A 700 year record of combustion-derived pollution in northern Spain: Tools to identify the Holocene/Anthropocene transition in coastal environments

Eduardo Leorri [a,*], Siddhartha Mitra [a], María Jesús Irabien [b], Andrew R. Zimmerman [c], William H. Blake [d], Alejandro Cearreta [e]

[a] Department of Geological Sciences, East Carolina University, Graham Building 103B, Greenville, NC 27858, USA
[b] Departamento de Mineralogía y Petrología, Facultad de Ciencia y Tecnología, Universidad del País Vasco UPV/EHU, Apartado 644, 48080 Bilbao, Spain
[c] Department of Geological Sciences, University of Florida, 241 Williamson Hall, P.O. Box 112120, Gainesville, FL 32611, USA
[d] Consolidated Radioisotope Facility, University of Plymouth, Plymouth, UK
[e] Departamento de Estratigrafía y Paleontología, Facultad de Ciencia y Tecnología, Universidad del País Vasco UPV/EHU, Apartado 644, 48080 Bilbao, Spain

HIGHLIGHTS

- Historic records of atmospheric pollutant emissions in SW Europe are needed.
- PAH and Pb concentrations and ratios from a north Spain salt marsh core were used.
- Atmosphere emissions mainly from regional coal burning increased in the early 1800s.
- Emissions associated with leaded gasoline peaked in 1975 CE.
- The results suggest 1800 CE as the Holocene/Anthropocene transition.

GRAPHICAL ABSTRACT
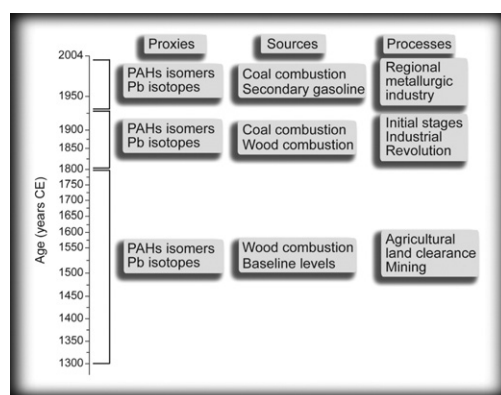
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ABSTRACT

There is an uneven geographical distribution of historic records of atmospheric pollutants from SW Europe and those that exist are very limited in temporal extent. Alternative data source is required to understand temporal trends in human impacts on atmospheric pollution. Polycyclic aromatic hydrocarbons (PAHs), heavy metal content and stable Pb isotopic ratios in a sediment core from a salt marsh in northern Spain were used to reconstruct the regional history of contaminant inputs over the last 700 years. Pre-1800s concentrations of Pb and PAHs represented baseline concentrations, i.e. pre-Industrial, conditions. During the initial stages of the Industrial Revolution, 1800s to 1860s, PAH concentrations increased by a factor of about two above baseline levels in the sediment column. By the 1930s, PAH levels reached ca. 10 times pre-Industrial levels and, along with Pb, reached a peak at ca. 1975 CE. Since then, sedimentary PAH and Pb concentrations decreased significantly. A combination of PAH isomer and Pb stable isotope ratios suggests that the contaminant sources are regional, likely derived partially from wood, but mainly coal used by the metallurgic industry in the Basque country since the 1800s and until the 1970s when leaded petrol saw increased use. This chronology of regional atmosphere-derived pollution

* Corresponding author. Tel.: +1 252 737 2529; fax: +1 252 328 4391.
E-mail addresses: leorrie@ecu.edu (E. Leorri), mitras@ecu.edu (S. Mitra), mariajesus.irabien@ehu.es (M.J. Irabien), azimmer@ufl.edu (A.R. Zimmerman), william.blake@plymouth.ac.uk (W.H. Blake), alejandro.cearreta@ehu.es (A. Cearreta).

expands current southwest Europe emission records and shows coastal salt marsh sediments to be useful in reconstructing the Anthropocene.

1. Introduction

Historical atmospheric pollutant emissions data are very limited for SW Europe and consist of country-specific emission records which are fairly recent (i.e. since the 1970s) (Pacyna et al., 2003, 2007). In the Iberian Peninsula, atmospheric pollutant records have been mainly restricted to cores from high altitude lake sediments (Fernandez et al., 2002) and peat bogs (Martinez-Cortizas et al., 1997, 2002), leaving a very limited understanding of atmospheric emissions at regional scale. The historic patterns of these emissions may also be recorded in coastal salt marsh sediments through integration of the atmospheric and aquatic (watershed) deposition. Coastal wetlands are of great ecological value and rank among the most productive of all natural ecosystems, and coastal areas have been attractive sites for human settlement over several millennia (Perillo et al., 2009). Globally, 1.2 billion people (23% of the world's population) live within 100 km of the coast, and 50% are likely to do so by 2030 Common Era (CE) (Adger et al., 2005), highlighting the critical need to study the historical record of pollutant deposition and storage within coastal sediments. In this context, the study of undisturbed sediment cores offers great potential to reconstruct the history of contamination (Valette-Silver, 1993; Ridgway and Shimmield, 2002). Although interpretation of the obtained data may be challenging due to the complicating effects of sediment re-suspension, early diagenetic reactions or bioturbation (Farmer, 1991; Eggleton and Thomas, 2004), these problems can be overcome by a multi-proxy approach including various indicators such as heavy metals, organic chemicals, radionuclides and Pb isotopic signatures (Kim et al., 2004; Cantwell et al., 2007; Louchouarn et al., 2012).

