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RECENT COASTAL ANTHROPOGENIC IMPACT RECORDED IN THE BASQUE MUD PATCH (SOUTHERN BAY OF BISCAY SHELF)

María Jesús Irabien[1], Alejandro Cearreta[2], José Gómez-Arozamena[3], Jon Gardoki[2], Aitor Fernández Martín-Consuegra[2]

[1]Dpto. Mineralogía y Petrología, Universidad del País Vasco UPV/EHU, Apartado 644, 48080 Bilbao, Spain. mariajesus.irabien@ehu.eus

[2]Dpto. Estratigrafía y Paleontología, Universidad del País Vasco UPV/EHU, Apartado 644, 48080 Bilbao, Spain. alejandro.cearreta@ehu.eus, jonngardoki@gmail.com, aitor.fernandez@ehu.eus

[3]Dpto. Ciencias Médicas y Quirúrgicas, Universidad de Cantabria UC, Avenida Herrera Oria s/n, 39011 Santander, Spain. jose.gomez@unican.es

Abstract

The historical anthropogenic impact on sediments from the Basque Mud Patch (southern Bay of Biscay) is explored using a multidisciplinary approach including the analysis of natural (^{210}Pb) and artificial (^{137}Cs, $^{239/240}$Pu) radiotracers, major elements (Al, Mn), metals (Zn, Pb, Cu, Cr), Pb isotopic ratios, and foraminiferal and pollen contents. The study of three short cores (19-46 cm), despite being hindered by the effects of biomixing, allow the calculation of a sedimentation rate of 1 ± 0.1 mm yr^{-1}. Distribution with depth of Al-normalised concentrations of metals reflects an increasing trend since 1880 CE, related to the industrialization of the Basque coastal area. According to the Sediment Quality Guidelines applied, contents of Zn and Pb appear as a potential cause of concern, given that they exceed the values from which adverse biological effects can be occasionally expected. However, foraminiferal assemblages do not show recognizable changes along the cores following increasing trace metal concentrations. Finally, pollen results reveal an increasing trend of coniferous taxa and a parallel reduction of authochthonous Deciduous *Quercus*, probably as a

consequence of reforestation works. Data obtained confirm that effects of coastal anthropogenic activities extend to the adjacent shelf, where muddy deposits are likely to act as a trap for contaminants.

Keywords: Metals; Foraminifera; Radiotracers; Pollen; Mud depocenter; Bay of Biscay

1. Introduction

The world´s continental shelves, which underlie for little more than 8% of the global marine surface, are key interfaces between terrestrial sediment source areas and deep-sea depositional systems (Covault and Fildani, 2014). They are complex environments characterised by the interplay among many factors, such as tectonic setting, material inputs from landmasses, climate, hydrodynamic processes (tidal flows, waves, currents) and human activities (Nittrouer et al., 2007; Chiocci and Chivas, 2014). These marine areas can act as significant sinks not only for fluvial and estuarine materials, but also for anthropogenic contaminants and carbon compounds (Mahiques et al., 2016; Qiao et al., 2017), which are frequently associated with fine-grained particles (Förstner, 2002). Many clastic shelves host mud deposits (the so-called depocenters), showing different three-dimensional geometries and characteristics, where land-supplied fine-grained materials are retained (Hanebuth at al., 2015). In the Bay of Biscay (Fig. 1), mud deposits appear as isolated patches (Hanebuth at al., 2015), conditioned by the favourable morphological context, short-term events of high fluvial sediment discharge and oceanic current forcing factors (Lesueur et al., 2002; Jouanneau et al., 2008). Mud patches located on the French shelf have been largely investigated in previous works (Castaing and Allen, 1981; Jouanneau et al., 1989; Lesueur et al., 2001, 2002; Schmidt et al., 2005; Dubrulle et al., 2007; Mengual et al., 2019; Mojtahid et al., 2019), whereas that lying along the northern Iberian margin adjacent to the Basque coast (Fig. 1) has received much less attention (see references below). For this reason, the study of these fine-grained deposits represents the main goal of this work.

The Basque region is a relatively small area (7,234 km^2) located in the innermost part of the Bay of Biscay (Fig. 1). Its recent history has been decisively marked by the exploitation and processing of local iron ores by steel industry, upon which a sizeable chunk of the economic growth of the city of Bilbao and the whole region was based for over a century. Unfortunately, these activities were carried out within a historical framework of unsustainable development, and almost all river catchments, estuaries and coastal water bodies have been affected, to a different extent, by a wide array of anthropogenic pressures, including urban, mining and industrial discharges, hydromorphological modifications, dredgings, and disposal of solid wastes (Tueros et al., 2009; Borja et al., 2016). Consequences have been especially dramatic in coastal areas where, in the current scenario of climate change, changes due to sea-level rise are likely to be overwhelmed by human impacts (Chust et al., 2009).

In the Basque Country, people living in coastal areas (around 1,500,000 inhabitants) accounts for 70% of the total population (IHOBE, 2017). About 55% settles in two metropolitan zones around the cities of Bilbao and San Sebastian-Donostia (Fig. 1) that make up less than 10% of the whole Basque territory. Most original transitional domains have been lost as a result of land reclamation and all estuaries show, to a greater or lesser extent, evidences of sediment contamination (Cearreta et al., 2004; Legorburu et al., 2013b; Irabien et al., 2015). Increased concentrations of trace metals and PAHs appear also in nearshore samples (Belzunce et al., 2004; Borja et al., 2008; Tueros et al., 2009; Viñas et al., 2010; Legorburu et al., 2013a), but enrichment levels are in general distinctly lower than those determined within the estuaries. Evidences of human influence are likely to extend to deeper areas, given the high contents of priority and emerging micropollutants determined in the Capbreton canyon, on the French part of the Bay of Biscay (Boutier et al., 2011; Azaroff et al., 2020).

This is the first work to assess the potential impact left by human activities in the muddy deposits of the Basque continental shelf. For this purpose, three sediment cores were studied using a multiproxy approach that includes the analysis of radionuclides (^{210}Pb, ^{137}Cs and $^{239+240}Pu$), trace metals, isotopic signatures of Pb, foraminiferal assemblages and pollen contents.

