



# A millennial-scale record of Pb and Hg contamination in peatlands of the Sacramento–San Joaquin Delta of California, USA



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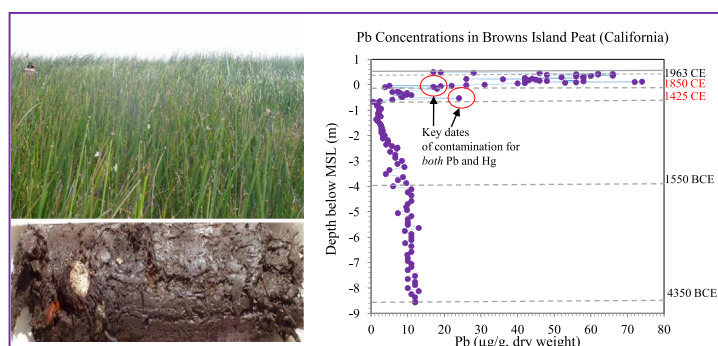
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## HIGHLIGHTS

- Micro-tidal peats were used to trace Pb and Hg contamination through the millennia.
- Anthropogenic Pb and Hg were first evident in California in ~1425 CE.
- Pb isotopes suggest early contamination may be from ore smelting in China.
- Pb ( $74 \mu\text{g g}^{-1}$ ) and Hg ( $990 \text{ ng g}^{-1}$ ) levels peaked during the California Gold Rush.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this paper, we provide the first record of millennial patterns of Pb and Hg concentrations on the west coast of the United States. Peat cores were collected from two micro-tidal marshes in the Sacramento–San Joaquin Delta of California. Core samples were analyzed for Pb, Hg, and Ti concentrations and dated using radiocarbon and  $^{210}\text{Pb}$ . Pre-anthropogenic concentrations of Pb and Hg in peat ranged from  $0.60$  to  $13.0 \mu\text{g g}^{-1}$  and from  $6.9$  to  $71 \text{ ng g}^{-1}$ , respectively. For much of the past  $6000+$  years, the Delta was free from anthropogenic pollution, however, beginning in ~1425 CE, Hg and Pb concentrations, Pb/Ti ratios, Pb enrichment factors (EFs), and HgEFs all increased. Pb isotope compositions of the peat suggest that this uptick was likely caused by smelting activities originating in Asia. The next increases in Pb and Hg contamination occurred during the California Gold Rush (beginning ~1850 CE), when concentrations reached their highest levels ( $74 \mu\text{g g}^{-1}$  Pb,  $990 \text{ ng g}^{-1}$  Hg; PbEF = 12 and HgEF = 28). Lead concentrations increased again beginning in the ~1920s with the incorporation of Pb additives in gasoline. The phase-out of lead additives in the late 1980s was reflected in changes in Pb isotope ratios and reductions in Pb concentrations in the surface layers of the peat. The rise and subsequent fall of Hg contamination was also tracked by the peat archive, with the highest Hg concentrations occurring just before

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1963 CE and then decreasing during the post-1963 period. Overall, the results show that the Delta was a pristine region for most of its ~6700-year existence; however, since ~1425 CE, it has received Pb and Hg contamination from both global and regional sources.

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## 1. Introduction

Peatlands form slowly over thousands of years, incorporating organic and inorganic materials into their peat soils, which reflect ambient conditions at the time of formation (Clymo, 1983; Turner et al., 2001). Some peatland types, such as bogs, typically contain a small fraction of inorganic sediment (<5%, Shotyk, 1996a), while other peatland types, such as tidal freshwater marshes, may contain over 50% inorganic sediment (Drexler et al., 2009a). A body of research has been built on the premise that atmospheric contaminants within the peat profile, if well preserved and accurately dated, can be used as archives of atmospheric emissions (Shotyk, 1996b). For this reason, peatlands have been used widely as historic archives of atmospheric contamination from metals such as lead (Pb) and mercury (Hg) (e.g., Shotyk, 1996a,b; Shotyk et al., 1998, 2002a,b; Weiss et al., 1999, 2002a,b; Martínez-Cortizas et al., 1999, 2002; Klaminder et al., 2003; Biester et al., 2003, 2006, 2007, 2012; Kylander et al., 2010).

Bogs have long been the preferred peatland type for establishing histories of metal contamination because they are generally classified as ombrotrophic (solely atmospherically fed) at the surface and at depth (Shotyk, 1996b). Even if these conditions are met, however, it is important to note that such an approach still includes several key assumptions. First of all, the assumption of ombrotrophy may not hold for all bogs, because, depending on their hydrogeology, raised bogs may be subject to occasional groundwater discharge (Siegel and Glaser, 1987). Furthermore, once deposited, it is assumed that most minerals held within the acidic bog peat, with the exception of calcite and apatite, are resistant to weathering (Le Roux et al., 2006; Smieja-Król et al., 2010). However, exceptions to this, such as chemical weathering of alkali feldspars by bacteria, can be found in the literature (Bennett et al., 1996). Another important assumption is little to no mobility of metals subsequent to deposition. Plentiful evidence exists for the effective immobility of Pb and Hg in bog and minerotrophic peat, due to the strong affinities of these metals to organic matter (e.g., Shotyk, 1996b; Benoit et al., 1998; Martínez-Cortizas et al., 1999, 2002; Weiss et al., 2002a,b; Novak et al., 2011). However, such immobility in peat may not always be assured as both Pb and Hg can become associated with dissolved organic matter and be subsequently lost from the system via leaching and runoff (Urban et al., 1990; Bindler and Klaminder, 2006).

Another assumption, which may prove particularly difficult to demonstrate, is that the peat archive is generally stable through time and that mineralization and humification cause little change in the chemical content of the peat (Biester et al., 2012). It is well known that during periods of seasonal or extended drought, the water table in a bog can drop precipitously, changing ambient conditions in the peat from anaerobic to aerobic status. Such a transformation can greatly increase rates of decomposition, resulting in mass loss of carbon through mineralization and large changes in the particle density of the remaining peat as organic matter oxidizes and decomposes (Rausch et al., 2005; Biester et al., 2012). This sequence of events can ultimately result in the concentration of elements within surface layers of peat or even the loss of some elements via surface and subsurface drainage (Tipping et al., 2003).

Minerotrophic (fen) peats are generally assumed to be inferior to ombrotrophic peats as archives of metal contamination because of their groundwater inflows and the metals contained therein, which can conflate the signal from atmospheric contamination (Shotyk, 1996b). However, the steady groundwater flows, which give rise to minerotrophic peatlands, may also serve to stabilize hydrologic

conditions, thus preserving the peat structure through time. Several studies have shown that fens can successfully be used as archives for particular elements (e.g., Cu and Zn; Shotyk, 1996b; Pb; Espi et al., 1997; Weiss et al., 1999; Monna et al., 2004). These studies demonstrate that, if the concentration of the contaminant is very low in the pre-anthropogenic record, then the anthropogenic component of the contaminant will clearly dominate the total budget, allowing for successful tracking through time (Weiss et al., 1999).

This same line of reasoning can be applied to using tidal marsh peats and coastal sediments as archives of atmospheric metal contamination. In these systems, contaminants may be delivered from the greater watershed as well as from the atmosphere. For this reason, flux calculations of Pb or Hg may not be possible from the record; however such studies can be instrumental in establishing the onset and pattern of contamination in a region. Other complicating factors in coastal systems, including the possibility of bioturbation, sediment resuspension, and/or early diagenetic changes, must also be considered (Alfonso et al., 2001; Leorri et al., 2014). Bioturbation of peat is little discussed in the archive literature even though it is a possibility in all peatland types. The impact of sediment resuspension and early diagenetic changes on peat archives depends strongly on the particular chemical species involved and the stability of redox conditions as changes in redox can liberate certain chemical species into the water column (Farmer, 1991; Spencer et al., 2003). Fortunately, researchers working in coastal systems have largely overcome these problems by carefully cross-comparing their results to ombrotrophic archives and/or using multi-proxy approaches. For example, Elbaz-Poulichet et al. (2011) established a 3500-year record of Hg and Pb contamination in the Pierre Blanche Lagoon of southern France and then cross-compared their results to a variety of other records in Europe. In addition, Alfonso et al. (2001) used salt marsh peat to establish a 5700-year contamination history in the Gironde estuary in southwest France. To dispel any doubt on the integrity of their archive, they cross-checked dates of particular events or periods of high Pb contamination with other available archives. Serrano et al. (2011, 2013) studied sediment cores from seagrass (*Posidonia oceanica*) mats on the Iberian Peninsula to show the history of Hg, Pb, Cu, As, Zn, and other metals over a period of four millennia. They demonstrated that the peaks in their chronologies were coincident with increases in metal use during the Greek and Roman empires and the Industrial Revolution, and they cross-compared their Hg seagrass mat record to peat and sediment archives from the same region. Finally, Leorri et al. (2014), working in a salt marsh in northern Spain, used Pb concentrations, Pb isotopes, and polycyclic aromatic hydrocarbons (PAHs) to establish a 700-year record of combustion-derived pollution. They justified their approach by citing the minimal mobility of Pb in sediments, the strong correlation between PAHs and Pb, and the similarity of their Pb profile to previously published records.

