of core BB1 (Figure 3a). Excess $^{210}\text{Pb}$ increased near-exponentially upcore from 1.3 Bq/kg at 31 cm to 166 Bq/kg at the top, a pattern consistent with steady-state sediment accumulation and radioactive decay. The accretion rate based on regression of the decay profile is 0.25 cm/yr. The $^{137}\text{Cs}$ profile (Figure 3b) broadly mirrors the record of $^{137}\text{Cs}$ atmospheric fallout in northern temperate latitudes (Warneke et al., 2002). Activity of $^{137}\text{Cs}$ increased upcore from the depth of first occurrence above the detection limit (20–22 cm) to a peak centered at 9 cm, above
which activity decreased to the core top. The accretion rate based on the AD 1963-64 peak is 0.25 cm/yr, identical to the $^{210}$Pb-based rate. Accumulation histories were developed for BB1 using the CIC and CRS models (Figure 3). This yielded age dates from AD 1901 to the time of core collection (AD 2009).

4.2 Total Pb and Sb concentration and ratios of stable Pb isotopes

The average Pb concentration of samples between 93 cm and 43 cm in BB1 was 11.2 mg/kg and represents background levels (Figure 2c). Samples at 41, 39 and 37 cm had an average Pb concentration of 23.8 mg/kg. From 35 cm to 21 cm, it increased from 20.5 to 93.3 mg/kg. The interval from 21 cm to 17 cm was characterized by a decline in Pb concentration to 76.5 mg/kg. Maximum Pb concentration (164 mg/kg) occurred at 9 cm and declined to 65.8 mg/kg at the modern marsh surface. Antimony (Sb) concentrations paralleled those of Pb (Figure 2c). Below 41 cm, total Sb concentration was 0.09-0.36 mg/kg. It increased to a peak of 1.44 mg/kg at 23 cm before declining to 1.13 mg/kg at 13 cm. Maximum Sb concentration was at 9 cm (1.63 mg/kg) and declined to 0.86 mg/kg at the core top.

Measured concentrations of Pb isotopes are expressed as ratios. From 93 cm to 51 cm $^{206}$Pb:$^{207}$Pb varied between 1.197 and 1.226 (Figure 2d). It reached a minimum of 1.174 at 43 cm before increasing to a maximum value of ~1.234 at 33-35 cm. There was a decline in $^{206}$Pb:$^{207}$Pb between 33 cm and 11 cm (1.186) prior to another increase to 1.207 at 9 cm and a subsequent decrease to the modern marsh surface value of 1.200.
5 DISCUSSION

5.1 $^{210}\text{Pb}$ and $^{137}\text{Cs}$ accumulation histories

The CRS model, which was originally developed for lake sediments (Krishnaswamy et al., 1971) and only later applied to salt marshes (McCaffery and Thomson, 1980), is best suited to marshes that sequester $^{210}\text{Pb}$ primarily by direct atmospheric deposition. In highly allochthonous marsh systems, particle-borne $^{210}\text{Pb}$ transported tidally to the marsh platform supplies activity in addition to that derived atmospherically. Because flux of tidal $^{210}\text{Pb}$ to the sediment surface is highly discontinuous, the steady-state assumption of the CRS model is frequently contradicted in minerogenic marshes. In Barnegat Bay marshes, the sediment inventory of excess $^{210}\text{Pb}$ is comparable to the theoretical inventory supported by the regional atmospheric flux, suggesting that tidal supply of $^{210}\text{Pb}$ is minimal (Velinsky et al., 2011).

Age-depth relationships predicted by the CIC and CRS $^{210}\text{Pb}$ models were in agreement (Figure 3c), suggesting that the accretion rate at site BB1 has been roughly constant over the past century. The CRS model is particularly sensitive to sediment compositional changes that influence the cumulative inventory of excess $^{210}\text{Pb}$, and this explains minor divergences between the CRS and CIC models where the core changes from rooted to non-rooted muddy peat. Considering the different assumptions associated with $^{210}\text{Pb}$ modeling and $^{137}\text{Cs}$ chronology, the concordance of the methods for core BB1 indicates that the sediment column is unmixed and stratigraphically complete.