Pollution sources (e.g., burning of wood, coal, and oil-derivate products) may vary greatly but the atmosphere is the predominant route for combustion derived contaminants, including organic molecules such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals such as Pb (Gallon et al., 2005; Louchouarn et al., 2012). The measurement of PAHs (and their isomer ratios) and Pb stable isotope ratios can yield information about contaminant sources and distribution pathways (Louchouarn et al., 2012). For instance, PAH isomer ratios can be used to differentiate between pyrogenic (combustion) and non-pyrogenic (petrogenic) sources of these compounds (Reddy et al., 2002). Moreover PAH isomer ratios can also be used to indicate the 'fuels' combusted (e.g., coal versus oil-derivate products) (Vane et al., 2011). Likewise, different sources of atmospheric Pb, such as wood burning, fossil fuel combustion or metal smelting, can be identified by their distinct Pb isotopic signatures (Gallon et al., 2005; Sturges and Barrie, 1987). Another advantage of the use of Pb as a proxy is that its stable isotope ratios are minimally altered by physical or chemical processes within the sediments (Gallon et al., 2005). Lead is considered immobile in peat sediments, peat bogs and lake sediments (see Shotyk et al., 1998 and references therein). The few studies which have examined ratios of Pb stable isotopes in conjunction with PAHs in sediments have been successful in identifying the types of fuel that contributed combustion-derived contaminants to the sediment (e.g. charcoal, wood, coke, coal, smelting, gasoline) (Gallon et al., 2005; Louchouarn et al., 2012; Vane et al., 2011). Further, the combination of several proxies allows assessment of the mobility and stability of each proxy within sediment cores (Brandenberger et al., 2008, 2011; Kuo et al., 2011; Louchouarn et al., 2012).

This study aims to produce a reliable sedimentary record of atmospheric pollution from coastal sediments in northern Spain using a multi-proxy approach. Concentrations of a wide range of PAHs and heavy metals were determined in a sediment core collected in the Kanala salt marsh. From this, a 700 year record of combustion-derived inputs for this estuarine area of southwestern Europe was reconstructed, providing a high resolution historical record of the transition from the Holocene (last interglacial, ca. last 11,500 years) to the Anthropocene (sensu Crutzen and Stoermer, 2000) in this region.

2. Materials and methods

2.1. Study site

The study site was selected based on previous sedimentological studies on the Atlantic Iberian coast which have identified zones of consistent and uniform accretion i.e. Kanala salt marsh, Urdaibai estuary, N. Spain (Leorri et al., 2010). The Urdaibai estuary represents the tidal portion of the Oka River, covers an area of 7.65 km^2, and occupies the flat bottom of the 11.6 km long, 1 km wide alluvial valley. The local and regional characteristics have been described elsewhere (Leorri and Cearreta, 2009; Cearreta et al., 2013; Leorri et al., 2013). This area is dominated by detrital sedimentation (mainly silt) with very little autochthonous organic matter (Cearreta et al., 2002b; Leorri et al., 2013), where Al, a proxy for clay minerals, and metal concentrations show a strong linear relationship ($r = 0.85$; Cearreta et al., 2002a). Thus, clays, and not organic matter, likely control heavy metal sorption in these sediments (see also Bradl, 2004). In addition, this estuary is highly valuable from an ecological perspective since it is the most extensive and pristine coastal area in the Basque region and was included within the Biosphere Reserve declared by UNESCO in 1984 CE (Cearreta et al., 2013).

2.2. Sample collection

One core, 39-cm long, was collected in 2004 CE from the Kanala salt marsh (Supporting Information [SI] Fig. 1), located in the mid reaches of the Urdaibai estuary at 4.055 m above local ordnance datum (LOD). Two PVC tubes (12.5 cm diameter) were inserted into the sediment in order to obtain sufficient material to determine grain size, sediment geochemistry (PAHs, elemental analysis, and lead stable isotope ratios), and provide a geochronology. The outmost 2–3 mm of the sediments was removed to minimize contamination from the PVC tube and downcore smearing during coring. The core was described and photographed before being sectioned into 1 cm intervals. Topographic elevation (Leica station; elevation error: ± 0.005 m) was measured, and this information is presented relative to the LOD (lowest tide at the Bilbao Harbour on 27th September 1878). Samples were dried at 40 °C over 24 h and then stored in sealed containers until analyzed. Compaction of the sediment during sampling was considered to be negligible and autocompaction (loss of porosity due to the load of overlying sediments) was considered minimal due to its dominance of detrital sediments (Leorri et al., 2008; Brain et al., 2011). In this study, we assume that sediment re-suspension, early diagenetic reactions and bioturbation minimally affect downcore profiles of the targeted proxies. This is based on the minimal mobility of Pb in sediments (see references above), strong correlation between PAHs and Pb, the similarity of the Pb profile and previously published records (e.g., Leorri et al., 2008) and the strong correlation between Fe (redox sensitive element) and Al ($r^2 = 0.91$) which suggests grain-size control of elemental distributions rather than post-depositional changes.