The literature thus demonstrates that non-ombrotrophic peatlands can be quite useful as archives of metals such as Pb and Hg. This is particularly important for expanding research into geographic areas that may not contain ombrotrophic peatlands. Here we provide the first record of millennial patterns of Pb and Hg concentrations on the west coast of the United States. Because no bogs exist in California due to the semi-arid climate, we chose to study peats from micro-tidal freshwater marshes at the landward end of the San Francisco Estuary called the Sacramento–San Joaquin Delta (hereafter, the Delta) (Fig. 1). Our main goal was to chronicle the transition from a largely pristine watershed to one highly impacted by Hg and Pb contamination during and after the California Gold Rush (Holmes et al., 1915; Schuster et al., 2002; Flegal et al., 2010).

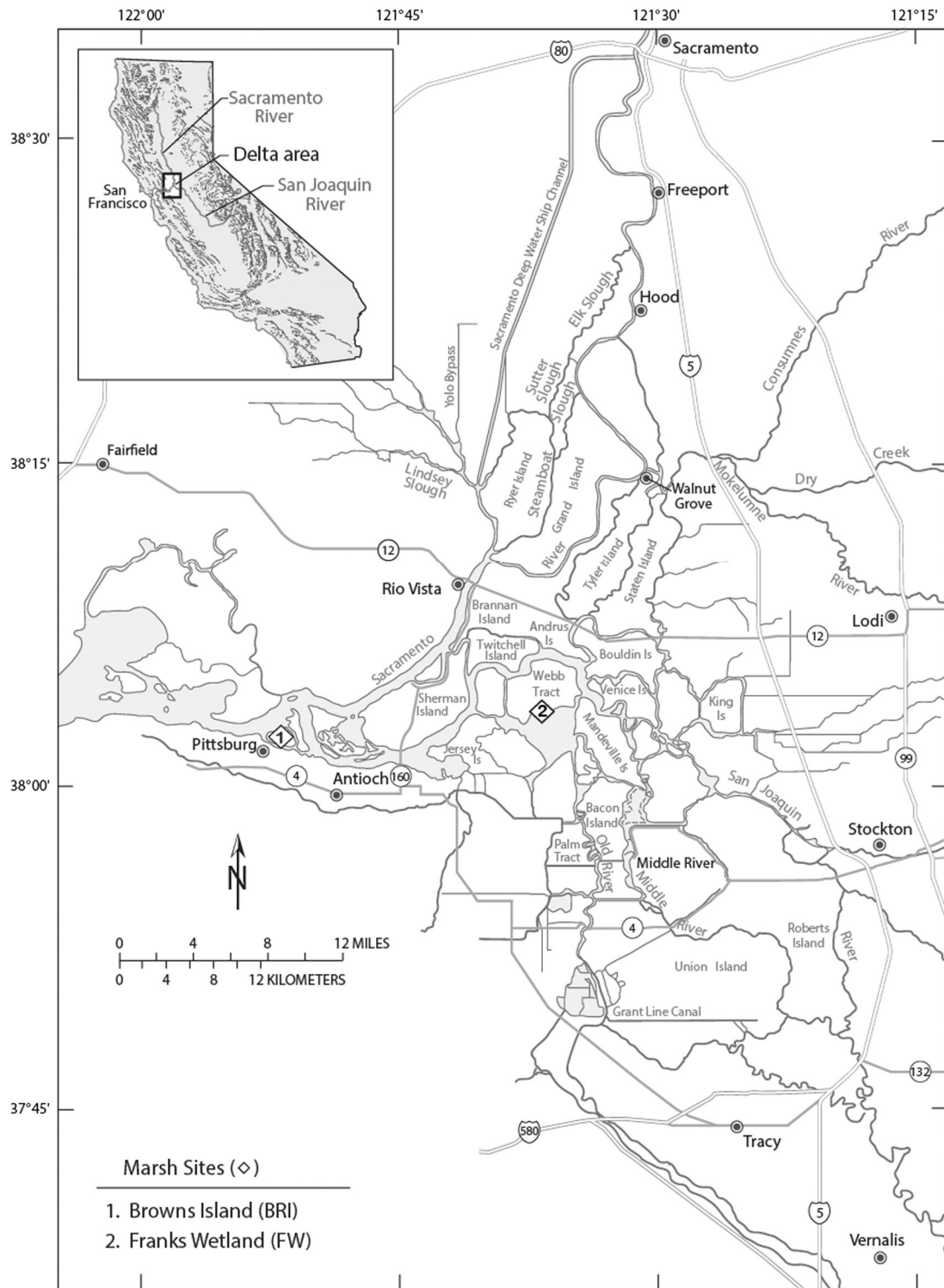


Fig. 1. Map showing Browns Island (BRI) and Franks Wetland (FW) in the Sacramento–San Joaquin Delta and inset map of California, USA.

## 2. Materials and methods

### 2.1. Site description

The Delta is part of a 163,000 km<sup>2</sup> watershed, bounded by the Sierra Nevada and Cascade Ranges of California (Cloern et al., 2011). It was once a 1400 km<sup>2</sup> micro-tidal peatland region that began forming approximately 6800 years ago (Drexler et al., 2007). The region receives runoff from more than 40% of the land area of California (California

Department of Water Resources, 1995) (Fig. 1). Tides in the Delta are semidiurnal and micro-tidal with a normal tidal range of approximately 1 m (Shlemon and Begg, 1975; Atwater, 1980). The climate of the region is characterized as Mediterranean with cool winters and hot, dry summers (Atwater, 1980). Mean annual precipitation is approximately 36 cm, but actual yearly precipitation varies from half to almost four times this amount. More than 80% of precipitation occurs from November to March and most freshwater inflow to the Delta occurs from January to June because of storage in the snowpack and releases



from reservoirs (Knowles, 2002). Beginning in the mid-1800s, the Delta was almost entirely drained for agriculture (Thompson, 1957; Atwater, 1980), resulting in its current configuration of more than 100 islands and tracts surrounded by 2250 km of man-made levees and 1130 km of waterways (Prokopovich, 1985). Islands that have been drained and farmed have experienced up to 8 m of land-surface subsidence (Deverel and Leighton, 2010).

Two remnant, relatively undisturbed marshes from contrasting hydrogeomorphic settings were chosen for this study. The first site, Browns Island (BRI), is a slightly brackish micro-tidal marsh situated at the confluence of the Sacramento and San Joaquin Rivers (Fig. 1). The second site, Franks Wetland (FW), is a micro-tidal freshwater marsh, sheltered by natural breakwaters and situated along a tributary of the San Joaquin River (Fig. 1). The peat at BRI is relatively high in inorganic sediment (~60% throughout the past 6300 years), whereas FW has a much lower inorganic sediment content (~28% over the past 5400 years) (Drexler et al., 2009a). In the past 150+ years, the level of inorganic sediment increased in the surface layers of these two sites due to the legacy of hydraulic gold mining during the California Gold Rush (Drexler et al., 2009a, 2013a). Regardless, the two sites still fall under the definition for organic soil (peat) or histosols (USDA, 2015), which requires greater than 12 to 18% organic carbon depending on the particular clay content and greater than half of the upper 80 cm of the soil profile containing such organic material.

Marsh vegetation in the Delta is dominated by emergent macrophytes and scrub-shrub wetland species. At BRI vegetation is dominated by *Schoenoplectus americanus* (American bulrush) and *Distichlis spicata* (salt grass). Vegetation on FW is dominated by *Cornus sericea* (red osier dogwood) and *Salix lasiolepis* (arroyo willow) and the coring site has a large population of *Athyrium filix-femina* (western lady fern). All botanical nomenclature follows Hickman (1993).

## 2.2. Coring and sample handling

Peat cores measuring 5 cm in diameter were collected during 2005 using a Livingstone corer, as described by Drexler et al. (2007, 2009a). The BRI core was 922 cm long. The FW core was 718 cm, however, only the first 608 cm were used because of a section of age reversals between 620 and 718 cm (Drexler et al., 2009b). At the BRI site, the top 50 cm of the core was excavated manually (in a 50 × 50 × 50 cm monolith) from the marsh surface due to a great presence of root material. The rest of the core was retrieved from the same exact location with the corer. Prior to analyses, cores, samples, and subsamples were stored at or below 5 °C. Sampling for determination of bulk density and loss on ignition (LOI) was done at 2-cm intervals, with continuous sampling in the top and bottom ~100 cm of each core and sampling approximately every 10 cm in the mid-core (Drexler et al., 2009b; Drexler, 2011). Duplicate analyses of LOI were run for approximately 10% of the samples and the average variability was 0.7%.