5.2 Pb concentrations

Comment [ak2]: But it's actually CIC that agrees with the $^{137}\text{Cs}$ depth.
Four features of historic U.S. Pb production and consumption (Figure 4a) are recognized in BB1 (Figure 2c; Table 1). Prior to AD 1935, U.S. consumption of Pb was equal to primary production. Pb production and consumption increased dramatically in the second half of the 19th century, although some anthropogenic Pb was released to the atmosphere much earlier in North America (Heyl et al., 1959) and Europe (Rosman et al., 1997). During this period inefficient furnaces and smelting coupled with development of taller stacks caused large amounts of Pb to be released to the atmosphere (Nriagu, 1998).

National Pb production increased from an annual average of 15,703 tons between AD 1830 and AD 1871 to 106,218 tons in AD 1881 (Figure 4a). The pronounced increase in Pb concentration at 33 ± 3 cm in BB1 represents this onset of large-scale, national Pb production and consumption. To accommodate uncertainty in establishing the timing of this change we assigned the sample a date of AD 1875 ± 5 years. The vertical uncertainty reflects difficulty in attributing the start of a trend to a specific sample (those at 35, 33 or 31 cm could represent this event). U.S. Pb production peaked in AD 1925 (620,913 tons) and consumption peaked in AD 1928 which is recorded at 21 cm in BB1 with an estimated uncertainty of ± 5 years.

The period from AD 1933 to AD 1962 was characterized by lower Pb production (average 319,244 tons annually). Coincident with the Great Depression, Pb consumption declined from 683,655 tons in AD 1930 to 378,024 in AD 1932 (Figure 4a). However, it had recovered to 952,544 tons in AD 1941. This divergence between production and consumption was a consequence of increasing consumption of secondary and imported Pb. A minimum Pb concentration at 17 cm in BB1 was interpreted as corresponding to
the consumption decline and assigned a date of AD 1935 ± 6 years. A second peak in Pb production (602,253 tons) and consumption (1,450,976 tons) occurred in AD 1974, since when it followed a declining trend. Peak Pb concentration in BB1 at 9 cm was assigned a date of AD 1974 ± 5 years.

5.2 Pre-AD 1920 stable Pb isotopes

Prior to the 1920s, the principal source of anthropogenic Pb released to the atmosphere was industrial activity. Between AD 1830 and AD 1870 most U.S. Pb (average 79% ± 17%, 1σ) was sourced from the Upper Mississippi Valley (UMV) Pb and Zn district (Figure 4b), principally in Illinois, Iowa and Wisconsin where it was smelted close to mines (Heyl et al., 1959). Three features of historic UMV Pb production are recognized in BB1 (Figure 2c; Table 1). UMV ores are distinctive because of their unusual isotopic composition with high (1.3 to 1.5) $^{206}$Pb/$^{207}$Pb values (Heyl et al., 1966; Doe and Delevaux, 1972; Heyl et al., 1974). Changes in $^{206}$Pb/$^{207}$Pb measured in BB1 likely record changes in UMV Pb production because of the location of Barnegat Bay relative to this source and prevailing winds which carried UMV lead to regions north and south of New Jersey (Marcantonio et al., 2002; Lima et al., 2005b) as well as to Bermuda (Kelly et al., 2009). Therefore $^{206}$Pb/$^{207}$Pb measurements in New Jersey salt-marsh sediments can potentially be used as chronostratigraphic markers. Dates ascribed to depths in core BB1 using Pb concentrations are stratigraphic constraints on the timing of $^{206}$Pb/$^{207}$Pb changes (Figure 2). Samples below 43 cm show variability but do not represent anthropogenic Pb inputs because these samples have background Pb concentrations. Sb concentrations confirm that changes associated with UMV Pb production took place.
before the widespread use of automobiles because vehicles are a major source of anthropogenic Sb.

UMV Pb production increased rapidly between AD 1824 (301 metric tons) and AD 1830 (5,416 metric tons) (Heyl et al., 1959). We assigned the initial increase in measured \(^{206}\text{Pb}:^{207}\text{Pb}\) at 41 cm a date of AD 1827 ± 5 years to correspond with the start of UMV Pb production. Peak production (approximately 25,000 metric tons annually) occurred from AD 1845 to AD 1847 (Heyl et al., 1959). Peak \(^{206}\text{Pb}:^{207}\text{Pb}\) in BB1 was at 34 cm (± 2 cm). Measured \(^{206}\text{Pb}:^{207}\text{Pb}\) peaks in sediment may better reflect maximum proportional contribution than maximum absolute production (in tons) because this is the time when dilution of the UMV signal from other sources is minimal. UMV Pb made its maximum relative contribution to national production in AD 1857 and AD 1858. Therefore the peak at 34 cm was assigned a date of AD 1857.