2.3. Sediment dating

The geochronology of the top 10 cm of the core was calculated from the ^{210}Pb profile using the constant rate of supply method (CRS) (Appleby

and Oldfield, 1978) supported by ^{137}Cs activities and it is presented and discussed elsewhere (Leorri et al., 2010, 2013). Samples for ^{210}Pb and ^{137}Cs were analyzed following the methodology described by Appleby (2001) at the University of Plymouth (UK) Consolidated Radioisotope Facility, using an EG&G Ortec planar (GEM-FX8530-S N-type) HPGe gamma spectrometry system built to ultra-low background specification for ^{210}Pb detection (see Leorri et al., 2013). Additional information is provided in the SI Text and results are presented in SI Table 1. This core presented an unsupported [210]Pb ([210]Pb$_{xs}$) inventory of 6846 ± 416 Bq m^{-2} slightly greater than the average for the Basque coastal region (ca. 5806 ± 200 Bq m^{-2}; Cearreta et al., 2013; Leorri et al., 2013), had an exponential decay profile that suggested a constant sediment accumulation rate in the upper section (ca. 100 years), and did not show any signs of major mixing or disruption of the sedimentation. In order to extend the chronology downcore, two samples (at 24 and 38 cm depth) were carbon-14 dated by accelerator mass spectrometry-AMS at Beta Analytic Inc. (USA). Because the presence of black carbon (BC) could bias radiocarbon dating based on total organic carbon (TOC) leading to an overestimation of the age (Masiello and Druffel, 1998; Dickens et al., 2004), the radiocarbon age of the BC isolate (extracted using Kuhlbusch, 1995; see also SI Text) was also determined by AMS. The 'corrected' age of deposition was estimated using a mixing model that removed the influence of old recycled carbon (BC) stored within the sediments (Dickens et al., 2004) (see SI Text, SI Table 2, and SI Fig. 2).

2.4. Chemical analyses

Sediments were analyzed for concentrations of 33 PAH compounds, 36 elements, and four Pb stable isotopes as proxies for residues of combusted biomass and fossil fuels (Hites et al., 1980; Rosman et al., 1997) resulting from vehicle exhaust, heating, cooking, large-scale power generation and open burning (CPSA, 1983; Dunlap et al., 1999). Analysis and quantification of PAHs were carried out at East Carolina University (USA) on a Shimadzu QP 2010s gas chromatograph/mass spectrometer (GC/MS) in selected ion monitoring (SIM) mode (see Mitra et al., 2012). PAHs were extracted using a Dionex Accelerated Solvent Extractor (ASE 350) in 66 mL sample cell spiked with 1 mL of deuterated PAH surrogate standard consisting of deuterated naphthalene, anthracene, benz[a]anthracene, benz[a]pyrene, and benz[g,h,i]perylene, in acetone. Solvent [acetone:hexane cocktail (2:1 v:v)] heated at 100 °C was purged through the sample cell over three static cycles of 3 min. PAHs in the extracts were purified using silica open-column fractionation (Dickhut and Gustafson, 1995) and then quantified by gas chromatography–mass spectrometry (GC/MS) after adding 1 mL of deuterated PAH internal standard (deuterated acenaphthylene, phenanthrene, chrysene, perylene, and indeno[1,2,3-c,d]pyrene). Each extraction batch included a lab blank and a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1941b (Organic Marine Sediment) or 1649a, following the PAH extraction procedures as described above. Compounds were considered not quantifiable (NQ) if the PAH abundance in a sample was less than twice the abundance from the lab blanks (averaged over 6 months), if the recovery of the deuterated surrogate standard compared was less than 50% of the deuterated internal standard or if PAH concentrations deviated by more than 10% from certified values in the SRM.

Metal concentrations were determined at Activation Laboratories Ltd. (Canada) by inductively coupled plasma-optic emission spectrometry (ICP-OES) after microwave digestion with aqua regia (Cearreta et al., 2013; Leorri et al., 2013). Sediment samples for stable lead isotopic ratios were analyzed using a multi-collector-inductively coupled plasma-mass spectrometer (Neptune, Thermo Scientific), at the Geochronology and Isotope Geochemistry Research Facility of the University of the Basque Country (Spain) (following Irabien et al., 2012). The contribution of anthropogenic sources above baseline values was calculated using two sets of mixing models (see Alvarez-Iglesias et al., 2012 and references therein).

Geochemical fluxes were calculated as the product of sediment accumulation rate and the concentration of each component. Fluxes of PAHs were calculated for both total PAH (TPAH) and high molecular weight PAH (HMW-PAH; those with four or more aromatic rings). The SI Text describes the methods used in greater detail, including a compilation of data from Spain and Europe regarding several isomer ratios and downcore total organic carbon, $\delta^{13}C$ and total N, and all data are presented in SI Table 3a and b (PAHs), 4 (metals) and 5 (Pb isotopes), supported by SI Figs. 3–9.

3. Results and discussion

3.1. Sediment chronology

Sedimentation rate estimates derived from the CRS (Appleby and Oldfield, 1978) method indicate that the uppermost 10 cm was deposited over about 100 years. The downcore profile of ^{137}Cs shows a clear subsurface maximum in activity at 3.5 cm depth. Assuming this subsurface ^{137}Cs maximum to be 1963 CE, i.e., during peak atmospheric bomb testing, it corroborates the [210]Pb$_{xs}$-derived age estimates. Considering the apparent minimal sediment mixing in this core, the ages of each sediment depth were calculated by linear interpolation between the C-14 dated horizons. The resulting geochronology yielded three zones of different sediment accumulation rates: 0–10 cm depth, 0.055 ± 0.022 g cm^{-2} year^{-1}; 10–25 cm depth, 0.056 ± 0.006 g cm^{-2} year^{-1}; and 25–39 cm depth, 0.039 ± 0.003 g cm^{-2} year^{-1} (SI Fig. 2).

