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

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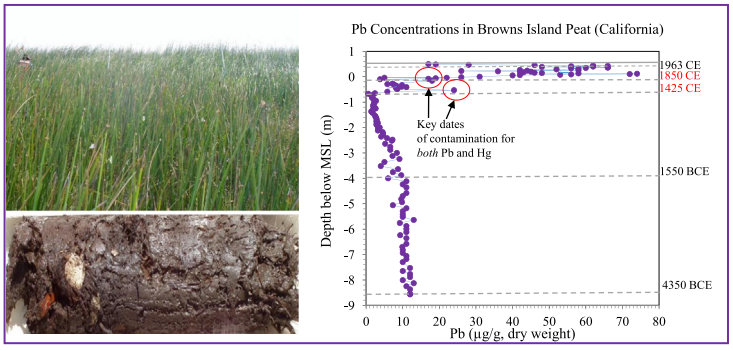
HIGHLIGHTS

- 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 μg g^{-1}) and Hg (990 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}Pb. Pre-anthropogenic concentrations of Pb and Hg in peat ranged from 0.60 to 13.0 μg $g^{-1}$and from 6.9 to 71 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 μg g^{-1} Pb, 990 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).