Production of Pb in the UMV declined during the late 19\(^{th}\) century from 47% of national output in AD 1871 to less than 5% by AD 1878. It had fallen to AD 1827 levels by the middle of the AD 1880s and by AD 1895 to 1905 average annual production was 180 tons annually equating to <1% of national production. We assigned a date of AD 1880 ± 20 years to this decline. Identifying its effect on measured \(^{206}\text{Pb}:^{207}\text{Pb}\) in BB1 is challenging; a minimum occurred at 21 cm although the decline to background values (approximately 1.207) occurred at 26 cm. This is further complicated by rapidly increasing national production which masks and overprints changes in the UMV. We assigned the sample at 23 cm a date of AD 1880 ± 20 years with an added vertical range.
of ± 3 cm to capture the uncertainty described. Disassociation of these changes with Sb concentrations suggests that they were not caused by emissions from automotive transport and occurred prior to AD 1920. Although absolute production of UMV Pb increased during the 20th century (e.g. World War One) it did not exceed 1.5% of the national total.

Following isotopic analysis of other potential sources including coal and Pb from other regions, they concluded that this change corresponded to historical Pb production in the UMV. Marcantonio et al. (2002) showed that Chesapeake Bay estuarine sediments deposited in the middle of the 19th century had a broad, shallow $^{206}\text{Pb}:{^{207}\text{Pb}}$ peak (Figure 5a). Great Lake sediments dated using $^{210}\text{Pb}$ and pollen had peak anthropogenic $^{206}\text{Pb}:{^{207}\text{Pb}}$ in AD 1883 in Erie, AD 1863 in Michigan and AD 1895 in Ontario (Graney et al., 1995). In Florida, a core of peat dated using $^{210}\text{Pb}$ and $^{14}\text{C}$ did not show significant increase in $^{206}\text{Pb}:{^{207}\text{Pb}}$ during the 19th century (Kamenov et al., 2009). Annually-banded corals provide an independently dated archive of historical Pb deposition (Shen and Boyle, 1987). At John Smith’s Bay (Bermuda), $^{206}\text{Pb}:{^{207}\text{Pb}}$ increased from 1.187 in AD 1826 to 1.211 in AD 1854, which was attributed to UMV Pb production (Kelly et al., 2009). In Rhode Island, (Lima et al., 2005b; Lima et al., 2005a) identified an increase in measured $^{206}\text{Pb}:{^{207}\text{Pb}}$ from 1.211 (AD 1815) to 1.325 (AD 1842) in lake sediments dated using varve counting confirmed by $^{210}\text{Pb}$ with $^{137}\text{Cs}$ peaks (Figure 5a). They concluded that differences among timing of mid 19th century $^{206}\text{Pb}:{^{207}\text{Pb}}$ maximums are caused by problems with age models and that the peaks actually represent simultaneous deposition of UMV Pb. Differences in the magnitude of $^{206}\text{Pb}:{^{207}\text{Pb}}$ peaks were proposed to reflect
mixing of multiple, spatially variable Pb sources (Lima et al., 2005b). For example, prevailing winds caused less UMV Pb to be deposited in the Chesapeake Bay than in New England and to have been absent in Florida. Consequently, Lima et al. (2005a) proposed that three chronological horizons (initiation, peak and decline) associated with deposition of UMV Pb could be identified in sedimentary archives in the northeastern U.S. (Figure 5). These horizons narrow the chronological hiatus between radiocarbon and \(^{210}\text{Pb}\) accumulation histories.