3.2. Pollutant delivery

While it is assumed that the high marsh sediments contain a record of atmosphere-delivered contaminants, the possibility of other sources is examined here. High salt marshes are affected by sporadic flooding, mainly during spring tides, accumulating pollutants from both atmospheric and aquatic sources. River-derived pollutants might be stored in intermediate reservoirs (e.g., soils) providing a time lag between emissions and the final deposition in the salt marsh, biasing the temporal reconstructions. In Kanala, the sporadic tidal flooding controls the sedimentation. The Urdaibai watershed is small and steep with the rainfall evenly distributed during the year (Bruschi et al., 2013). These characteristics most likely minimize large variations in sediment source. To assess the contribution of atmospheric versus watershed inputs, we have calculated a focusing factor which can indicate augmentation of [210]Pb$_{xs}$ inventory by allochthonous sediments enriched in [210]Pb$_{xs}$ (Callender and Van Metre, 1997; Chillrud et al., 1999). Based on the constant rate of supply (CRS) model (Appleby and Oldfield, 1978) the [210]Pb$_{xs}$ at year 0 flux is 21 ± 1.3 mBq cm^{-2}. The modeled flux was then used to reconstruct the theoretical inventory which was within 1% of the measured inventory of 6846 ± 416 Bq m^{-2}, suggesting a constant source dynamics. [210]Pb$_{xs}$ fluxes up to 18.3 mBq cm^{-2} year^{-1} from ombrotrophic peats ([210]Pb$_{xs}$ derived from atmospheric deposition) in the NW Iberian Peninsula (Olid et al., 2013; less than 400 km to the west of Kanala) seem an adequate regional reference for atmospheric [210]Pb$_{xs}$ fluxes based on the similarity of the averaged inventories between NW Spain and the Basque region (5443 ± 340 Bq m^{-2} and 5806 ± 200 Bq m^{-2} in, respectively). Kanala presents greater fluxes and inventory than the regional estimates, although within global ^{210}Pb flux calculated range (15.5 ± 7.5 mBq cm^{-2} year^{-1}) (Turekian et al., 1977; Baskaran, 2011). Taken together, the regional and global estimates suggest combined atmospheric and aquatic (transported in the watershed) sources for the [210]Pb$_{xs}$, with the atmosphere contributing $86 \pm 13\%$ of [210]Pb.

During transport, PAH signatures can be modified, for instance, fluxes and concentrations of individual PAHs when normalized to TPAH generally decrease as a function of increasing PAH molecular weight. For example, phenanthrene (PHEN)/TPAH is generally higher than pyrene (PYR)/TPAH, followed by coronene (COR)/TPAH values (SI

Fig. 3). These differences in relative abundances across PAH molecular weight may either be due to varying relative intensity of atmospheric to estuarine-derived influx or to changing source of combustion. In that direction, sedimentary concentrations of total PAHs and Pb are very strongly correlated ($r^2 = 0.99$) (e.g., SI Fig. 4 indicates the concomitant increase of PYR and Pb since the 1820s to 1975 CE), implying a common combustion-derived source which suggest that changes in the patterns are related to changing sources of combustion rather than being associated to changes in the transport pathways of pollutants.

Below we consider downcore profiles of PAH isomer ratios, PAH flux, metal concentrations and fluxes, as well as Pb stable isotopes for three time intervals with distinct geochemical signatures: 1300–1800 CE, 1800–1930 CE, and 1930–2000 CE.

3.2.1. 1300 to 1800 CE

Geochemical variables in the Kanala core sediments deposited prior to the 19th century show similar temporal variations in TPAH, Pb, and Zn concentration and fluxes (Fig. 1). During the period from 1300 to 1800 CE, high molecular weight PAH isomer ratios benzo[a]anthracene (BaA) to chrysene (CHRY), and benzo[a]pyrene (BaP) to benzo[e]pyrene (BeP) are relatively uniform proceeding upcore (Fig. 2). The high molecular weigth PAH isomer pairs do not change when adjusted for photodegradation (SI Fig. 5) and present a strong correlation with each other (SI Fig. 6) confirming their application to reconstruct historical sources.

The vertical dashed lines in Fig. 2 represent the atmospheric signal of regional combustion throughout Spain as represented by downcore profiles of PAH isomer ratios in sediments from high mountain lakes (Fernandez et al., 2000) (SI Fig. 7). The remarkably uniform PAH isomer ratios from 1830 to ca. 2000 CE would suggest that the combustion-derived aeolian sources of PAHs throughout Spain were constant during that time period. From 1300 to 1800 CE, BaA/CHRY and BaP/BeP in the Kanala core are notably similar to the ratios between 1830 and 2000 CE in high mountain lake sediments throughout Spain (Fig. 2). Organic matter properties of bulk sediments in the Kanala core also remain

relatively constant from 1300 to 1800 CE (SI Fig. 9). Together, these observations suggest that the sources of PAHs to the Kanala salt marsh from 1300 to 1800 CE were predominantly aeolian. Thus, the enriched relative abundance of low molecular weight compounds such as PHEN in contrast to PYE or COR is driven by the type of fuel used from 1300 to 1800 CE. A similar enrichment of low molecular weight PAHs was documented in sediments from an ombotrophic bog of the Iberian Peninsula from 1000 to 1750 CE (Pontevedra-Pombal et al., 2012).