## 2.3. Dating by $^{14}\text{C}$ , $^{137}\text{Cs}$ , and $^{210}\text{Pb}$

Radiocarbon ( $^{14}\text{C}$ ) analyses were done on both cores at the Lawrence Livermore National Laboratory using accelerator mass spectrometry (AMS) methods, as previously described by Drexler et al. (2009a). Fruiting bodies or achenes (*Schoenoplectus* spp.) recovered from the peat cores were chiefly used as these macrofossils are considered to be the most reliable materials available (Drexler et al., 2009a). Radiocarbon dates from the BRI and FW cores (Table A1) were used to create spline-fit age-depth models for each core profile using the statistical approach of Heegaard et al. (2005). The models are considered reliable for peat older than approximately 250 cal years BP (prior to 1700 CE) based on uncertainty analysis.

The activities of  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  in the top 50 cm of the BRI and FW cores were measured in order to date the profiles. Core samples were analyzed using gamma spectroscopy as described in Drexler et al.

(2013b). Both  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  have been used successfully for dating lake sediments and wetland soils (Armentano and Woodwell, 1975; Appleby et al., 1997). The first elevated levels of  $^{137}\text{Cs}$  appeared in the atmosphere and in fallout in the early 1950s, with peak activities occurring at the height of atmospheric nuclear testing in 1963 (Ritchie and McHenry, 1990). A date of 1963 is assigned to the depth interval with the highest  $^{137}\text{Cs}$  activity. For  $^{210}\text{Pb}$  dating, we used the constant flux: constant sedimentation rate model to assign dates to each of the core profiles (Appleby and Oldfield, 1983; Craft and Richardson, 1998).

## 2.4. Trace and major element determinations

Concentrations of trace and major elements in peat were determined at the U.S. Geological Survey laboratory in Boulder, CO, by inductively coupled plasma mass spectrometry (ICP-MS) using a Perkin Elmer Elan Model 6000 and inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Perkin Elmer Optima Model 3300DV. Due to the great length of the cores, 2-cm sections for trace and major element analysis for the BRI core were taken approximately every 2 cm for the first meter, every 6 cm for 1–3 m, and every 12 cm for the rest of the core. This regimen was followed in order to take the most samples during periods of rapid change in metal concentrations, while taking fewer samples during stable periods. For the FW core, samples were taken every 10 cm or less in the top m of the core. Samples deeper in the core were taken at specific depth ranges that corresponded to the main time periods examined (see below) in order to provide comparative information for the BRI core. For each core section, a sub-sample of approximately 100 mg was completely dissolved in an HCl–HNO<sub>3</sub>–HF acid mixture using a microwave total-digestion procedure (Roth et al., 1997; Barber et al., 2003; Hart et al., 2005). The digested samples were diluted at 1:10 (volume:volume, digest:water) with 18 MΩ-cm deionized water and were preserved with triple-distilled HNO<sub>3</sub>, prepared using the method of Kuehner et al. (1972). Aerosols of acidified aqueous samples were introduced into both spectrometers using a high-solids Burgener pneumatic nebulizer. Multiple internal standards (In, Ir, and Rh), which covered the mass range, were used to correct for instrumental drift. Standard reference materials (SRM) from the National Institute of Standards and Technology (NIST) were digested and analyzed with each batch and included NIST SRM 8704 (Buffalo River Sediment) and NIST SRM 2702 (Marine Sediment) for trace and major elements, and NIST SRM 1630a (Trace Mercury in coal) and NIST SRM 1635 (Trace Elements in Coal, subbituminous) for Hg. Additional details regarding the specific analysis techniques, procedures, and instrumental settings for ICP-MS analyses can be found in Garbarino and Taylor (1996) and Taylor (2001); and for ICP-AES in Garbarino and Taylor (1979), Boss and Fredeen (1999), and Hart et al. (2005). Mercury was determined by direct combustion–amalgamation–atomic absorption spectrometry using a Milestone Model DM80 spectrometer following EPA method 7473 (USEPA, 2007).

For all trace and major elements analyzed, concentrations for each sample were determined in triplicate on an aliquot of the digested, freeze-dried, homogenized sample. The mean relative standard deviations (RSD = the standard deviation divided by the average times 100 (%)) for the triplicate analyses of Pb, Hg, and Ti were all <7%. In addition, replicate digestions (n = 21) of separate aliquots were made to test homogeneity of the material and reproducibility of the digestion procedure. The mean RSD values for Pb, Hg, and Ti concentrations were 5%, 19%, and 8%, respectively.

Lead concentrations were normalized to Ti in order to factor out the fluctuating sediment content in the peat contributed by the Sacramento and San Joaquin Rivers (Wright and Schoellhamer, 2005) and to better determine the onset of anthropogenic contamination. Several inorganic proxy elements were tested for normalization (Sc, Ga, Zr, Ti, and Al), but Ti was chosen because it had consistently strong correlations with ash content (Spearman rank coefficient ( $r_s$ ) = 0.90 at BRI and  $r_s$  = 0.97 at FW) and with Pb in the oldest, “pre-anthropogenic” peat in both cores.

## 2.5. Calculation of Pb and Hg enrichment factors

In order to understand the transition of the Delta from a pristine region to one impacted by Hg and Pb contamination, we calculated enrichment factors, EFs, (e.g., Duce et al., 1975; Kylander et al., 2006) as follows:

$$\text{PbEF}_{\text{Reference},X} = (\text{Pb}/X)_{\text{Sample}} / (\text{Pb}/X)_{\text{Reference}} \quad (1)$$

where X is the lithogenic element primarily found in the inorganic fraction of soils and not likely introduced by anthropogenic contamination (Ti in this study). For the BRI profile, the internal reference concentrations were based on the average of 36 samples in the age range from 1550 BCE to 4350 BCE (−4.04 to −8.57 m MSL). For the FW profile, reference concentrations were based on an average of three samples in the age range from 2500 BCE to 3600 BCE (−5.17 to −5.83 m MSL).

## 2.6. Stable Pb isotopes

The isotopic composition of Pb in peat samples was determined at the USGS Isotope Laboratory in Denver, CO, on splits of sample aliquots digested for the ICP determinations. Aliquots were spiked with  $^{205}\text{Pb}$ -enriched isotope tracer (Neymark and Amelin, 2008) followed by purification using anion-exchange columns and loading of Pb salts and silica gel (Gerstenberger and Haase, 1997) on outgassed Re filaments. The Pb isotopic compositions were measured using a multi-collector ThermoFinnigan Triton thermal ionization mass spectrometer (TIMS) in static mode. All Pb isotopes were measured on Faraday-cup detectors with 2 $\sigma$  external error of ~0.1% for  $^{206}\text{Pb}/^{204}\text{Pb}$  and 0.05% for  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$ . A weighted-average Pb blank of  $0.02 \pm 0.01 \text{ ng mL}^{-1}$  was measured by isotope dilution TIMS on eight splits prepared for ICP blanks. Raw Pb-isotope ratios were corrected for spike and blank contributions, and for mass fractionation of  $0.0010 \pm 0.0003$  per mass unit using data for NIST Pb-isotope standards SRM-981 and SRM-982 measured under the same run conditions. Lead concentrations in peat samples determined by ICP-MS and isotope dilution by TIMS were in excellent agreement (Spearman rank correlation coefficient,  $r_s = 0.995$ ).

## 2.7. Statistical analyses

Correlations between parameters that did not have normal or log-normal distributions are described using non-parametric statistics. In these situations, the Spearman rank correlation coefficient ( $r_s$ ) was computed using SigmaPlot, version 11 (Systat Software, Inc., 2008).

All parameters with normal or log-normal distributions were evaluated using linear least-squares regressions with SigmaPlot.

## 3. Results

### 3.1. Determination of peat age

At BRI, the 1963 peak in  $^{137}\text{Cs}$  was observed at 14 cm of depth below land surface (0.373 m MSL) (Table A2). The results were very similar using  $^{210}\text{Pb}$  dating by the constant flux: constant sedimentation method; the mid-section age for this section was assigned the date of 1964.5 (Table A2). At FW, the  $^{137}\text{Cs}$  peak was observed at 24 cm of depth below land surface (0.030 m MSL) (Table A2), which is much deeper than at BRI. The activities of  $^{137}\text{Cs}$  at FW were quite low (all <0.35 pCi/g), suggesting that the noise:signal ratio may have been too high to achieve good results with  $^{137}\text{Cs}$  at this site. Therefore, we relied on  $^{210}\text{Pb}$  dating for FW. The section dated to 1964.5 was found at 13 cm below land surface (0.110 m MSL).

Table 1 contains the key dates used to create a framework for the history of Pb and Hg concentrations in the Delta. These dates were determined from  $^{210}\text{Pb}$  analyses (Table A1) and spline fit models created using radiocarbon analyses of macrofossils from BRI and FW

**Table 1**

Key depths, corresponding dates, and estimated error for the BRI and FW core profiles.