5.3 Post-AD 1920 stable Pb isotopes

Two \(^{206}\text{Pb} : ^{207}\text{Pb}\) features associated with leaded gasoline are recognized in BB1. Leaded gasoline was a significant source of anthropogenic Pb following its introduction in AD 1923 (Facchetti, 1989; Nriagu, 1990). Peak U.S. production occurred in AD 1970 (exceeding 250,000 tons annually; Figure 4c). Following the Clean Air Act (AD 1970) consumption of leaded gasoline declined to 17,000 tons in AD 1988 (Nriagu, 1990). By AD 1993 U.S. Pb emissions from gasoline were 1% of those in AD 1970 (Bollhöfer and Rosman, 2001). Up to two thirds of Pb added to gasoline entered the atmosphere as fine particulate matter that was transported long distances through the atmosphere (Facchetti, 1989). The Pb ore(s) used in gasoline production and released to the atmosphere varied over time and also among regions in the U.S. depending on the mixture used by each manufacturer (Shirahata et al., 1980; Facchetti, 1989; Rosman et al., 1993; Graney et al., 1995), although geological records of Pb deposition and direct measurements of atmospheric Pb isotopes suggest that a regional-scale patterns can be discerned for the northeastern U.S. (Marcantonio et al., 2002).
From the introduction of leaded gasoline until the mid-1960s, \( ^{206}\text{Pb}:{^{207}\text{Pb}} \) values declined slightly as non-radiogenic Pb was added to gasoline (Lima et al., 2005b). Direct measurements of the isotopic composition of gasoline or atmospheric emissions are sparse for this period. The ALAS model (Hurst, 2000) suggests that \( ^{206}\text{Pb}:{^{207}\text{Pb}} \) in gasoline declined from 1.175 in the 1920s to 1.145 in the mid-1960s (Figure 5c). These values are in agreement with atmospheric measurements for eastern North America and California of 1.15 in AD 1967 (Shirahata et al., 1980; Rosman et al., 1993). In Rhode Island lake sediments, Lima et al. (2005a) reported a decline from 1.197 in AD 1922 to 1.190 in AD 1964 (Figure 5b). Similarly, sediments from the Chesapeake Bay (core MD) showed a \( ^{206}\text{Pb}:{^{207}\text{Pb}} \) decline from 1.207 in AD 1898 to a minimum of 1.193 in AD 1956. Coral records from Bermuda showed no trend in isotopic ratio (Kelly et al., 2009). Decreased \( ^{206}\text{Pb}:{^{207}\text{Pb}} \) from 19 cm to 11 cm in BB1 (Figure 2d) was caused by the introduction (and dominance until the mid 1960s) of leaded gasoline with a relative constant isotopic signature of 1.165 (Hurst, 2000; Lima et al., 2005b). This had the effect of diluting other contributions resulting in the minima of 1.185 at 11cm in BB1. We assigned this \( ^{206}\text{Pb}:{^{207}\text{Pb}} \) minimum a date of AD 1965 ± 5 years (Table 1; Figure 2d and 6a).

After approximately AD 1965, \( ^{206}\text{Pb}:{^{207}\text{Pb}} \) ratios in gasoline increased (Figure 5) because Pb ores from Missouri were increasingly used (Graney et al., 1995; Hurst, 2000). Shirahata et al. (1980) showed an increase in measured atmospheric \( ^{206}\text{Pb}:{^{207}\text{Pb}} \) from 1.15 in AD 1967 to 1.23 in AD 1977, whilst the averaged record of Rosman et al. (1993)
showed a U.S. aerosol peak of 1.22 in AD 1980. Peak $^{206}\text{Pb}:^{207}\text{Pb}$ in Greenland snow occurred between AD 1972 and AD 1984 (Rosman et al., 1993). Since the decline of leaded gasoline, no clear regional pattern of changing $^{206}\text{Pb}:^{207}\text{Pb}$ values has emerged and records show variability since AD 1980 (Figure 5). The $^{206}\text{Pb}:^{207}\text{Pb}$ peak in BB1 at 7 cm was given a date of AD 1980 ± 5 years (Table 1; Figure 6). The sedimentary record from Rhode Island showed a $^{206}\text{Pb}:^{207}\text{Pb}$ rise from 1.192 in AD 1966 to a peak of 1.205 in AD 1981 (Lima et al., 2005b). In the Chesapeake Bay, $^{206}\text{Pb}:^{207}\text{Pb}$ values increased from 1.197 in AD 1967 to a peak of 1.204 in AD 1981. Bermudan corals show a pronounced increase in $^{206}\text{Pb}:^{207}\text{Pb}$ between AD 1964 (1.174 and 1.183 at John Smith’s Bay and North Rock respectively) and AD 1977 (1.191 and 1.205).