Similar to PAHs, concentrations of Pb deposited during this pre-19th century period are low (average 24 mg kg^{-1}) as are Pb fluxes (11 μg m^{-2} year^{-1}) and the ^{208}Pb/^{206}Pb ratios are uniform (Fig. 2), similar to PAH data. The materials analyzed from this period present Pb concentrations similar to background data in the region (Cearreta et al., 2013) and S. Spain (Garcia-Alix et al., 2013) and Pb isotopic ratios are similar to background values in Greenland ice cores (Rosman et al., 1997), in a peat bog from Switzerland (Shotyk et al., 2002) (Fig. 3) and coastal salt marshes from SW France (^{207}Pb/^{206}Pb = 0.835) (Alfonso et al., 2001). In that sense, the period 1300 to 1800 CE could be used as baseline data (i.e., pre-Industrial) to assess the impact during the Industrial period. Baseline values would be differentiated from background values (i.e., pre-Anthropogenic) based on the fact that background values of atmospheric emissions are usually estimated from materials older than 5000 years B.P. (Monna et al., 1997; Shotyk et al., 2002) although vary region to region (Garcia-Alix et al., 2013). In addition, previous work has indicated four deviations from background concentrations of Pb during the late Holocene of the Basque region (Monna et al., 1997), some concomitant with other records in the NW Iberian Peninsula (Martinez-Cortizas et al., 1997, 2002; Pontevedra-Pombal et al., 2012), Europe (Shotyk et al., 2002) and Greenland (Rosman et al., 1997) related to the mining activities in western Europe (Pontevedra-Pombal et al., 2013). Locally, these excursions have been associated with deforestation via wood burning (Monna et al., 1997). In this context, the period 1300 to 1800 CE most likely reflects atmospheric emissions of wood burning, supported by the similarities with high altitude lakes in Spain (also associated with
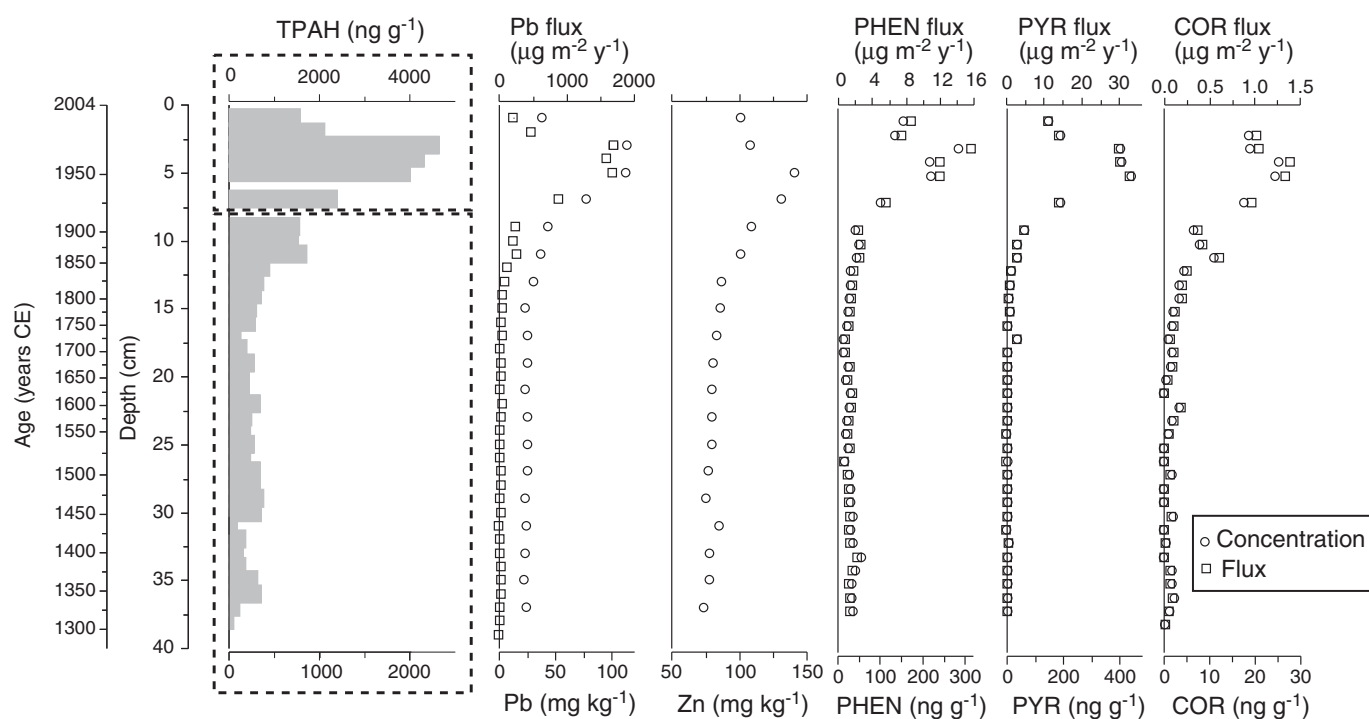