2. Regional setting and background

The continental shelf adjacent to the Basque Country (Fig. 1) is a narrow area (7-20 km) about 150 km long which receives the discharge of suspended material (around 1.57×10^6 t yr^{-1}) of twelve different river systems (Pascual et al., 2004; Uriarte et al., 2004). As early observed by De Buen (1933), coarse to medium-sized sandy materials occur in the western part, while in the eastern section the mid- and outer shelves (50-<150 m depth) are covered by an extended unit of fine-grained sediments (Rey and Mendialdea, 1989; Jouanneau et al., 2008; Galparsoro et al., 2010), henceforth expressed as the Basque mud patch (BMP) (Fig. 1). It is bounded by rocky outcrops in a shoreward direction and extends to the shelf-break and the edges of the Capbreton Canyon. According to Jouanneau et al. (2008), this deposit is about 680 km^2 in size and has a maximum thickness of 7 m.

The study of the benthic microfauna in surface sediments from the BMP developed by Pascual et al. (2008) evidenced that distribution of foraminifera and ostracod assemblages were mainly controlled by environmental variables such as calcium carbonate, particulate organic carbon and silt-clay proportion. These authors found specimens affected by the oil-spill derived from the sinking of the tanker MV *Prestige*, which introduced about 63,000 metric tonnes of heavy fuel in the Bay of Biscay between November 2002 and February 2003 (Laffon et al., 2006). In addition, data provided by Fernández Martín-Consuegra (2018) from the analysis of both surface and cored sediment samples pointed out the role of cool-waters upwelling through the San Sebastian Canyon to explain foraminiferal distribution during the last 4000 years.

3. Materials and methods

3.1. Sampling

Sediment cores were obtained during the EUSKASED (Euska2) scientific cruise of the R/V *Côtes de la Manche* in July 2004 from the central area of the BMP, in front of the city of San Sebastian-Donostia (Fig. 1). Cores KS-04 (43º25.45N, 2º0898W, 44 cm long) and KI-03 (43º25.69N, 2º09.18W, 19 cm long) were retrieved at 135 m depth using a Kullenbeg corer, whereas core KI-06 (43º25.424N, 1º57.747W, 46 cm long) was obtained at 119 m depth using an interface corer (Champilou, 2005). Sediment cores were cut in 1 cm-thick intervals at the University of Bordeaux (France).

3.2. Radiometric analysis

Specific activities of both natural (^{210}Pb y ^{226}Ra) and artificial (^{137}Cs, $^{239/240}$Pu and ^{238}Pu) radiotracers were measured in samples from core KS-04. In addition, activity concentrations of other natural radionuclides such as ^{232}Th, ^{212}Pb and ^{228}Ac, which occur in the disintegration chain of ^{235}U, and ^{40}K were also determined. Except $^{239/240}$Pu and ^{238}Pu, they were analysed in the University of Cantabria (Spain) by gamma spectrometry, using a low-background high purity HPGe detector (see procedural details in Alvarez-Iglesias et al., 2007 and Cearreta et al., 2013). Sediment samples were homogenised, hermetically sealed and stored for at least 25 days to ensure secular equilibrium between ^{226}Ra, ^{222}Rn and the short-lived daughter nuclides of the latter. Excess ^{210}Pb activities (^{210}Pb$_{xs}$) were determined by subtracting the ^{226}Ra activity (assumed to equal the supported ^{210}Pb activity) from the total ^{210}Pb activity. Measures of $^{239/240}$Pu and ^{238}Pu were carried out in the Laboratory of Environmental Radioactivity of the University of Valencia (Spain) using alpha spectrometry, after a sequential chromatographic separation process (analytical details are described in Sáez-Muñoz et al., 2020).

Dating methods using $^{210}Pb_{xs}$ are based on the assumption that the tracer cycle is a closed system, so that the flux of $^{210}Pb_{xs}$ to the sediments is constant and there is no post-depositional remobilization (Goldberg, 1963; Krishnaswami et al., 1971). In coastal and marine environments, which are considered as open systems (Pfitzner et al., 2004), flux of ^{210}Pb to the sediments is mainly due to direct atmospheric deposition, but contributions can also be produced by advection, the flow of suspended matter from river discharges and the disintegration of ^{226}Ra dissolved in the water column, although this last process is likely to be significant only at great depths (Cochran et al., 1990). These factors may introduce certain limitations in the application of the method as well as in the different models for dating. However, and despite these uncertainties, ^{210}Pb activities along the studied core showed a clearly exponential decrease with depth, reflecting that accumulation rates were constant. Therefore, both sediment accumulation rates (SAR) and mass accumulation rates (MAR) were estimated through the Constant Flux (CF:CS) model (Koide et al., 1973; Robbins, 1978), which assumes constant ^{210}Pb flux and sedimentation rates.

3.3. Geochemical analysis

Sediment samples from all cores were mechanically homogenised using an agate mortar and pestle. Elemental concentrations were analysed in Activation Laboratories Ltd. (Actlabs, Ontario, Canada). An amount of 0.5 gr of sample was digested with aqua regia (a combination of concentrated hydrochloric and nitric acids) for 2 hours at 95ºC. Samples were then cooled, diluted with deionized water and analysed using a Varian ICP. Detection limits were 0,01% for Al, 5 mg kg^{-1} for Mn, 2 mg kg^{-1} for Zn and Pb, and 1 mg kg^{-1} for Cu and Cr. Quality Control for the digestion was 15% for each batch, 2 method reagent blanks, 6 in-house controls, 8 sample duplicates and 5 certified reference materials. An additional 20% CQ was performed as part of the instrumental analysis to ensure quality in the areas of the instrumental drift.

When dealing with sediments, it is an extended practice to normalize trace metal concentrations to the contents of a conservative element such as aluminium to compensate for the potential effects of granulometric and mineralogical differences (e.g. Mil-Homens et al., 2006; Ho et al., 2012). Sediments along each core are fairly homogeneous, and vertical profiles displayed by measured concentrations and Al-normalised values for metals are remarkably similar. However, only Al-normalised concentrations are represented to facilitate inter-core comparisons.