Core	Depth in meters MSL	Date in cal year BP (error estimate <sup>a</sup> )	Date in calendar years	
BRI	0.51 (land surface)		2007 CE	
	0.37		1963 CE	
	−0.16	100	1850 CE (initiation of Gold Rush)	
	−0.65	525 (105)	1425 CE (initiation of "Modern Period")	
	−1.86	1950 (155)	0 CE	
	−2.23	2300 (150)	350 BCE	
	−4.04	3500 (95)	1550 BCE	
	−8.57 (basal peat)	6300 (125)	4350 BCE	
	FW	0.27 (land surface)		2005 CE
		0.11		1963 CE
−0.33		100	1850 CE (initiation of Gold Rush)	
−0.77		525 (125)	1425 CE (initiation of "Modern Period")	
−2.59		1950 (85)	0 CE	
−2.91		2300 (100)	350 BCE	
−4.30		3500 (50)	1550 BCE	
−5.83 (base of datable peat due to inversions)		5550 (125)	3550 BCE	

<sup>a</sup> Total error was estimated using the approach developed by Heegaard et al. (2005).

(Table A1; Drexler et al., 2009a). The surface and basal dates show the timespan that each core represents. The remaining dates bookmark important time periods in the Delta that were used to differentiate pre-anthropogenic from anthropogenic time periods. The onset of anthropogenic contamination was determined by careful study of upticks in Hg and Pb concentrations as well as Pb/Ti ratios (details regarding normalization are found in the next section) in the cores.

### 3.2. Pb and Hg concentrations

At BRI concentrations of Pb were relatively high ( $>15 \mu\text{g g}^{-1}$ ) near the top of the peat column and lower ( $<15 \mu\text{g g}^{-1}$ ) in the older peat at depths greater than approximately −0.5 m MSL (Fig. 2, Table A3). From approximately −4.0 MSL to 0.5 m MSL, there was a decrease in Pb concentrations in the BRI core. This gradual decrease is coincident with a concomitant decrease in bulk density and Ti and an increase in LOI (loss on ignition), demonstrating that during this period the relative organic content of the peat was increasing relative to earlier in the record.

At FW, similar to BRI, concentrations of Pb were also relatively high ( $>15 \mu\text{g g}^{-1}$ ) near the top of the peat column and lower ( $<15 \mu\text{g g}^{-1}$ ) in the older peat at depths greater than approximately −0.5 m MSL (Fig. 3, Table A3). In contrast to the BRI core, there were no long-term increasing or decreasing trends in LOI, bulk density, and Ti in the FW core.

Pb concentrations in the FW profile had a similar pattern to the BRI profile, but values were generally lower both near the surface and at depth (Figs. 2 and 3). There are two time horizons when Pb increased sharply in the BRI profile—one at approximately 1425 CE and another at about 1850 CE. The FW core, which was not subsampled as intensively as the BRI core, only shows a sharp increase at the 1850 CE time horizon. There is a decrease in the Pb concentration of peat in the top ~10 cm of both cores (Figs. 2 and 3), which corresponds to peat formed after 1963 CE.

The vertical distribution of total Hg concentrations at the two study sites was similar to that of Pb, in that the highest concentrations were found in a zone just beneath the shallowest, most recently formed peat (Figs. 2 and 3, Table A3). At depths greater than about 0.5 m below MSL, Hg concentrations were consistently  $<75 \text{ ng g}^{-1}$  at the BRI site and  $<40 \text{ ng g}^{-1}$  at the FW site (Figs. 2 and 3). In contrast, nearly all samples from the top ~60 cm of both profiles had Hg  $>100 \text{ ng g}^{-1}$ .

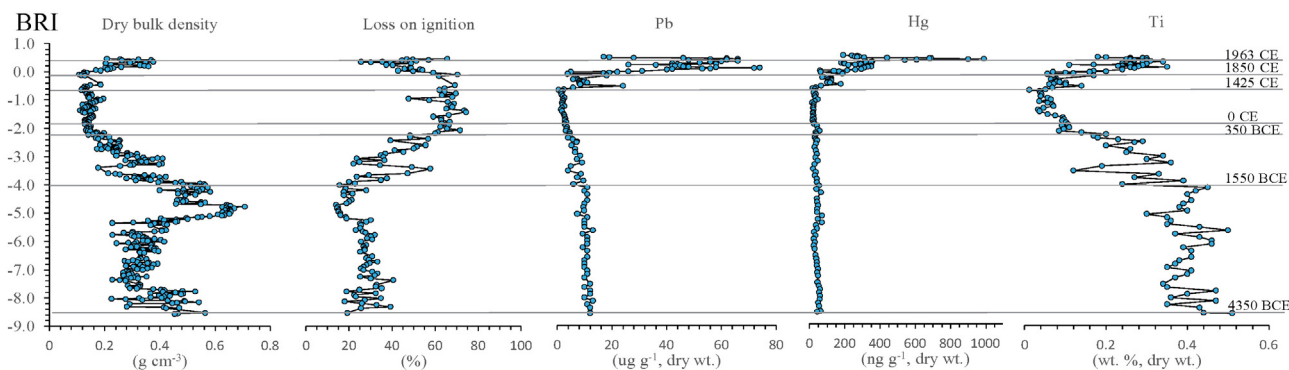


Fig. 2. Dry bulk density, loss on ignition, and Pb, Hg, and Ti concentrations in the BRI core. Land surface is at 0.51 m MSL.

As with Pb, sharp increases in Hg concentration were observed at about 1425 CE and about 1850 CE in the BRI core. The FW core also had sharp upticks at both of these time periods. The highest Hg concentrations (greater than  $400 \text{ ng g}^{-1}$ ) were in peat from 0.15 to 0.07 m MSL, an interval that includes 1963 CE (Fig. 3). Just as for Pb, the patterns in Hg concentrations were similar between the two cores, but the concentrations were greater overall in the BRI core.

3.3. Normalized Pb concentrations

Ti concentrations used to normalize Pb are provided in Table A3. In the BRI core, Pb/Ti values were nearly constant (0.002 to 0.003) in the peat ranging in age from 4350 to 350 BCE (Fig. 4). Peat ranging in age from approximately 350 BCE to 1424 CE showed increasing Pb/Ti values (0.003 to 0.006). The values in the FW core during these pre-anthropogenic time periods were quite similar to that of BRI. The greatest Pb/Ti values occurred in both cores beginning at ~1850 (the start of the California Gold Rush) (Fig. 4b and c). The maximum Pb/Ti values in the FW core were less than half of those in the BRI core. Overall, the Pb/Ti data in the BRI core older than ~1425 CE had Pb/Ti < 0.006, and those younger than 1425 CE had Pb/Ti > 0.006 (Fig. 4a).

Samples in the time period from 350 BCE to 1424 CE had much lower inorganic content (as represented by Ti) than other samples in the BRI profile and plot closer to the origin (Figs. 2 and A1). An examination of the relationship between Ti vs. Pb for BRI revealed that inorganic proxy elements may not provide a clear distinction between anthropogenic and pre-anthropogenic peat at very low concentrations (Fig. A1b).

Analysis of the relationship between Ti vs. Hg at BRI (Figs. 2 and A2) revealed a pattern similar to that of Ti vs. Pb. In peat older than 1425 CE, the ratio Hg/Ti was predominantly  $< 10^{-4}$ , whereas in peat younger than 1425 CE, the ratio was predominantly  $> 10^{-4}$ . At very low concentrations of Hg and Ti, it was difficult to discern the anthropogenic vs. pre-anthropogenic peat samples (Fig. A2b).

3.4. Enrichment factors for Pb and Hg

Maximum values of PbEFs in both the BRI and FW profiles occurred in the time period from 1850 to slightly after 1963 CE (Fig. 5). Maximum PbEF values at BRI ranged from 10 to 12, whereas maximum PbEF values at FW were ~3. Only the BRI core showed an uptick in PbEF at both critical junctures: 1425 CE and 1850 CE. Overall, PbEF values in the FW core were generally lower than those observed at the BRI site and didn't have the level of dramatic increase seen in the BRI core post-1850 CE (Fig. 5a). The most recent PbEF values (post-1963 CE) in both cores had a steadily decreasing pattern, with the top layers having the lowest values.

Values of HgEF were generally greater than those for PbEF at the same site (Fig. 5). At BRI, maximum values of HgEF ranged between 20 and 28 and occurred just before and after 1963 CE. There was an unusual increase to 11 in the BRI HgEF at approximately -1.07 m MSL (with a slight uptick in PbEF as well at this time), which corresponds to approximately 1065 BP (885 CE). Computed HgEF values for the FW site were lower than the corresponding values for the BRI core, similar to the case for PbEF values. Maximum HgEF values at FW (between 7 and 9) were from the period ~1425 to ~1850 CE. In more recent sections of the FW core, HgEF values were all in a relatively narrow range (4 to 6). The most recent peat in the BRI core had a steady decrease in HgEF values after the extremely high value of 28 reached at ~1963 CE.