Fig. 1. Downcore profiles of total PAH concentration (ng g^{-1}), total lead flux (μg m^{-2} y^{-1}) and concentration (mg kg^{-1}), zinc concentration (mg kg^{-1}), phenanthrene (PHEN), pyrene (PYR), and coronene (COR) flux (μg m^{-2} y^{-1}) and concentration (ng g^{-1}). Age expressed in years Common Era (CE). Circles indicate concentrations, squares indicate fluxes.
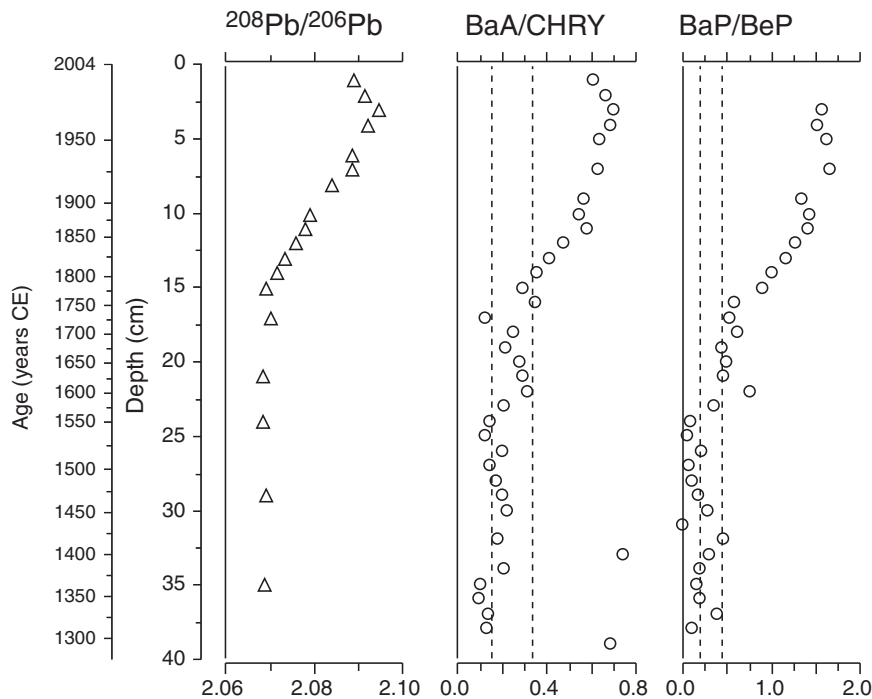
Fig. 2. Downcore profiles of lead isotope ratios (^{208}Pb/^{206}Pb), benzo[*a*]anthracene/chrysene (BaA/CHRY), and benzo[*a*]pyrene/benzo[*e*]pyrene (BaP/BeP). Dashed lines in BaA/CHRY and BaP/BeP plots are representative of each respective isomer ratio from mountain lakes throughout Spain (see SI Fig. 6).
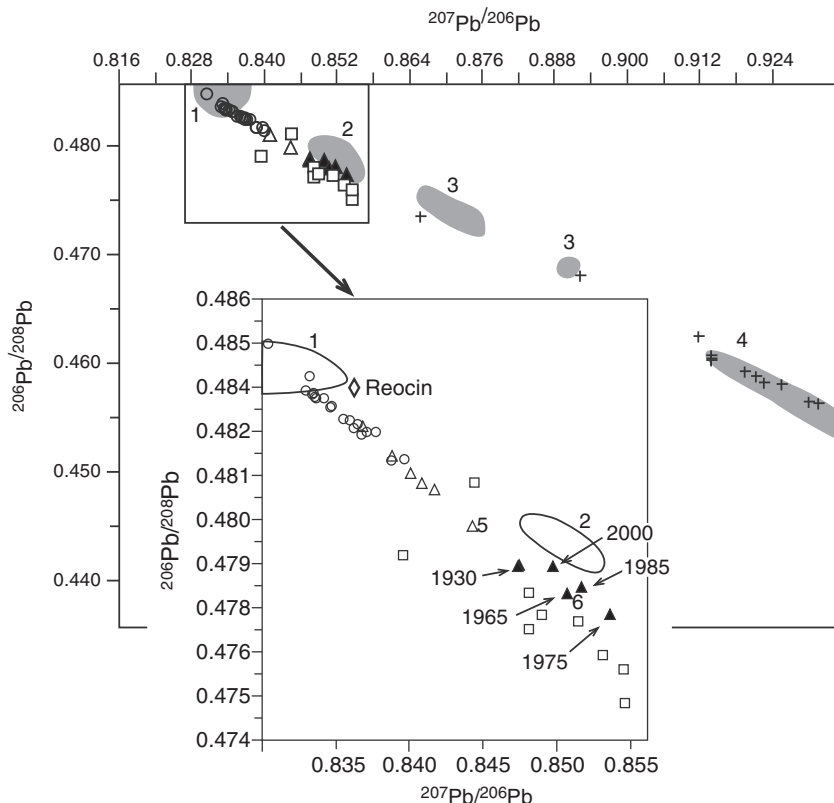

Fig. 3. Pb isotope ratio correlation diagram between ^{207}Pb/^{206}Pb and ^{206}Pb/^{208}Pb. White circles represent samples older than 1800 CE and samples from other nearby cores considered un-impacted. Open triangles represent samples between 1800 and 1930 CE. Black triangles (with associated ages) represent samples younger than 1930 CE that are bracketed by samples representing coal isotopic ratios from both Spain (Díaz-Somoano et al., 2007) and the United Kingdom (Farmer et al., 1999) (white boxes). The plus signs represent additional reference values such as air quality, industrial and gasoline signals (also shaded area number 4) (Monna et al., 1997; Dunlap et al., 1999; Alvarez-Iglesias et al., 2012). Background values are from Greenland Ice Holocene samples (number 1) (Rosman et al., 1997) and the Basque Region (Monna et al., 1997). Norwegian peat bog samples from 1800 to 1950 CE are indicated by number 2, whereas samples from 1960 to latter than 1980 CE are indicated by number 3 (Dunlap et al., 1999). Numbers 5 and 6 represent the isotopic signal at 1300 and 1500 CE from Greenland Ice samples (Rosman et al., 1997). See also Alvarez-Iglesias et al. (2012). Reocin lead and zinc ore values are indicated for reference (located ca. 120 km from Kanala).

wood burning) (Fernandez et al., 2000), and recorded in both NW Spain (Pontevedra-Pombal et al., 2012) and the Basque region (Monna et al., 1997).