Lead isotope analyses were carried out at the Geochronology and Isotope Geochemistry-SGIker facility of the University of the Basque Country UPV/EHU (Spain) using a Thermo Fisher Scientific MC-ICP-MS Neptune, after digestion of the samples with Aqua Regia. NBS981 standard was used for calibration and accuracy check measurements.

3.4. Microfaunal study

Benthic foraminiferal analysis was performed for a 1-cm sample every two, from 0-1 cm to 16-17 cm depth in core KI-03 and from 0-1 cm to 18-19 cm depth in core KI-06. Samples were sieved through a 63 μm mesh and washed with tap water to remove clay- and silt-size (mud) fractions. They were dried at 40 °C and preliminarily observed under a stereoscopic binocular microscope using reflected light. All contained a great abundance of well-preserved foraminifera and tests were picked until a representative amount of >300 individuals was obtained for each sample. In total, 19 samples and >6,500 foraminiferal tests were studied and taxonomically classified following Loeblich and Tappan (1988) updated in the World Register of Marine Species (WoRMS).

3.5. Pollen analysis

Samples from core KI-03 were analysed at each 1-cm layer every two from 1-2 cm to 17-18 cm depth (alternating with those of foraminifera) and in core KI-06 pollen samples coincided with those of foraminifera. They were chemically (HCl, KOH, HF) and densimetrically (Thoulet solution) treated for the extraction of pollen and non-pollen palynomorphs (NPPs) at the Institute of History-CSIC in Madrid. In addition, each sample was mounted in glycerine for the correct observation and identification of palynomorphs under an optical microscope at 400x and 600x magnification. Taxonomic classification was performed following Goeury and de Beaulieu (1979), Moore et al. (1991), Reille (1992) and Cugny et al. (2010). A minimum of 500 pollen grains were counted per sample while aquatic taxa, fungal spores and other NPPs were excluded from the terrestrial pollen sum (Robles-López et al., 2018).

4. Results and discussion

Ranges of Mn and trace metal concentrations in the three studied cores and regional background values proposed by different authors are included in Table 1.

4.1. Core KS-04

Sediments from this core are fine-grained (mean granulometry ranges from 14.8 to 26.6 µm), exhibit rather constant contents of $CaCO_3$ (15.8-23.6%), and X-ray radiograph reveals undisturbed horizontal lamination, pointing out low bioturbation intensity (Champilou, 2005). Moreover, concentrations of ^{232}Th, ^{212}Pb, ^{228}Ac and ^{40}K display almost vertical profiles, pointing out the absence of significant compositional changes along the core. Unfortunately, samples from the topmost 3 cm and those corresponding to 12-13 cm and 16-18 cm depth were not available for analysis. Therefore, the lack of the uppermost sediments prevents processes of near surface biomixing to be discarded. In any case, the exponential decrease with depth observed for the excess activity of ^{210}Pb (Fig. 2) allows, using the slope of the line derived from the linear regression between $\ln^{210}Pb_{xs}$ and depth (Appleby and Oldfield, 1992) a mean sedimentation rate of 1 ± 0.1 mm yr^{-1} to be calculated. If some mixing were occurring throughout the core, the estimated sedimentation rate would be biased high (Silverberg et al., 1986). However, the obtained value is similar to the lowest rates determined by Jouanneau et al. (2008) in the sedimentary deposits of the BMP (between 1.3 and 5.0

mm yr^{-1}) and by Schmidt et al. (2005) in the adjacent mud depocenters of the French shelf (from nearly 1 mm yr^{-1} up to almost 3 mm yr^{-1}).

Transient tracers, such as ^{137}Cs and to a much lesser extent $^{239/240}Pu$, have been widely applied in dating sediments, usually to corroborate sedimentation rates determined using ^{210}Pb. In undisturbed cores, the first occurrence of both radioisotopes should correspond to the beginning of atmospheric nuclear weapons testing in the early 1950s, whereas highest values are usually attributed to the maximum global fallout in 1962-64 CE. In this core, ^{137}Cs and significant amounts of $^{239/240}Pu$ appear for the first time at 6 cm depth (Fig. 2), slightly deeper (1 cm) than expected according to the ^{210}Pb-derived ages and yielding a comparable but somewhat higher sedimentation rate (~1.3 mm yr^{-1}). However, ^{210}Pb-based chronological model is likely to provide a better resolution for the maximum concentrations of both radioisotopes found at around 4 cm depth (mid-1960s) than that derived from the first appearance of ^{137}Cs (which should indicate that they were deposited later in time, in the 1970s), given that they probably reflect the peak flux preceding the ban of atmospheric testing of nuclear weapons (year 1963). The anomalous penetration of radiotracers to greater depths than expected, previously described in several works (Livingston and Bowen, 1979; Jaakkola et al., 1983; Cochran, 1985; Crusius et al., 2004) confirms that sediment accumulation may not be the only factor controlling their distribution in sediments (Moon, 2003). Biomixing is probably the most powerful mechanism for displacement, being ^{137}Cs (and virtually every other contaminant of interest) a lot more sensitive to mixing than ^{210}Pb (Johannessen and Macdonald, 2012). Moreover, vertical profiles of ^{137}Cs can be also distorted by other phenomena such as desorption from sediment grains and diffusive transport (Hancock et al., 2011) or vertical displacement of pore-waters caused by changes in density of the overlying column (Holby and Evans, 1996).

Vertical profiles displayed by Al-normalised concentrations of Zn, Pb and Cu are very similar in shape, showing low and almost constant values below 13 cm depth and a progressive increase towards more recent sediments (Fig. 3). The chronological framework built on the basis of the ^{210}Pb-derived sedimentation rate indicates that these sediments were deposited before 1880 CE. Although the Basques´ knowledge on iron mining and forging probably antedated Roman times (Douglass and Bilbao, 2005), the change to the modern steel industry began in 1848 with the launch of the first blast furnace near the city of Bilbao. However, the main expansion took place in the 1880s owing to the implementation of new technologies that enabled the conversion of local low-phosphorous iron ores to high-quality steel (Bilbao, 1983). Therefore, concentrations of Zn, Pb and Cu in these bottom sediments seem to represent well pre-industrial levels, whereas those deposited above reflect the increasing impact of recent anthropogenic activities. This is supported by the vertical evolution of Pb isotopic ratios, which exhibit a significant shift towards depleted values as concentrations of this metal increase (Fig. 4a). While samples deposited before 1880 CE appear together within the field associated with pre-industrial estuarine sediments, thereafter there is an increasing input of sources less radiogenic than the background component (Fig. 4b). For comparison, potential mixing end-members have been plotted (Fig. 4b), and they include local galenas from the Arditurri district (see Fig. 1 for location), coal, metallurgical emissions, and leaded gasolines. Obtained data tend to fall along a linear array with tighter adherence for the greater ratios, representative of background values, and a greater spread at the smaller ratios, indicative of the increasing contribution of anthropogenic sources (most probably metallurgical works) since 1880 CE.