3.5. Stable isotopes of Pb

The major changes in lead isotopes at BRI (Table A4), shown with a plot of  $^{206}\text{Pb}/^{204}\text{Pb}$  vs. depth/age, occurred at 1425 and 1825 CE (Fig. 6). The variability in Pb concentrations in pre-anthropogenic peat as well as the divergence of the anthropogenic samples into two major linear distributions (1425 to 1849 CE (red triangles) and 1850 to 1962 CE (green squares)) are evident in the plot of  $1/\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  (Fig. 7). In Fig. 8,

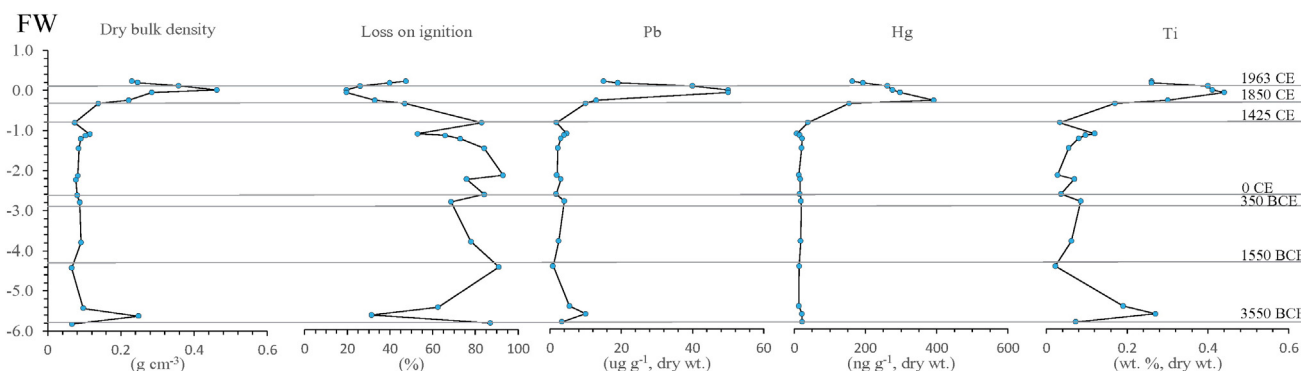


Fig. 3. Dry bulk density, loss on ignition, and Pb, Hg, and Ti concentrations in the FW core. Land surface is at 0.27 m MSL.



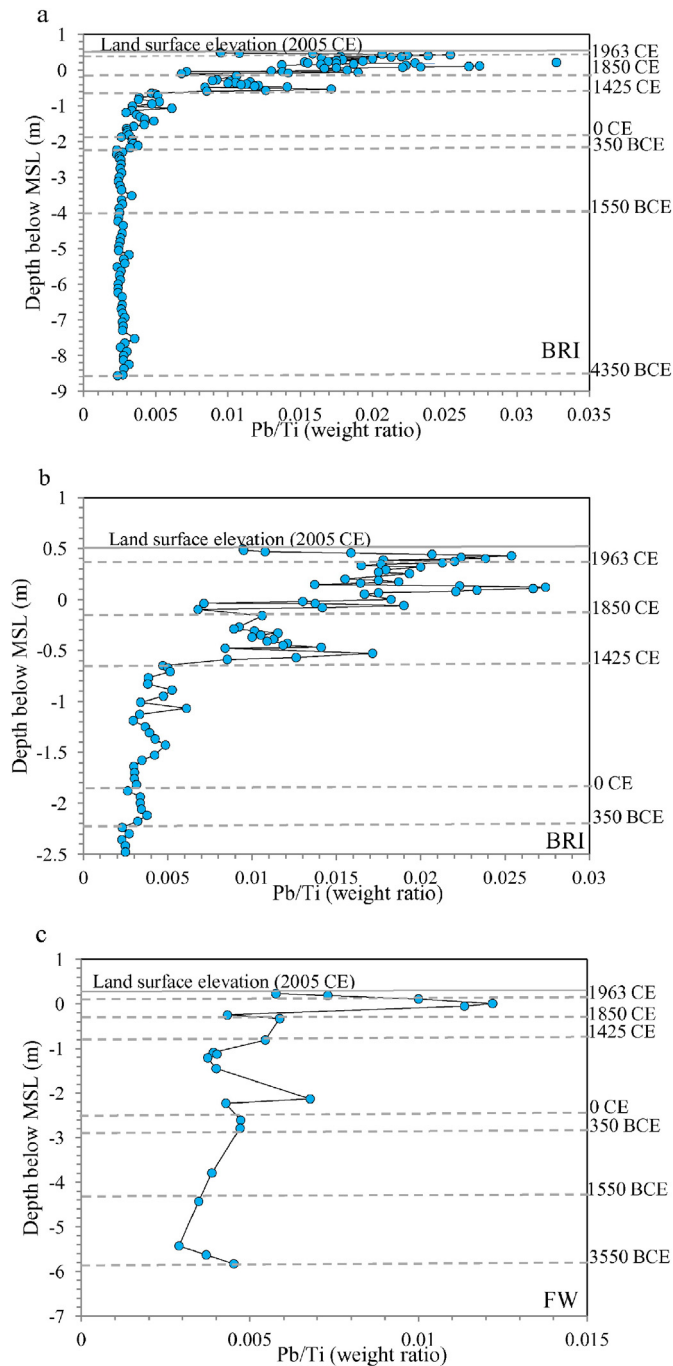


Fig. 4. Pb/Ti ratios for the BRI core (a), the top 2 m of the BRI core (b), and the FW core (c).

all the BRI samples from before 1425 CE plot rather close together. Beginning in 1425 CE, the Pb isotope compositions of BRI samples started to extend out toward less radiogenic values in all plots (indicating anthropogenic influence; Fig. 8). In addition to the BRI samples, potential local (West Shasta Mining District ores from the eastern Klamath Mountains; Fig. 8a) and global sources (a range of ores from China, Fig. 8b and c) of Pb contamination are included in the plots.

A plot of  $^{208}\text{Pb}/^{207}\text{Pb}$  vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  (Fig. 9) provides detailed Pb isotope data from BRI as well as isotopic values of potential local influences from the Gold Rush and onward. The pre-anthropogenic samples from BRI plot very close to previously published data from deep sediment cores from San Francisco Bay (Fig. 9). Samples from 1850–1962 plot near local Cu mining and leaded gasoline from the time period between 1964 and 1979. Three recent samples (1963 CE and younger) have

$^{206}\text{Pb}/^{207}\text{Pb}$  values between 1.2004 and 1.2082, which fall near values for leaded gasoline from the 1980s (Fig. 9).

#### 4. Discussion

The extensive peats in the Delta provide a unique archive of Hg and Pb contamination on the west coast of the United States. Unlike Europe, in which anthropogenic Pb contamination began ~2000–3500 years before present (Shotyk et al., 1998; Alfonso et al., 2001; Martínez-Cortizas et al., 2002; Baron et al., 2005; Bindler and Klaminder, 2006; Kylander et al., 2006), the Delta has been a region free from metal pollution for much of the past ~6700 years since its formation. The following sections provide an explanation of the major trends in Hg and Pb contamination through time in the Delta.