5.4 Development of age-depth profiles for BB1

We used the nine samples with ages estimated from Pb concentrations or $^{206}\text{Pb}:^{207}\text{Pb}$ (Table 1) as the input for an age-depth model (Figure 6). In addition, year of core collection (AD 2009) was added as a surface data point (0-1 cm depth), but was not specified as a fixed constraint. The sample at 34 cm was assigned a date of AD 1857 ± 5 years in favor of when the UMV made its maximum proportional contribution to national Pb production. Results from $^{210}\text{Pb}$ and $^{137}\text{Cs}$ were not included. Age-depth models use dated samples to provide downcore age estimates with sample-specific uncertainty at 1 cm intervals. We applied the “Clam” model of (Blaauw, 2010) executed in R and using a locally weighted spline. Model age uncertainties (2σ) ranged from 4 to 15 years with an average of 8 years. The Clam model estimates an approximately linear rate of sediment accumulation in core BB-1 since AD 1827 (lowest date), although a period of slightly
reduced sedimentation is predicted between approximately AD 1910 and AD 1940 (Figure 6b). The age-depth model developed using CIC $^{210}$Pb accumulation lies within the 95% confidence interval of the Clam model at all depths. This agreement suggests that $^{210}$Pb accumulation histories developed from high salt-marsh peat are accurate.

5.5 Implications for dating the onset of accelerated sea-level rise in salt marsh sediments

Accelerated sea-level rise recorded by tide gauges is often reported as occurring at approximately AD 1920 (Church and White, 2006). Reconstructions of RSL from salt-marsh sediment can extend instrumental histories and resolve the timing of this important change if adequate chronologies can be developed. The nine, regional, chronostratigraphic markers recognized in salt-marsh sediment from New Jersey using Pb concentrations and stable Pb isotopic ratios help meet the need for a dating technique in the hiatus between $^{14}$C and $^{210}$Pb. These markers dating back to AD 1827 are of fixed age and unaffected by the moving, 100 year window limitation of $^{210}$Pb. In the near future tide-gauge records will span a longer interval than can be resolved using $^{210}$Pb. Indeed, some tide-gauge records in the northeastern U.S. already exceed 100 years (e.g. New York City, Philadelphia and Baltimore). Therefore concentrations and isotopic ratios of Pb are useful to use salt-marsh sediment to bridge the gap between instrumental and geological records of RSL change.

6 Conclusions

Reconstructions of sea-level rise from salt-marsh sediments span the interval between long term geological and recent instrumental records. Anthropogenic Pb emissions
preserved in salt-marsh sediment can be used as chronologic markers. Changing
downcore Pb concentrations from a salt marsh in New Jersey, USA reflected prominent
Stable Pb isotopes transported by prevailing winds correlated with production in the
Upper Mississippi Valley where Pb ores have an unusual and distinctively high
\[^{206}\text{Pb} : {^{207}\text{Pb}}\text{ ratio (AD 1827, 1857 and 1880). Changes in leaded gasoline are recognized}
at AD 1965 and 1980. These markers meet the need for geochronological horizons in the
radiocarbon plateau of the last 400 years and also extend and independently corroborate
accumulation histories derived from \[^{210}\text{Pb}]. Use of Pb concentrations and stable isotopes
to date salt-marsh sediment helps extend high resolution sea-level reconstructions beyond
the instrumental period of tide-gauge measurements and more precisely identify when
modern rates of rise began.

Acknowledgements

Funding for this study was provided by NICRR grant DE-FC02-06ER64298, National
Science Foundation award EAR-0951686 and NOAA grant NA11OAR4310101 (to B.
Horton) and New Jersey Department of Environmental Protection Grant SR-0111 (to D.
Velinsky and C. Sommerfield). C.H. Vane and S. Chenery publish with permission of
the Executive Director of British Geological Survey. This research was supported by
Earthwatch Institute Student Challenge Award Programs. Kemp thanks a post-doctoral
fellowship at the Yale University Climate and Energy Institute. This paper is a
contribution to IGCP project 588 “Preparing for coastal change” and PALSEA.
Figure Legends

Figure 1: Location of the Barnegat Bay study site in New Jersey, USA. Core BB1 has the geographic coordinates 40° 01.793’ N, 74°04.797’W

Figure 2: Downcore measurements of stable Pb concentrations in Core BB1. (A) Gravimetric dry-bulk density. (B) Organic matter mass content estimated by loss on ignition (LOI). (C) Concentration of Pb (closed circles, black line) and Sb (open circles, grey line). (D) Measured ratio of $^{206}$Pb to $^{207}$Pb.