With regard to Cr, when compared to Zn, Pb and Cu, it can be observed that the onset of clearly increased contents is located upwards in the sedimentary column (Fig. 3). This is consistent with the results obtained in sediment cores collected from the Bilbao estuary, main industrialised area of the Basque Country, which indicated that Cr and Ni entered into the estuarine domains later in time (Cearreta et al., 2002). Finally, it is noteworthy that values of Mn/Al with depth mimic the behaviour observed for the other trace metals, showing a gradual increase above 10 cm depth (Fig. 3). Mn is a redox-sensitive element that has been extensively used to test potential post-depositional remobilization in sediment cores, given that it can be solubilized in the anoxic environment and redeposited in the upper oxic layers (Valette-Silver, 1993; McKay et al., 2007; Kuzyk et al., 2017). In fact, previous studies developed on sediments from the French sector of the Bay of Biscay have identified marked peaks of this element in the upper section of the cores (at depths between 0 and 5 cm) related to early diagenetic processes, with maximum contents located at the oxygen penetration depth (Hyacinthe et al., 2001; Mouret et al., 2009; Boutier et al., 2011). Notwithstanding this, in this core potential diagenetic effects are likely to be masked by anthropogenic inputs of Mn (frequently used in steelmaking), as enhanced concentrations of this element (accompanied by high contents of other pollutants such as Zn, Pb or Cu) have been detected in coastal and estuarine sediments from the Basque Country (Ramos et al., 1990; Tueros et al., 2009; Larreta et al., 2012; Legorburu et al., 2013a; Rodríguez-Iruretagoiena et al., 2016; Garmendia et al., 2019), particularly in areas of slag disposal adjacent to the Bilbao estuary (Borja et al., 2008).

Assuming the constant flux of $^{210}Pb_{xs}$ and the CF:CS model, a constant mass accumulation rate of 97 ± 6 mg cm^{-2} yr^{-1} was estimated. Calculation of the metal fluxes for sediments deposited before 1880 CE, which are supposed to represent pre-industrial contributions, yielded the following values (in mg m^{-2} yr^{-1}): 407 for Zn, 116 for Pb, 68 for Cu, 136 for Cr and 1,510 for Mn. These values are within the ranges proposed by Álvarez-Vázquez et al. (2017) as natural fluxes for estuarine sediments of Galician Rias (northwestern Spain). However, the intense industrialization of the Basque coastal area is likely to have resulted in an increase of the metal fluxes to the BMP, since they are currently around 6 times higher for Pb, 4 for Zn, 3.5 for Cu, 2 for Mn and 1.5 for Cr.

4.2. Cores KI-03 and KI-06

Sediments from cores KI-03 and KI-06 are composed by fine-grained materials (13.7-19.2 µm and 14.1-16.6 µm respectively) and exhibit almost constant contents of

$CaCO_3$ (19.6-23.0% and 17.2-19.7% respectively) and evidences of bioturbation (deformed horizontal lamination) (Champilou, 2005).

In both cores distribution patterns of Al-normalised concentrations of Mn and trace metals with depth bear striking similarities (Fig. 5). They show low values in bottom sediments, which increase irregularly upwards until reaching constant levels in the upper layer (about 10 cm thick). These flattened uppercore profiles are likely to reflect not only the anthropogenic inputs of metals during the last decades, but also the homogenization effect exerted by biomixing. The only exception to this trend is Mn, which exhibits enhanced contents in surface samples. This enrichment could be related to the diagenetic remobilization of this element from reducing subsurface sediment layers and the subsequent precipitation upwards under oxic conditions. Moreover, in both cores there is a marked horizon at 16 cm depth with elevated Al-normalised concentrations of Mn, Zn, Cu and Pb, which can reflect both an anthropogenic origin (an episode of contamination) or a post-depositional effect (migration of the redox front and scavenging of metals by Fe-Mn oxyhydroxides). Therefore, further studies involving pore waters and metal speciation should be made in this area to gain insight into the Mn redox cycling, as it can lead to remobilization of elements within the sedimentary column and trigger/accelerate the transfer of trace elements from sea water (Tribovillard et al., 2006).

A total number of 81 different foraminiferal species were found in both cores. The relative abundance of porcellaneous (average 3.4%, range 0.6-6.9%) and agglutinated tests (1.6%, 0.3-4.6%) was minor compared to dominant hyaline forms (95.0%, 90.9-99.1%). The average number of species per sample was 37 (range 22-54) and those taxa present more abundantly in all samples were *Bolivina difformis* (11.2%, 4.5-19.5%), *Bolivina spathulata* (10.6%, 2.3-19.9%), *Globocassidulina subglobosa* (9.1%, 2.8-20.4%), *Bolivina pseudoplicata* (7.6%, 3.8-10.5%), *Rosalina irregularis* (7.1%, 3.2-16.1%), *Gavelinopsis praegeri* (7.1%, 2.7-10.9%), *Cibicidoides lobatulus* (6.9%, 3.6-11.8%), *Cassidulina laevigata* (5.3%, 1.9-10.3%), *Bulimina marginata* (4.4%, 3.2-5.7%)

and *Hyalinea balthica* (2.3%, 0.3-5.4%) (Fig. 6). This assemblage is made mainly of species tolerant to low oxygen conditions and does not exhibit a significant variation through time along the cores. Pascual et al. (2008) and Martínez García (2012) found these same taxa as dominant in the surface samples of this muddy area.