3.2.2. 1800 to 1930 CE

Exponential increase in PAH and Pb abundances and fluxes occurs upcore throughout this period. Concentrations of TPAHs increase from ca. 200 ng g^{-1} to more than 2400 ng g^{-1} by 1930 CE (Fig. 1). TPAH concentrations are 3.5 times greater than baseline levels by 1860 CE and ca. 10 times greater by 1930 CE, with the majority of the PAH increase being driven by changes in high molecular weight compounds. Both Pb and Zn (Fig. 1) and some other metals such as Cr similarly increase in abundance during this time period. Neither properties of bulk organic matter nor watershed human population changes are coincident with the timing of the changes in PAH and Pb concentrations and fluxes (SI Fig. 9). Fig. 2 indicates an increase in ^{208}Pb/^{206}Pb towards less radiogenic values beginning at 1800 CE. These increases in PAH and Pb concentrations from baseline levels and less radiogenic Pb isotope ratios are likely related to the initial stages of the Industrial Revolution in Europe (Bindler et al., 2001; Eades et al., 2002; Renberg et al., 2002; Gabrieli et al., 2010). For example, in the nearby region around the city of Bilbao the first metallurgical furnace was already established in 1841 CE followed by a second one in 1857 CE. At this time, the metallurgical industry became one of the dominant economic drivers in the region (Cearreta et al., 2002a). However, the progressive increase of Pb, Zn (Fig. 1) and Cu (SI Table 2) could also reflect a more local effect. For instance, the establishment of local industry (weapons and cutlery manufacturers) around the town of Gernika (SI Fig. 1) occurred between 1913 and 1917 CE (Leorri et al., 2013). The departure from baseline values reported here occurring at 1800 CE has been previously pinned at 1850 CE (Olid et al., 2010) and ca. 1900 (Martinez-Cortizas et al., 2012) in the NW Iberian Peninsula. Following the methods described in Alvarez-Iglesias et al. (2012), the Pb contribution from Industrial pollution in the Kanala salt marsh was calculated to surpass 80% by 1930 CE. This value is greater than those reported from NW Iberian Peninsula peat bog sediments that suggest the industrial contribution to be between 24 and 35% also by the 1930s (Martinez-Cortizas et al., 2012). The greater and earlier signs of industrial pollution in Kanala could be related to the focusing factor of coastal sediments versus peat bogs, a more intense industrialization in the Basque region, or both. Nevertheless, ^{210}Pb$_{xs}$ fluxes and inventory indicate a minimal contribution from the focusing factor.

The dramatic shifts in Pb isotope ratios and high molecular weight PAH ratios that occur during this time period (Fig. 2) imply that sources of combustion dramatically changed at the beginning of this time interval. The trends in PAH isomer ratios and Pb stable isotope ratios in Kanala are coeval, suggesting that they may be used to discern sources of combustion. Unfortunately, historical data on fuel consumption from the Basque region are not available. However, since the 1850s there has been an exponential increase in coal use in Spain (Rubio, 2005). This suggests that coal was replacing wood as the primary fuel at this time as reported elsewhere in Europe (Elmquist et al., 2007). These changes in PAH isomer ratios during this time are not observed in high mountain lakes throughout Europe (Fernandez et al., 2000) but are observed in an ombrotrophic bog in the Iberian Peninsula (Pontevedra-Pombal et al., 2012), and it could represent a further evidence that from 1800 to 1930 CE, local atmospheric deposition dominates the sediment profiles at this site. In fact, the lack of record of similar changes in PAH isomer ratios in Spain's high altitude mountain lakes may be explained by the fact that the residue from coal combustion is enriched in coarse grained aerosols (>1 μm) (Kauppinen and Pakkanen, 1990). Most likely, these coarse grained aerosols would deposit before traveling to high mountain areas.

Lead stable isotope ratios that become less radiogenic from 1800 CE onwards (Figs. 2 and 3) are also indicative of increasing influence of coal. A Pb isotope mixing model was applied for this time assuming only two end members of combustion, baseline values (associated with wood burning) and coal. Samples from this core older than 1930 CE (Fig. 3 inset, open triangles) cluster together with baseline data (white circles) except for one sample (Fig. 3). This mixing model indicates a clear switch from wood to coal with the latter becoming dominant after 1900 CE. Unfortunately, the overlap of the PAH isomer ratios in our study of wood and coal precludes their ability to distinguish between these sources during this time interval.

3.2.3. 1930 to 2000 CE

This time period is marked by an increase in sedimentation rate (SI Fig. 2), decrease in Al and Fe concentrations, a depletion in δ^{13}C values (down to −27.3‰ compared to an averaged value of −24.5‰ before 1930 CE; SI Fig. 9) and higher total organic carbon to nitrogen ratio. All, this suggests changes in land use (land clearance and soil erosion), likely associated with increasing human population during this time period (Bruschi et al., 2013), reflected in the sediments through more depleted δ^{13}C values and higher TOC/N ratios.

Concentrations and fluxes of PAHs increase from ~1930 to 1970 CE, followed by a gradual decrease proceeding to 2000 CE (Fig. 1), a pattern observed both regionally and globally (Van Metre et al., 2000; Dreyer et al., 2005; Gallon et al., 2005; Vane et al., 2011). This pattern of increasing PAH from early to mid 1900s followed by a decrease in the latter half of the 20th century has been attributed to increasing residential and industrial development followed by greater governmental controls on fuel combustion emission (Van Metre et al., 2000; Lima et al., 2003; Gallon et al., 2005). The sedimentary flux of TPAHs during this time period ranges from ca. 1300 μg m^{-2} y^{-1} in the early 1930s to ca. 2500 μg m^{-2} y^{-1} during the 1970s. These values are significantly higher than those reported for high altitude Alpine snow and ice (Gabrieli et al., 2010), high altitude lakes in Western and Central Europe (Fernandez et al., 1999, 2000), ombotrophic bogs in Spain (Pontevedra-Pombal et al., 2012), or remote lakes in the USA (Fernandez et al., 1999; Quiroz et al., 2005), but similar to sedimentary fluxes in urban and industrial lakes (Quiroz et al., 2005).