Figure 3: Downcore activity profiles of $^{210}$Pb and $^{137}$Cs. (A) Profile of excess $^{210}$Pb with a fitted exponential curve and the accretion rate ($S$) computed following Eq. 1 in the text. (B) Profile of $^{137}$Cs showing an activity peak presumed to be concordant with AD 1963-1964, and the accretion rate based in the age-depth relationship. Analytical uncertainty is smaller than symbol. (C) Age depth models developed for core BB1 using the $^{210}$Pb CIC and CRS models. See text for description.

Figure 4: Historical records of Pb production and consumption. (A) U.S. Pb primary production and consumption. Data from the USGS Lead Statistical Compendium (AD 1830 to AD 1990) and the USGS Minerals Yearbook (AD 1991 to AD 2008). Vertical grey bands labeled A-D mark historic features used to assign ages to Pb concentrations in BB1. (B) Pb production from Upper Mississippi Valley ores (solid line from (Heyl et al., 1959), also shown as a percentage of the U.S. total (grey diamonds, right axis). Vertical
Figure 5: Records of \( ^{206}\text{Pb}:^{207}\text{Pb} \) changes through time. (A, B) Historic fluctuations in \( ^{206}\text{Pb}:^{207}\text{Pb} \) preserved in river basin (Pettaquamscutt, RI) and estuarine (Chesapeake Bay) sediment cores and in annually-banded corals (Bermuda). Chronological control in each case was from an independent dating method such as varve or band counting, \( ^{210}\text{Pb} \) or pollen changes of known age. Changes in \( ^{206}\text{Pb}:^{207}\text{Pb} \) were not used as a dating technique. (C) Historic record of \( ^{206}\text{Pb}:^{207}\text{Pb} \) in US leaded gasoline and atmospheric measurements. The Anthropogenic Pb ArchaeoStratigraphy (ALAS) model (dashed line) is reproduced from (Hurst, 2000). Data points are atmospheric measurements of \( ^{206}\text{Pb}:^{207}\text{Pb} \) from locations in the USA (and in particular the northeast) reported by (1) (Rosman et al., 1993) (2) (Shirahata et al., 1980) (3) (Sturges and Barrie, 1987) (4) (Bollhöfer and Rosman, 2001). Vertical grey bands show inferred ages (H and I) for BB1 at AD 1965 and 1980.

Figure 6: Age-depth estimates for core BB-1. (A) Downcore changes in Pb concentration (open circles) and \( ^{206}\text{Pb}:^{207}\text{Pb} \) ratios (filled squares) were used to assign dates to specific depths on the basis of documented changes in national Pb production and consumption and the contribution of Upper Mississippi Valley Pb with its unusual isotopic signature. Isotopic changes at 34 cm could reflect maximum absolute production in the Upper Mississippi Valley (AD 1846) or maximum proportional contribution (AD
1857), both are shown for comparison. Dashed grey line shows age-depth relationship from a constant initial concentration (CIC) model of $^{210}$Pb accumulation that is supported by peak $^{137}$Cs activity (grey square). It is restricted to the upper 27 cm of the core because at lower depths excess $^{210}$Pb did not exceed analytical error. Vertical error bars represent sample thickness and uncertainty in selecting a single sample to assign an age to. Horizontal error bars represent uncertainty in assigning features in the historic record of Pb production an age, in most cases $\pm$ 5 years was used. (B) Age-depth model produced by “Clam” (Blaauw, 2010) using the nine horizons assigned ages based on changes in Pb concentration and $^{206}$Pb:$^{207}$Pb ratio and the known age of the surface. A date of AD 1857 was used at 34 cm. The model was developed a locally-weighted spline function. Grey error band is the 95% confidence interval for estimated ages (solid line). CIC accumulation model developed from $^{210}$Pb and $^{137}$Cs is shown as a dashed grey line.
## Table 1