Forty different pollen taxa were observed in both cores. Tree pollen shows the greatest dominance (83.5%, range 63.9-96.6%) whereas herbaceous (10.7%, 2.8-23.2%) and shrub (5.8%, 0.6-14.9%) pollen are secondary (Fig. 7). Hydro-hygrophytes (27.4%, 9.4-47.1%) and NPPs (1.8%, 0.3-4%) were also present in the samples but not included into the terrestrial pollen sum. The most significant taxa along both cores were *Pinus pinaster* (63.3%, 34.7-84.8%), Cyperaceae (6.3%, 1-14.5%), Deciduous *Quercus* (6.3%, 1.9-14.1%), *Pinus sylvestris* type (5.5%, 1.5-13.2%), Apiaceae (4.5%, 0.4-13.9%), *Erica* type (3.0%, 0.2-8.5%), *Betula* (2.6%, 0.8-6.5%), *Alnus* (2.2%, 0.6-5.9%), Poaceae (1.8%, 0.4-5.7%), *Arbutus* type (1.6%, 0.2-4.6%) and Cichorioideae (1.5%, 0.2-3.6%). There is a progressive increase in coniferous species (*P. pinaster* and *P. sylvestris* type) with time and a parallel reduction of Deciduous *Quercus*, herbaceous (Apiaceae and Poaceae) and shrub (*Arbutus* type and *Erica* type) taxa. It should be noted the testimonial appearance of *Eucalyptus* in some of the most superficial samples, a clearly exotic taxon introduced since mid-20th century for economic reasons.

4.3. Environmental assessment

According to Ridgway and Shimmield (2002), for most temperate zones the evidence suggests that the impacts of contaminated sediments on shelf seas tend to be small and largely confined to the coastal area adjacent to the estuaries, given that contaminants present in the suspended sediment load are rapidly spread and diluted by mixing with less contaminated marine sediment. However, results obtained in the studied cores reflect an increasing trend in metal concentrations. Table 1 provides an overview of the different background values proposed for coastal sediments of the Basque Country (Legorburu et al., 1989; Cearreta et al., 2002; Rodríguez et al., 2006) and the North-East Atlantic (OSPAR, 2006). It is well known that factors such as particle size, mineral composition and organic carbon content of the samples, as well as the analytical method used, can condition to a great extent the estimation of pre-industrial references and probably explain the observed differences. Therefore, in this work the consistently low concentrations found in downcore samples have been considered to represent pre-industrial conditions and, in order to provide a means to assess the relative role of anthropogenic impact on the BMP, enrichment factors have been calculated as follows (Herut and Sandler, 2006):

Enrichment factor (EF): [X(s)/Al(s)] / [X(b)/Al(b)]

where X is metal concentration, (s) is sample, and (b) is background value.

Ranges of metal concentrations in the three cores are very similar (Table 1), with the highest EFs oscillating between 1.3 and 1.4 for Cr, 1.9-2.2 for Mn, 2.5-3.2 for Cu, 2.9-3.8 for Zn and 4.7-5.8 for Pb. However, it is noticeable that, contrary to that observed in the historically polluted sediments from some Basque estuaries (Ramos et al, 1990; Cearreta et al., 2018; Irabien et al., 2018; 2019), metal contents in samples from the BMP do not exceed in any case the effects range-median (ERM) values proposed by Long et al. (1995) as sediment quality guidelines (see Table 1), which represent conditions where adverse biological effects occur frequently. In fact, levels of Cu and Cr in all samples remain even below the effect range-low (ERL) values, which correspond to concentrations below which adverse biological effects are rarely observed. Based upon this evaluation, Pb and Zn appear as main contaminants of environmental concern in this area, given that they exhibit concentrations above the ERLs and below the ERMs until 6 cm depth in core KS-04 and until 10 cm depth in cores KI-03 and KI-06. Therefore, they enter the "possible-effects" range, within which adverse biological effects would occasionally occur. In fact, foraminiferal assemblages do not show any significant variation through time in the cores despite trace metal concentrations increase towards more recent times. This situation was previously observed in the recent sedimentary record of the Bilbao estuary, where Cearreta et al.

(2002) concluded that occurrence of foraminifera in the recent industrial zones and along the modern estuary was not related to defined levels of trace metals.

As expected, concentrations of metals in the BMP are distinctly lower than those determined in some Basque estuaries (Belzunce et al., 2004; Montero et al., 2013), where high amounts of contaminated sediments remain accumulated (Cearreta et al., 2002; 2018). Nevertheless, an overall improvement in estuarine sediment quality has been observed over the last years as a consequence of the decrease of contaminant disposal activities and the implementation of efficient systems for wastewater treatment (Leorri et al., 2008; Tueros et al., 2009; Legorburu et al., 2013b). In historically polluted areas such as the Bilbao estuary, the study of sediment cores indicates that the gradual deposition of "cleaner" sediments is leading to a marked decline in trace metal concentrations towards recent samples (Irabien et al., 2018; 2019). Unfortunately, no similar trends can be recognised in cores from the BMP (Figs. 3 and 5).

Regarding the dynamics of the vegetation, the progressive increase of coniferous taxa is indicative of their extensive plantations carried out on the Cantabrian coastal area since the end of the 19th century resulting in the continuous decrease of authocthonous Deciduous *Quercus*. This was exacerbated from the 1940s, when the "National Reforestation Plan" was launched (Michel Rodríguez, 2006).

5. Conclusions

This work confirms that the influence of the anthropogenic activities developed in the Basque coast since late 19th century extends to the marine environment, where muddy deposits (BMP) act as a trap for the chemicals released. The similarity between the results obtained in the three studied cores seems to reflect that Mn and trace metals are widely distributed over the BMP. As expected, due to the mixing with uncontaminated marine sediments, concentrations are significantly lower than those determined historically in the nearby estuaries, which are the main source of sediments to the shelf. However, and contrary to that determined in these estuarine areas, no significant improvement is observed in recent times, probably as a consequence of the low sedimentation rates and the disturbing effects of biomixing processes. Therefore, confirming the extent of contamination within marine muddy deposits and monitoring its evolution in the future appear as essential tasks for the environmental assessment and responsible management of continental shelves adjacent to industrialised areas.