##### 4.1. Pre-anthropogenic period

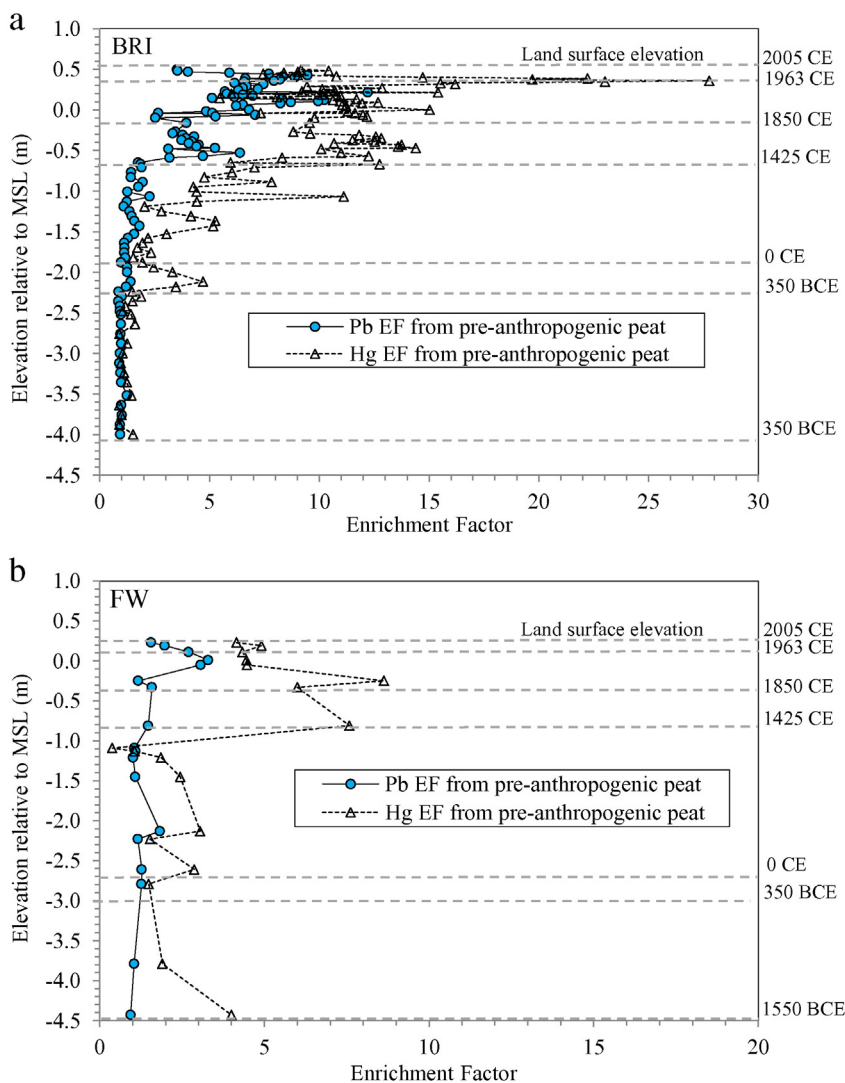
At BRI and FW from 4350 BCE to 1424 CE (pre-anthropogenic period), Pb and Hg concentrations were not only low but also quite stable (Figs. 2 and 3). Pb concentrations ranged from 0.60–13.0  $\mu\text{g g}^{-1}$  (Figs. 2 and 3), which is in between pre-anthropogenic concentrations measured in Chinese lake archives (15–18  $\mu\text{g g}^{-1}$ ; Lee et al., 2008) and European peats (0.10–0.78  $\mu\text{g g}^{-1}$ ; Shotyk et al., 1998, 2001; Klaminder et al., 2003; Le Roux et al., 2004). Pre-anthropogenic Hg concentrations at BRI and FW ranged from 6.9 to 71  $\text{ng g}^{-1}$  (Figs. 2 and 3), which is comparable to pre-anthropogenic concentrations in southern Ontario (13–35  $\text{ng g}^{-1}$ ; Givélet et al., 2003) and Europe (~10–50  $\text{ng g}^{-1}$ ; Roos-Barraclough et al., 2002).

##### 4.2. Initiation and source(s) of anthropogenic influence

At approximately 1425 CE, upticks appeared in Pb and Hg concentrations, Pb/Ti ratios, PbEFs, and HgEFs in the BRI profile, signaling the onset of detectable anthropogenic contamination (Figs. 2–5). In addition, the Pb isotope signatures of the BRI core also began to trend toward less and less radiogenic values starting at ~1425 CE (Figs. 6–8), another sign of anthropogenic influence. The linear relationship between  $1/\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  shows that, starting in 1425 CE, the natural Pb component began to mix with a source having a higher Pb concentration and lower  $^{206}\text{Pb}/^{204}\text{Pb}$  value (Fig. 7). Due to less frequent sampling intervals and lower overall Pb and Hg concentrations in the FW profile compared to the BRI profile, the ~1425 CE uptick can only be seen in Hg concentrations and HgEFs in the FW core (Figs. 2, 3, and 5). Nevertheless, the overall pattern of contamination in the FW profile mirrors that of BRI. The HgEFs at BRI have additional peaks prior to ~1425 CE: one at approximately 1065 CE (–1.07 m MSL) and one at 840 CE (–0.89 m MSL). These two earlier peaks in HgEFs may be related to eruptions of the Medicine Lake Volcano in northern California in  $885 \pm 90$  CE (Little Glass Mountain) and  $1065 \pm 40$  CE (Glass Mountain) (Donnelly-Nolan et al., 1990).

Plots of both Pb and Hg vs. Ti enabled us to identify thresholds for determining anthropogenic contamination (Pb/Ti values  $> 0.006$  and Hg/Ti  $> 1 \times 10^{-4}$ ; Figs. A1 and A2). This approach was generally highly effective at identifying anthropogenic Pb and Hg, *except* at very low concentrations of Hg, Pb, and Ti when this approach led to misleading results (Figs. A1b and A2b), likely due either to some Pb and Hg incorporated into the organic fraction of the peat or incomplete combustion in the LOI process.

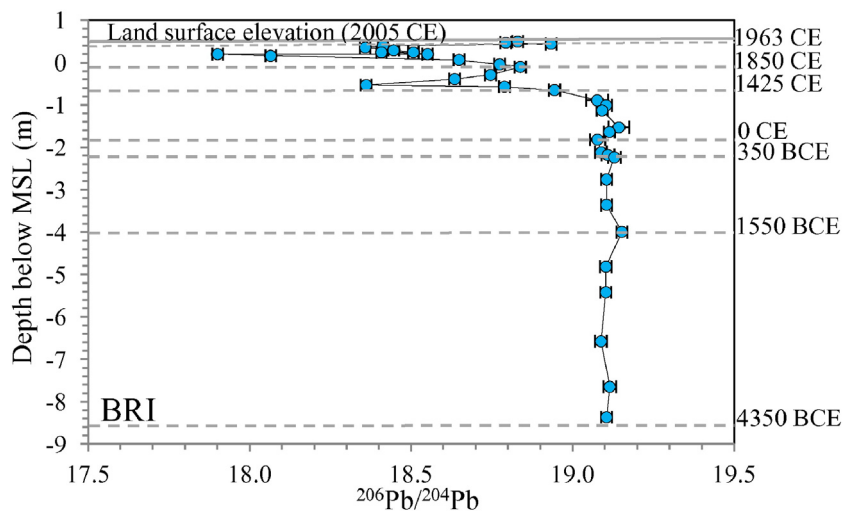
The provenance of anthropogenic Pb and Hg contamination in California beginning at ~1425 CE has yet to be established. We investigated the Pb isotope signatures of ores from the West Shasta Mining District in the eastern Klamath Mountains of California (Doe et al., 1985), which are located in the northwestern boundary of the Sacramento–San Joaquin watershed, but found no ores that fall along a two end-member mixing line with BRI samples (Fig. 8(a)). To our knowledge, there are no other obvious local anthropogenic sources from



**Fig. 5.** Pb and Hg enrichment factors (EFs) at (a) BRI and (b) FW. The mean Pb/Ti and Hg/Ti ratios of pre-anthropogenic peat in both BRI (from 1550 BCE to 4350 BCE) and FW (from 2500 BCE to 3600 BCE) were used as reference materials in calculating the EFs.

that period of time. The Spanish influence in California, which certainly included smelting, did not begin until 1775 (Starr, 2005). Increased biomass burning by native populations has previously been suggested as

possible source of heightened local metal concentrations in peat (Givelet et al., 2003); however, not only were there no notable increases in charcoal in the western US during this time (Marlon et al., 2013), but



**Fig. 6.**  $^{206}\text{Pb}/^{204}\text{Pb}$  vs. depth/age for the BRI profile. Error bars = 1 sd.



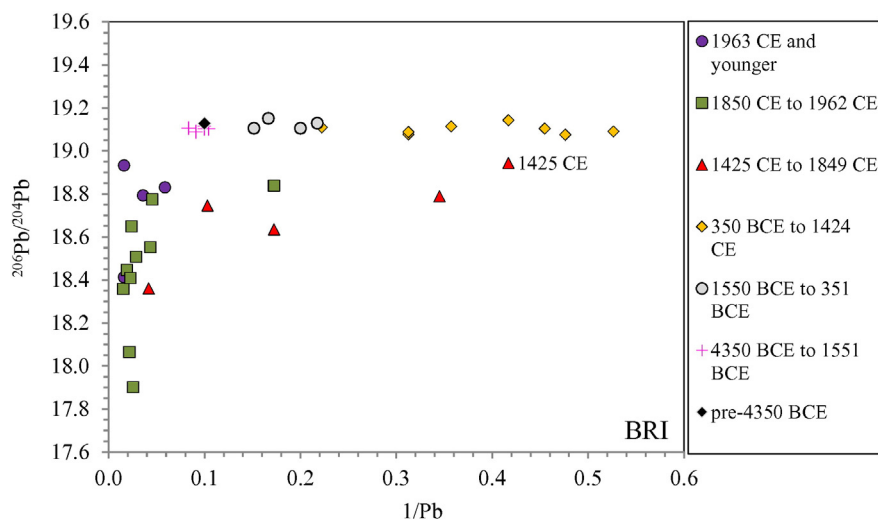


Fig. 7. Plot of  $1/\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  for the BRI profile.

biomass burning cannot explain the *less* radiogenic (anthropogenic) Pb isotope data in the BRI cores starting at  $\sim 1425$  CE (Figs. 6–9). This leaves global sources of Hg and Pb contamination including coal burning and smelting in Europe, Asia, Mexico, and South America. Prevailing winds in the San Francisco Estuary are westerly to north-westerly throughout the year (Conomos et al., 1985). If it is assumed that prevailing wind patterns between  $\sim 1425$  and 1849 CE were similar to the present (Barron et al., 2003), occasional southerly winds were likely insufficient for significant transport of Hg and Pb contamination from Mexico or South America to California. Europe is extremely distant and Delta peats do not contain the well-established peaks during Greek and Roman times found throughout European peatlands (e.g., Shotyk et al., 1998, 2001; Roos-Barraclough et al., 2002; Klaminder et al., 2003). For these reasons, an Asian source (China, Japan, and/or Korea) of contamination appears likely.