<table>
<thead>
<tr>
<th>Year</th>
<th>Type</th>
<th>Description</th>
<th>Depth in BB1 (cm)</th>
<th>Age Error (yrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1875 Pb concentration</td>
<td>Start of national Pb production</td>
<td>33 ± 3</td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td>1925 Pb concentration</td>
<td>Peak in national Pb production</td>
<td>21 ± 1</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td>1935 Pb concentration</td>
<td>Minimum in national Pb production and consumption</td>
<td>17 ± 1</td>
<td>6</td>
</tr>
<tr>
<td>D</td>
<td>1974 Pb concentration</td>
<td>Peak in national Pb production</td>
<td>9 ± 1</td>
<td>5</td>
</tr>
<tr>
<td>E</td>
<td>1827 206Pb:207Pb</td>
<td>Start of UMV Pb production</td>
<td>41 ± 1</td>
<td>5</td>
</tr>
<tr>
<td>F</td>
<td>1857.5 206Pb:207Pb</td>
<td>Peak contribution by UMV</td>
<td>34 ± 2</td>
<td>5</td>
</tr>
<tr>
<td>G</td>
<td>1880 206Pb:207Pb</td>
<td>Decline of UMV Pb production</td>
<td>25 ± 3</td>
<td>20</td>
</tr>
<tr>
<td>H</td>
<td>1965 206Pb:207Pb</td>
<td>Gasoline minimum</td>
<td>11 ± 1</td>
<td>5</td>
</tr>
<tr>
<td>I</td>
<td>1980 206Pb:207Pb</td>
<td>Gasoline peak</td>
<td>7 ± 1</td>
<td>5</td>
</tr>
</tbody>
</table>

Ages assigned to samples in core BB1 using measured lead concentrations and 206Pb:207Pb ratios in comparison with historical U.S. and Upper Mississippi Valley (UMV) lead production and consumption. Age error is an estimate of the uncertainty of identifying a specific date in historical records and is a minimum of 5 years to include a lag between Pb production and deposition. Depth has an uncertainty for sample thickness (±1 cm) and in some instances is larger because age horizons could be associated with a range of adjacent samples.
References


and varve chronologies validate record of 137Cs released by the Chernobyl accident.

Geochimica et Cosmochimica Acta 69, 1803-1812.

Eglinton, T.I., 2005b. High-resolution historical records from Pettaquamscutt River
basin sediments: 2. Pb isotopes reveal a potential new stratigraphic marker. Geochimica
et Cosmochimica Acta 69, 1813-1824.

Marcantonio, F., Zimmerman, A., Xu, Y., Canuel, E., 2002. A Pb isotope record of mid-
Atlantic US atmospheric Pb emissions in Chesapeake Bay sediments. Marine Chemistry
77, 123-132.

2007. The use of 'bomb spike' calibration and high-precision AMS C-14 analyses to date
salt-marsh sediments deposited during the past three centuries. Quaternary Research 68,
325-337.

McCaffrey, R.J., Thomson, J., 1980. A record of accumulation of sediment and trace
metals in a Connecticut salt marsh. In: Saltzman, B. (Ed.), Estuarine physics and

Recent chronologies for tree rings and terrestrial archives using 14C bomb fallout


Nriagu, J.O., 1990. The rise and fall of leaded gasoline. The Science of The Total

Nriagu, J.O., 1998. PALEOENVIRONMENTAL RESEARCH: Enhanced: Tales Told in

vertical marsh accretion in a southern New England tidal salt marsh. Estuarine, Coastal
and Shelf Science 47, 419-429.


Nriagu, J.O. (Ed.), The biogeochemistry of lead in the environment. Elsevier, Amsterdam,
pp. 285-393.

Isotopic evidence for the source of lead in Greenland snows since the late 1960s. Nature
362, 333-335.

from Carthaginian and Roman Spanish Mines Isotopically Identified in Greenland Ice
Dated from 600 B.C. to 300 A.D.â€. Environmental Science & Technology 31, 3413-
3416.


Schaele, B.K., Patterson, C.C., 1981. Lead concentrations in the northeast Pacific:
54, 97-116.


Figure 2

[Graph showing data and legend: mud, salt marsh peat, rooted salt marsh peat, with symbols and lines indicating concentration and depth]