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References

Álvarez-Iglesias, P., Quintana, B., Rubio, B., Pérez-Arlucea, M. 2007. Sedimentation rates and trace metal history in intertidal sediments from San Simon Bay (Ria de Vigo, NW Spain) derived from ^{210}Pb and ^{137}Cs chronology. J. Environ. Radioactivity 98, 229-250. https://doi.org/10.1016/j.jenvrad.2007.05.001

Álvarez-Vázquez, M.A., Caetano, M., Álvarez-Iglesias, P., Pedrosa.García, M.C., Calvo, S., De Uña-Álvarez, E., Quintana, B., Vale, C., Prego, R. 2017. Natural and Anthropocene fluxes of trace elements in estuarine sediments of Galician Rias. Estuar. Coast. Shelf Sci. 198, 329-342.https://doi.org/10.1016/j.ecss.2016.08.022

Appleby, P.G., Oldfield, F. 1992. Applications of 210Pb to sedimentation studies. In: Ivanovich, M., Harmon, R.S. (Eds.), Uranium-series disequilibrium. Applications to

Earth, Marine and Environmental Sciences, second ed. Oxford Science, Oxford. pp 731-778.

Azaroff, A., Miossec, C., Lanceleur, L., Guyoneaud, R., Monperrus, M. 2020. Priority and emerging micropollutants distribution from coastal to continental slope sediments: A case study of Capbreton Submarine Canyon (North Atlantic Ocean). Sci. Total Environ. 703, 135057. https://doi.org/10.1016/j.scitotenv.2019.135057

Belzunce, M.J., Solaun, O., González Oreja, J.A., Millán, E., Pérez, V. 2004. Contaminants in sediments. In: Borja, A., Collins, M. (Eds.), Environment of the Basque Country. Elsevier Oceanography Series 70,283-315.

Bilbao, L.M. 1983. La siderurgia vasca, 1700-1885. Atraso tecnológico, política arancelaria y eficiencia económica. In: Antecedentes próximos de la sociedad vasca actual. Siglos XVIII y XIX. Actas del IX Congreso de Estudios Vascos. Sociedad de Estudios Vascos/Eusko Ikaskuntza, pp 81-93. http://www.eusko-ikaskuntza.eus/es/publicaciones/la-siderurgia-vasca-1720-1885-atraso-tecnologico-politica-arancelaria-y-eficiencia-economica/art-8850/ (accesed January 2020)

Borja, A., Tueros, I., Belzunce, M.J., Galparsoro, I., Garmendia, J.M., Revilla, M., Solaun, O., Valencia, V. 2008. Investigative monitoring within the European Water Framework Directive: a coastal blast furnace slag disposal, as an example. J. Environ. Monit. 10, 453-462. https://doi.org/10.1039/b801269e

Borja, A., Chust, G., Rodríguez, J.G., Bald, J., Belzunce-Segarra, M.J., Franco, J., Garmendia, J.M., Larreta, J., Menchaca, I., Muxika, I. Solaun, O., Revilla, M., Uriarte, A., Valencia, V., Zorita, I. 2016. “The past is the future of the present”: learning from long-time series of marine monitoring. Sci. Total Environ. 566-567, 698-711. https://doi.org/10.1016/j.scitotenv.2016.05.111

Boutier, B., Quintin, J.Y., Rozuel, D., Dominique, A., Bretaudeau-Sanjuan, J. 2001. Retrospective study of metal contamination time trends in the French part of the Bay of Biscay. Environ. Technol. 33, 1807-1815.

Castaing, P., Allen, G.P. 1981. Mechanisms controlling seaward escape of suspended sediments from the Gironde: A macrotidal estuary in France. Mar. Geol. 40, 101-118. https://doi.org/10.1016/0025-3227(81)90045-1

Cearreta, A., Irabien, M.J., Ulibarri, I., Yusta, I., Croudace, I.W., Cundy, A.B. 2002. Environmental transformation of the Bilbao estuary, N. Spain: microfaunal and geochemical proxies in the recent sedimentary record. Mar. Pollut. Bull. 44, 487-503. https://doi.org/10.1016/S0025-326X(01)00261-2

Cearreta, A., Irabien, M.J., Pascual, A. 2004. Human activities along the Basque coast during the last two centuries: geological perspective of recent anthropogenic impact on the coast and its environmental consequences. In: Borja, A., Collins, M. (Eds.), Environment of the Basque Country. Elsevier Oceanography Series 70, 27–50.

Cearreta, A., García-Artola, A., Leorri, E., Irabien, M.J., Masque, P. 2013. Recent environmental evolution of regenerated salt marshes in the southern Bay of Biscay: anthropogenic evidences in their sedimentary record. J. Mar. Syst. 109–110, S203-S212. https://doi.org/10.1016/j.jmarsys.2011.07.013

Cearreta, A., Irabien, M.J., Gómez-Arozamena, J. 2018. Transformación antrópica reciente de la bahía de Pasaia (Guipúzcoa): análisis multidisciplinar de su registro sedimentario. Geogaceta 64, 107-110.

Champilou, N. 2005. Modelités de la sédimentation actuelle de la vasière de plateau LOI-GUNEA. Rapport de stage de master 2 ENVOLH. Université de Bordeaux. 28 pp.

Chiocci, F.L., Chivas, A.R. 2014. An overview of teh continental shelves of the World. In: Chiocci, F.L., Chivas, A.R. (Eds), Continental shelves of the world: their evolution during the Last Glacio-Eustatic Cycle. Geological Society, London, Memoirs 41, 1-5. https://doi.org/10.1144/M41.1

Chust, G., Borja, A., Liria, P., Galparsoro, I., Marcos, M., Caballero, A., Castro, R. 2009. Human impacts overwhelm the effects of sea-level rise on Basque coastal habitats (N Spain) between 1954 and 2004. Estuar. Coast Shelf Sci. 84, 453-462. https://doi.org/10.1016/j.ecss.2009.07.010

Cochran, K.J. 1985. Particle mixing rates in sediments from the eastern equatorial Pacific: Evidence from ^{210}Pb, ^{239,240}Pu and ^{137}Cs distribution at MANOP sites. Geochim. Cosmochim. Acta 49, 1195-1210. https://doi.org/10.1016/0016-7037(85)90010-9