Long-range dispersal at the scale of thousands of kilometers may initially seem more appropriate for Hg, due to its 0.5–2 year atmospheric residence time, than for Pb aerosols, whose maximum dispersal is usually  $< 500$  km (Kylander et al., 2010). However, recent research has demonstrated that long-range transport of Hg and Pb contamination from Asia to the west coast of the US (including the San Francisco Bay area) can occur in as little as 10 days (Steding and Flegal, 2002; Jaffe et al., 2005; Weiss-Penzias et al., 2006, 2007; Diaz-Somoano et al., 2009; Ewing et al., 2010). Thus, it is quite feasible that the anthropogenic Pb and Hg found in the peat beginning at  $\sim 1425$  in the Delta originated in Asia and is related to smelting and/or coal burning.

The use of coal, which contains both Hg and Pb, began in China around 350 BCE and has continued to the present (Thomson, 2003; Dastoor and Larocque, 2004). However, coal is unlikely to be the source of contamination at BRI, because average values of Chinese coal are between  $\sim 2.467$ – $2.479$  for  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $\sim 1.172$  to  $1.183$  for  $^{206}\text{Pb}/^{207}\text{Pb}$  (Mukai et al., 2001; Flegal et al., 2013), a range that does not fall on a two-end member mixing line with BRI samples from 1425 to 1849 CE (Fig. A3).

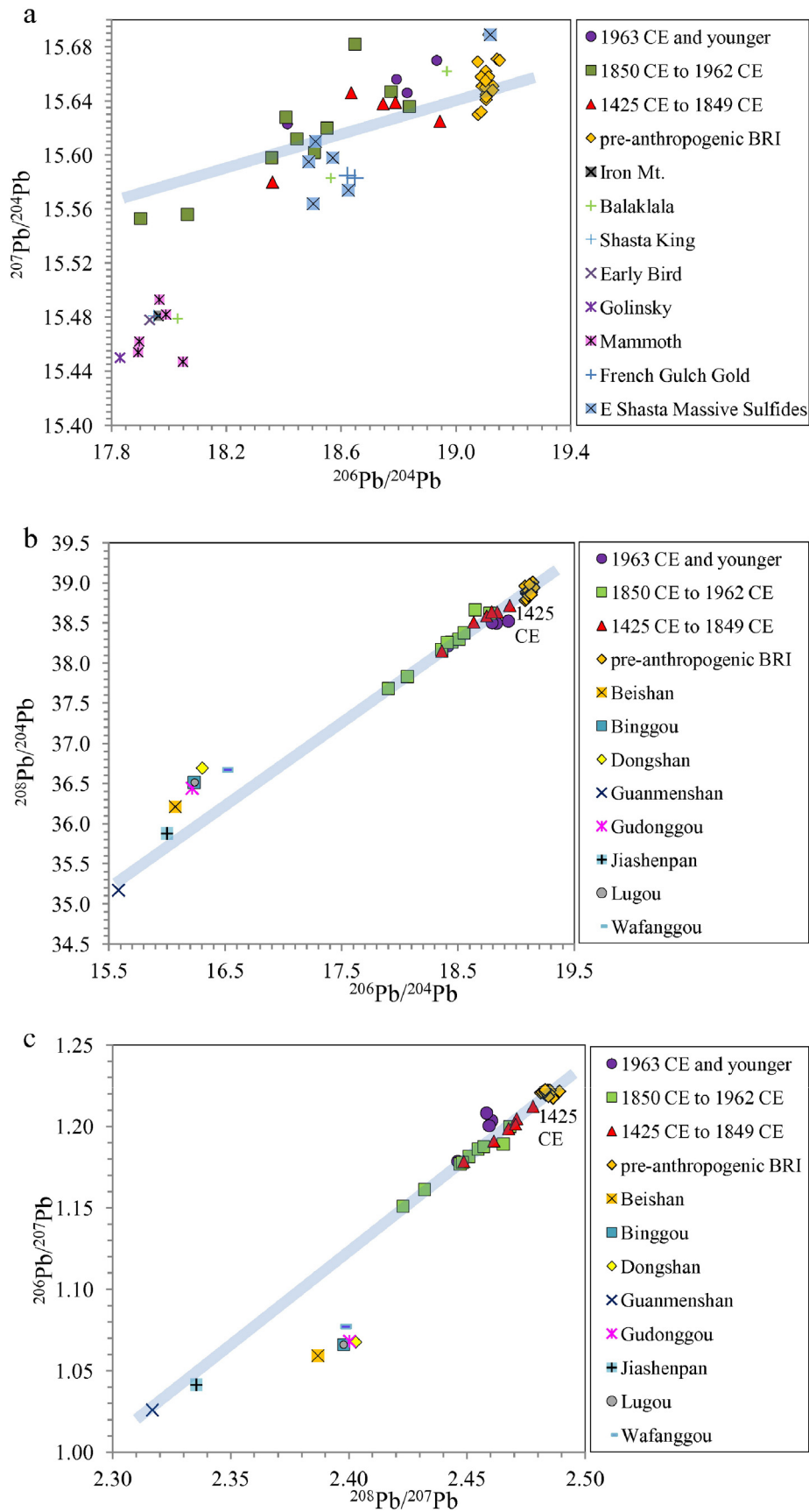
With regard to smelting, Lee et al. (2008), who studied a 7000-year sediment record from Liangzhi Lake in Hubei province in China, identified a period of increased Cu and Pb smelting for weapons and tools (dubbed the “modern period”) that began at approximately  $\sim 1370$  CE  $\pm 120$  years. This “modern period” in China is consistent with the onset of anthropogenic Pb and Hg in the Delta ( $1425$  CE  $\pm 105$  years and  $\pm 125$  years, respectively, for BRI and FW). We examined the Pb isotope signatures of a variety of Chinese ores to determine whether any could potentially be the source of contamination at BRI

(Zhu, 1995; Sangster et al., 2000; Dodson et al., 2009; Ferrat et al., 2012). We found two deposits, amongst a range of Chinese ore data in Sangster et al. (2000), which fall along a two end-member mixing line with pre-anthropogenic BRI samples: (1) a sedimentary-exhalative deposit from Jiashenpan, Inner Mongolia and (2) a Mississippi Valley-type deposit from Liaoning Province, China (Fig. 8b and c; Table A5). Therefore, for the above reasons, the source of early Pb and Hg contamination could very well be from China. However, due to the lack of data from throughout Asia, it is not currently possible to *definitively* assign provenance to this first instance of Pb and Hg contamination in the Delta.

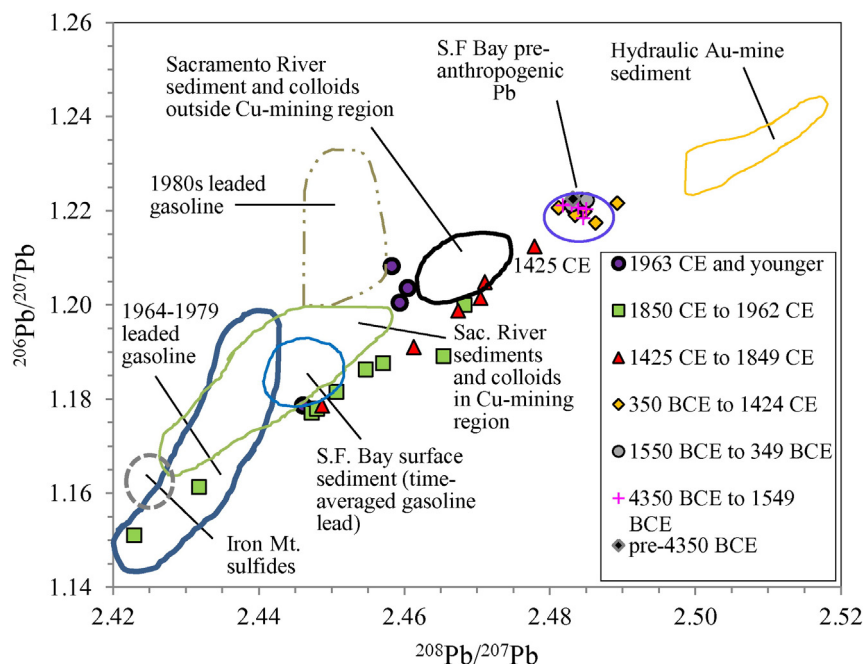
#### 4.3. The California Gold Rush period to 1962 CE

In this study, dramatic increases in Hg and Pb concentrations, Pb/Ti and Hg/Ti values, and EFs were used to establish the onset of the California Gold Rush period (Figs. 2–5). In addition, Fig. 7 demonstrates a transition to very high Pb concentrations with highly variable  $^{206}\text{Pb}/^{204}\text{Pb}$  during this time period. The peak Pb and Hg concentrations at BRI for this period were  $74 \mu\text{g g}^{-1}$  and  $990 \text{ ng g}^{-1}$ , respectively. Metal contamination stemming from the Gold Rush has previously been documented in benthic sediments in the San Francisco Estuary (Hornberger et al., 1999; Bouse et al., 2010) as well as Lake Tahoe and other smaller lakes in the Sierra Nevada (Heyvaert et al., 2000; Sanders, 2007).