Pb isotopic ratios in samples from this period (after 1930 CE) are the least radiogenic and cluster together with ratios very similar to those of coal reference materials from both Spain (Díaz-Somoano et al., 2007) and the United Kingdom (Farmer et al., 1999) (Fig. 3). Data from British coal are pertinent as this was the main source of coal used for the steel industry in the Basque region (Villanueva, 1991).

Leaded gasoline, which was introduced in the 1920s, became the major source of atmospheric emissions in Europe by the 1950s (Dunlap et al., 1999) and the major fuel source in Spain since 1970s (Rubio, 2005). Then, it seems reasonable to expect that PAH isomer ratios in this Kanala core will align with ratios available in the literature for petroleum combustion. Isomer ratios of fluoranthene (FL)/(FL + PYR) and indeno[1,2,3-cd]pyrene (IP)/(IP + benzo[ghi]perylene (Bghi)) from petroleum combustion are typically suggested to range from 0.4 to 0.5 and from 0.2 to 0.5, respectively (Yunker et al., 2002). Post-1930 CE average ratios of FL/(FL + PYR) and IP/(IP + Bghi) in the Kanala sediments are 0.55 and 0.57, respectively. The higher values in these materials would suggest that either the dominant source of PAHs from 1930 CE onwards is derived from grass/wood/coal combustion or that values of PAH isomer ratios denoted in Yunker et al. (2002) are not appropriate for interpreting PAH sources in Europe. In spite of the known post-Industrial Revolution record of petroleum use throughout Europe, two other studies reconstructing patterns of fossil fuel use in the 20th century detected no influence from petroleum combustion in PAH isomer ratios (Gabrieli et al., 2010; Pontevedra-Pombal et al., 2012). Another recent study noted that PAH composition in charcoals have, in some respects, source signatures similar to unburned fossil materials (i.e. crude oil), suggesting the potential for misinterpretations of the source signatures of natural PAHs in soils and sediments (Keiluweit et al., 2012). Thus, PAH isomer ratio data should be used with caution in intercontinental comparisons of pyrogenic pollutant types.

The contribution of anthropogenic sources is calculated to be ca. 90% by 1975 CE and the leaded gasoline influence increased from almost negligible in 1930 CE to 13–24% by 1975 CE (see Alvarez-Iglesias et al., 2012 for methods). The peak at 1975 CE occurred later than the one at 1955–1962 recorded in NW Spain (Olid et al., 2010; Alvarez-Iglesias et al., 2012) but contemporaneous to the maxima reported in Europe (1970s–1980s). While the Pb contribution from gasoline in Kanala is similar to the values reported from an estuarine system in NW Spain (Alvarez-Iglesias et al., 2012), the Pb contributions from gasoline are smaller than those at a peat bog from NW Spain (Martinez-Cortizas et al., 2012) and other European records (Dunlap et al., 1999; Shotyk et al., 2002). This reflects the greater importance of coal to local and regional combustion emissions in NW Spain.

The gradual decrease in PAH abundance from 1970s is accompanied by a decrease in isomer ratios of high molecular weight PAHs. The lead isotope ratios become more radiogenic and Pb and Zn concentrations also decrease after the 1970s (Figs. 1 and 2). All this is coincident with the general trend of Spain's decreasing emissions of BaP relative to those of the rest of Europe from 1970 CE onwards (Pacyna et al., 2003). While it is tempting to ascribe these recent changes to declining population throughout the watershed, on the contrary, human population has increased in the watershed of the estuary in recent years (SI Fig. 9). These changes suggest a transition to the use of non-BaP enriched fuels from 1970s up to the present. Similar decreases have been noted in several other regional and global studies and have been attributed to more effective emissions control, improved combustion technologies and/or substitution of coal combustion by cleaner fuels (Van Metre et al., 2000; Pacyna et al., 2003; Dreyer et al., 2005; Gallon et al., 2005).

3.3. Conclusions

This reconstruction of combustion-derived contaminant delivery from a SW Europe salt marsh over the past 700 years using PAHs and Pb isotopic data reveals temporal trends that bear a striking resemblance to records obtained in other regions. While it suggests that the record reflects global-scale changes, the large calculated fluxes and distinct geochemical signatures indicate a more regional source. In fact, PAH isomer and Pb isotopic ratios indicate a strong influence of regional coal use as a major factor in the observed local patterns of metal and PAH delivery since the 1800s. This coal use was most likely associated with the regional iron and steel industries and paralleled the local economic development (Villanueva, 1991).

This study also shows that salt marshes contain potentially valuable records of regional atmosphere delivery of contaminants. Furthermore, this study demonstrates the value of a combined organic geochemistry and metal chemistry approach, which makes use of isomer and isotope ratio analyses, in reconstructing this type of records.

This record from the Urdaibai estuary has captured a regional fingerprint of pollution that fills an important data gap towards reconstructing the chronology of pollution in coastal sediments. This information can be used to narrow down chronological uncertainties in other records with a less continuous sedimentary accumulation using the history of the pollutants emissions. Crutzen and Stoermer (2000) have called for a new epoch, the Anthropocene, referring to the interval of human alteration of global biogeochemical cycles beginning after the invention of the steam engine in the late 18th century. The record in coastal sediments reconstructed here would suggest a date of ca. 1800 CE for the boundary between the Holocene and the Anthropocene epochs in northern Spain.

Conflict of interest

The authors declare that there is no any actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.

Appendix A. Supplementary data

Supporting Information (SI). The provided SI Text describes the methods with greater detail, are supported by SI Figs. 2 to 10, and data analyzed are presented in SI Tables 1 to 5. SI Fig. 1 indicates the location of the study site. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.09.064.

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