Cochran, K.J., McKibbin-Vaughan, T., Dornblaser, M.M., Hirschberg, D., Livingston, H.D., Buesseler, K.O. 1990. ^{210}Pb scavenging in the North Atlantic and North Pacific Oceans. Earth Planet. Sc. Lett. 97, 332-352. https://doi.org/10.1016/0012-821X(90)90050-8

Covault, J.A., Fildani, A. 2014. Continental shelves as sediment capacitors or conveyors: source-to-sink insights from the tectonically active Oceanside shelf, southern California, USA. In: Chiocci, F.L., Chivas, A.R. (Eds), Continental shelves of the world: their evolution during the Last Glacio-Eustatic Cycle. Geological Society, London, Memoirs 41, 315-326. https://doi.org/10.1144/M41.23

Crusius, J., Bothner, M.H., Sommerfield, C. 2004. Bioturbation depths, rates and processes in Massachusetts Bay sediments inferred from modelling of ^{210}Pb, and $^{239+240}$Pu profiles. Estuar. Coast. Shelf Sci. 61, 643-655. https://doi.org/10.1016/j.ecss.2004.07.005

Cugny, C., Mazier, F., Galop, D. 2010. Modern and fossil non-pollen palynomorphs from the Basque mountains (western Pyrenees, France): the use of coprophilous fungi to reconstruct pastoral activity. Veg. Hist. Archaeobot. 19, 391–408.

De Buen, F. 1933. Campaña del Xauen en aguas de Gipúzcoa (Julio-Agosto 1932). Notas y Resúmenes del Instituto Español de Oceanografía, ser. II, 72, 1-40.

Díaz-Somoano, M., Suárez-Ruiz, I., Alonso, J.I.G., Ruiz Encinar, J., López-Antón, M.A., Martínez-Tarazona, M.R. 2007. Lead isotope ratios in Spanish coals of different characteristics and origin. Int. J. Coal Geol. 71, 28-36. https://doi.org/10.1016/j.coal.2006.05.006

Douglass, W.A., Bilbao, J. 2005. Amerikanuak: Basques in the New World. University of Nevada Press, 519 p.

Dubrulle, C., Jouanneau, J.M., Lesueur, P., Bourillet, J.F., Weber, O. 2007. Nature and rates of fine-sedimentation on a mid-shelf: "La Grande Vasière" (Bay of Biscay, France. Cont. Shelf. Res. 26, 2099-2115.https://doi.org/10.1016/j.csr.2007.05.002

Elbaz- Poulichet, F., Holliger, P., Huang, W.W., Martin, J.M. 1984. Lead cycling in estuaries, illustrated by the Gironde estuary, France. Nature 308, 409-414.

Fernández Martín-Consuegra, A. 2018. Cambios oceanográficos en el Cuaternario final detectados por medio de microfauna frente al Geoparque de la Costa Vasca (sur del Golfo de Vizcaya). Estudios de Cuaternario CKQ 8, 35-64.

Förstner, U. 2002. Sediment sampling, sample preparation, grain size corrections, and chemical criteria. In: Burden, F.R., McKelvie, I., Förstner, U, Guenther, A. (Eds), Environmental Monitoring Handbook. McGraw-Hill. Chapter 14.

Galparsoro, I., Borja, A., Legorburu, I., Hernández, C., Chust, G., Liria, P., Uriarte, A. 2010. Morphological characteristics of the Basque continental shelf (Bay of Biscay, northern Spain): their implications for Integrated Coastal Zone Management. Geomorphology 118, 314-329. https://doi.org/10.1016/j.geomorph.2010.01.012

Garmendia, M., Fdez-Ortiz de Vallejuelo, S., Liñero, O., Gredilla, A., Arana, G., Soto, M., de Diego, A. 2019. Long term monitoring of metal pollution as a tool to investigate the effect of engineering works in estuaries. A case study, the Nerbioi-Ibaizabal estuary (Bilbao, Basque Country). Mar. Pollut. Bull. 145, 55-563. https://doi.org/10.1016/j.marporbul.2019.06.051

Goeury, C., de Beaulieu, J.L. 1979. À propos de la concentration du pollen à l'aide de la liqueur de Thoulet dans les sédiments minéraux. Pollen et Spores 21, 239–251.

Goldberg, E.D. 1963. Geochronology with lead-210. In: Radioactive dating, IAEA, Vienna, 121-131.

Hancock, G.J., Leslie, C., Everett, S.E., Tims, S.G., Brunskill, G.J., Haese, R. 2011. Plutonium as a chronomarker in Australian and New Zealand sediments: a comparison with 137Cs. J. Environ. Radioactivity 102, 919-929. https://doi.org/10.1016/j.jenvrad.2009.09.008

Herut, B., Sandler, A. 2006. Normalization methods for pollutants in marine sediments: review and recommendations for the Mediterranean. IOLR Report H18/2006, 23 pp.

Hanebuth, T.J.J., Lantzsch, H., Nizou, J. 2015. Mud depocenters on continental shelves - appearance, initiation times, and growth dynamics. Geo-Mar. Lett. 35, 487-503.

Ho, H.H., Swennen, R., Cappuyns, V., Vassilieva, E., Van Tran, T. 2012. Necessity of normalization to assess the contamination by heavy metals and arsenic in sediments near Haiphong Harbor, Vietnam. J. Asian Earth Sci. 56, 229-239. https://doi.org/10.1016/j.jseaes.2012.05.015

Holby, O., Evans, S. 1996. The vertical distribution of Chernobyl-derived radionuclides in a Baltic Sea sediment. J. Environ. Radioactivity, 33, 129-145. https://doi.org/10.1016/0265-931X(95)00089-S

Hyacinthe, C., Anschutz, P., Carbonel, P., Jouanneau, J.M., Jorissen, F.J. 2001. Early diagenetic processes in the muddy sediments of the Bay of Biscay. Mar. Geol. 177, 111-128. https://doi.org/10.1016/S0025-3227(01)00127-X

IHOBE, 2017. Climate change in the Basque Country: 28 best practices. 68 pp. In: https://www.regions4.org/resources/climate-change-in-basque-country-28-good-practices/

Irabien, M.J., García-Artola, A., Cearreta, A., Leorri, E. 2015. Chemostratigraphic and lithostratigraphic signatures of the Anthropocene in estuarine areas from the eastern Cantabrian coast (N. Spain). Quat. Int. 364, 196-205. https://doi.org/10.1016/j.quaint.2014.08.056