The specific sources of Hg and Pb contamination can be traced to the mining practices of the time. Prior to the early 20th century, Hg was used extensively to amalgamate fine gold in both placer and hard-rock gold mining operations (Alpers et al., 2005). An estimated 4.5 million kg of Hg was lost to rivers of California, mostly in the Sierra Nevada (Churchill, 2000; Alpers et al., 2005). Some of this load was transported through the Delta to the San Francisco Bay, where elevated Hg concentrations have been noted in sediments deposited after 1850 CE (Fuller et al., 1999; Hornberger et al., 1999). With respect to Pb, several possible sources related to mining and smelting in northern California exist including auriferous tertiary gravels mobilized during the hydraulic mining period, Pb aerosol fallout from the Selby smelter in Pittsburg, CA (operational between 1885–1971), and mine drainage and sediment from sulfide copper–zinc deposits of the West Shasta mines near Redding, CA (Holmes et al., 1915; Gilbert, 1917; Rabinowitz and Wetherill, 1972; Flegal et al., 2010). During its operation, the Selby smelter processed ores, scrap, and bullion from several states as well as foreign sources with the relative proportion of these varying through time, thus precluding clear identification of a Pb isotope signature from this source (Rabinowitz, 2002). Regardless, Rabinowitz and Wetherill (1972) used Pb isotopes to determine that



**Fig. 8.**  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{207}\text{Pb}/^{204}\text{Pb}$  values of BRI samples and ores from the West Shasta Mining District in the eastern Klamath Mountains of California (in the Sacramento-San Joaquin watershed; data from Doe et al. (1985) and (b)  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{208}\text{Pb}/^{204}\text{Pb}$  and (c)  $^{206}\text{Pb}/^{207}\text{Pb}$  vs.  $^{208}\text{Pb}/^{207}\text{Pb}$  values of BRI samples and select Chinese ores (data from Sangster et al. (2000); Table A5). A wide blue line represents the two end-member mixing line that is required between pre-anthropogenic BRI samples and potential contaminant sources.



**Fig. 9.** Plot of  $^{208}\text{Pb}/^{207}\text{Pb}$  vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  from peat samples in the BRI profile with additional data from Sacramento River and San Francisco Bay sediments (Dunlap et al. (2008) and references therein).

smelter-derived Pb was the dominant Pb source in grasses found within 20 miles downwind from the smelter and that the smelter still contributed a portion of the Pb found in grasses at 30 miles distance. BRI is approximately 18 miles downwind from the Selby smelter and FW is approximately 30 miles. Therefore, the main sources of Pb from 1850 to 1962 CE are likely a combination of Sacramento River sediments/colloids both from inside and outside of the Cu-mining region and aerosols from the Selby smelter (Rabinowitz and Wetherill, 1972; Dunlap et al., 2008; Fig. 9).

The use of alkyl lead in gasoline began in the 1920s and evidence of contamination from this source can be seen in less and less radiogenic values in peat samples (Robert, 1984; Fig. 9). Other studies in the San Francisco Estuary have also found evidence of lead contamination in sediments beginning in the 1930s from the use of alkyl lead additives (Rabinowitz and Wetherill, 1972; Ritson et al., 1999; Dunlap et al., 2000; Steding et al., 2000).

As the impact of the Gold Rush began to decline mid-century, Hg contamination in the Delta was no longer dominated by local sources. Hg concentrations and HgEFs in Delta peats between ~1940–1962 reflect the period of highest global production and industrial emission (Figs. 2, 3 and 5; Engstrom and Swain, 1997; Schuster et al., 2002).

#### 4.4. Post-1963 period

In this period, there was a decline in Pb/Ti values (Fig. 4b) and a shift in Pb isotope compositions, which is consistent with the elimination of alkyl lead additives in U.S. gasoline by the late 1980s (Fig. 9; Steding et al., 2000; Dunlap et al., 2008). The least radiogenic, post-1963 Pb isotope data from BRI are consistent isotopically with leaded gasoline used in the U.S. from 1964 to 1979 CE and are also similar isotopically to Pb in sulfide ore from Iron Mountain, the largest producing copper mine in California (Fig. 9; Dunlap et al., 2008). The three most recent BRI samples appear to contain Pb from both the 1980s leaded gasoline and Sacramento River sediment and colloids outside the Cu-mining region (Fig. 9).

During the post-1963 period, global sources of Hg declined, resulting in decreases in Hg concentrations in Delta peat (Figs. 2 and 3). A reduction in Hg levels in sediment samples from eight stations in the San

Francisco Estuary was also found by Conaway et al. (2007) in a study conducted from 1993 to 2001.

#### 4.5. Comparison of BRI and FW

Beginning in 1425 CE and continuing to the present, BRI had a similar pattern of contamination to FW, however actual values for Hg and Pb concentrations and EFs were quite different. Pre-anthropogenic Pb and Hg concentrations in the FW core were roughly half that of the BRI core (Figs. 2 and 3). During the Gold Rush period, the PbEFs at FW were less than half and the HgEFs were about half of the values at BRI (Fig. 5). This is not surprising as these two marsh sites are situated in contrasting hydrogeomorphic zones (Drexler, 2011). The BRI marsh is situated in a higher energy site at the confluence of the Sacramento and San Joaquin Rivers, whereas the FW site is located in a quiescent tributary of the San Joaquin River behind a natural breakwater. Because of its position, BRI has had a higher and much more variable inorganic sedimentation rate through the millennia than FW (BRI:  $552 (\pm 667)$  g sediment  $\text{m}^{-2} \text{year}^{-1}$  and FW:  $27.0 (\pm 33.1)$  g sediment  $\text{m}^{-2} \text{year}^{-1}$ ; Drexler, 2011). The greater importance of inorganic sediment in peat formation and its variability through time in BRI vs. FW can be seen in the plots of bulk density, loss on ignition and Ti (Figs. 2 and 3). The difference in inorganic sedimentation rates as well as the greater distance of FW from the Sacramento River (which received and carried most Gold Rush sediments) likely led to the differences in contamination levels between the marshes.

## 5. Conclusions

In this study, the peat archive from the Sacramento–San Joaquin Delta of California was used to trace the history of Pb and Hg contamination. Pre-anthropogenic concentrations of Pb and Hg in marsh peat ranged from  $0.60$  to  $13.0 \mu\text{g g}^{-1}$  and  $6.9$  to  $71 \text{ ng g}^{-1}$ , respectively. Anthropogenic Pb and Hg contamination was first identified in ~1425 CE using Hg and Pb concentrations, Pb/Ti ratios, PbEFs, HgEFs, and Pb isotope values. The source of this first instance of Pb and Hg pollution on the west coast of the United States was likely smelting activity in Asia. The next peak in contamination occurred during the California Gold Rush (beginning ~1850 CE), when Hg and Pb contamination

reached its highest levels ( $74 \mu\text{g g}^{-1}$  Pb,  $990 \text{ ng g}^{-1}$  Hg,  $\text{PbEF} = 12$ , and  $\text{HgEF} = 28$ ). Another uptick in Pb contamination occurred when alkyl Pb was first added to gasoline in the ~1920s. The phase-out of Pb additives was reflected in Pb isotope ratios and reductions in Pb concentrations in post-1963 peat. The rise and subsequent fall of Hg contamination was also tracked by the peat archive, with the highest Hg concentrations occurring just before 1963 CE and then decreasing during the post-1963 period. Overall, the results of this study show that micro-tidal peats in the Delta provide a highly useful archive for establishing the onset of anthropogenic contamination and chronicling the transition from a pristine to a polluted watershed.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.01.201>.

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