Irabien, M.J., Cearreta, A., Serrano, H., Villasante-Marcos, V. 2018. Environmental regeneration processes in the Anthropocene: The Bilbao estuary case. Mar. Poll. Bull. 135, 977-987. https://doi.org/10.1016/j.marpolbul.2018.08.022

Irabien, M.J., Cearreta, A., Gómez-Arozamena, J., Serrano, H., Sanchez-Cabeza, J.A., Ruiz-Fernández, A.C. 2019. Geological record of extreme floods and anthropogenic impacts on an industrialised bay: The Inner Abra of Bilbao (northern Spain). Sci. Total Environ. 696, 133946. https://doi.org/10.1016/j.scitotenv.2019.133946

Jaakkola, T., Tolonen, T., Huttunen, P., Leskinen, S. 1983. The use of fallout ^{137}Cs and $^{239/240}Pu$ for dating of lake sediments. In: Meriläinen, J., Huttunen, P., Battarbee, R.W. (eds) Paleolimnology, Developments in Hydrobiology 15, 15-18.

Johannessen, S.C., Macdonald, R.W. 2012. There is no 1954 in that core! Interpreting sedimentation rates and contaminant trends in marine sediment cores. Mar. Pollut. Bull. 64, 675-678. https://doi.org/10.1016/j.marpolbul.2012.01.026

Jouanneau, J.M., Weber, O., Champilou, N., Cirac, P., Muxika, I., Borja, A., Pascual, A., Rodríguez-Lázaro, J., Donard, O. 2008. Recent sedimentary study of the shelf of the Basque Country. J. Mar. Sys. 72, 397-406. doi: 10.1016/j.jmarsys.2007.03.013

Jouanneau, J.M., Weber, O., Latouche, C., Vernet, J.P., Dominik, J. 1989. Erosion, non-deposition and sedimentary processes through a sedimentological and radioisotopic study of surficial sediments from the "Ouest-Gironde vasière" (Bay of Biscay). Cont. Shelf Res. 9, 325-342. https://doi.org/10.1016/0278-4343(89)90037-X

Koide, M., Bruland, K.W., Goldberg, E.D. 1973. Th-228/Th-232 and Pb-210 geochronologies in marine and lake sediments. Geochim. Cosmochim. Acta 37, 1171-1187

Krishnaswami, S., Lal, D., Martin, J., Meybeck, M. 1971. Geochronology of lake sediments. Earth Planet. Sci. Lett. 11, 407–414.

Kuzyk, Z.Z.A., Gobeil, C., Goñi, M.A., Macdonald, R.W. 2017. Early diagenesis and trace element accumulation in North American Artic margin sediments. Geochim. Cosmochim. Acta 203, 175-200. https://doi.org/10.1016/j.gca.2016.12.015

Laffon, B., Rábade, T., Pásaro, E., Méndez, J. 2006. Monitoring of the impact of *Pr*estige oil spill on *Mytilus galloprovincialis* from Galician coast. Environ. Inter. 32, 342-348. https://doi.org/10.1016/j.envint.2005.07.002

Larreta, J., Solaun, O. Menchaca, I., Rodríguez, J.G., Valencia, V. 2012. Estado de la contaminación en los sedimentos de los estuarios del País Vasco (1998-2001 / 2009-2012). Technical Report of AZTI-Tecnalia, URA, 223 pp.

Legorburu, I., Ramos, A., Sola, M. 1989. Heavy metals in coastal sediments in Guipuzcoa (Spain). Toxicol. Environ. Chem. 23, 129-134.

Legorburu, I., Galparsoro, I., Larreta, J., Rodríguez, J.G., Borja, A. 2013a. Spatial distribution of metal accumulation areas on the continental shelf of the Basque Country (Bay of Biscay): a GIS-based approach. Estuar. Coast. Shelf Sci. 134, 162-173. https://doi.org/10.1016/j.ecss.2013.05.024

Legorburu, I., Rodríguez, J.G., Borja, A., Menchaca, I., Solaun, O., Valencia, V., Galparsoro, I., Larreta, J. 2013b. Source characterization and spatio-temporal evolution of the metal pollution in the sediments of the Basque estuaries (Bay of Biscay). Mar. Pollut. Bull. 66, 25-38. https://doi.org/10.1016/j.marpolbul.2012.11.016

Lesueur, P., Jouanneau, J.M., Boust, D., Tastet, J.P., Weber, O. 2001. Sedimentation rates and fluxes in the continental shelf mud fields in the Bay of Biscay (France). Cont. Shelf Res. 21, 1383-1401. https://doi.org/10.1016/S0278-4343(01)00004-8

Lesueur, P., Tastet, J.P., Weber, O. 2002. Origin and morphosedimentary evolution of fine-grained modern continental shelf deposits: the Gironde mud fields (Bay of Biscay, France). Sedimentology 49, 1299-1320.

Leorri, E., Cearreta, A., Irabien, M.J., Yusta, I. 2008. Geochemical and microfaunal proxies to assess environmental quality conditions during the recovery process of a heavily polluted estuary: The Bilbao estuary case (N. Spain). Sci. Total Environ. 396, 12-27. https://doi.org/10.1016/j.scitotenv.2008.02.009

Leorri, E., Mitra S., Irabien M.J., Zimmerman A.R., Blake, W.H., Cearreta, A. 2014. A 700 yr record of combustion-derived pollution in northern Spain: tools to identify the Holocene/Anthropocene transition in coastal environments. Sci. Total Environ. 470-471, 240-247. https://doi.org/10.1016/j.scitotenv.2013.09.064

Livingston, H.D., Bowen, V.T. 1979. Pu and ^{137}Cs in coastal sediments. Earth Planet. Sc. Lett. 43, 29-45. https://doi.org/10.1016/0012-821X(79)90153-5

Loeblich, A.R., Tappan, H. 1998. Foraminiferal genera and their classification. Van Nostrand Reinhold Company, New York. 970 pp.

Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manage. 19, 81-97.

Mahiques, M.M., Hanebuth, T.J.J., Martins, C.C., Montoya-Montes, I., Alcántara-Carrió, J., Figueira, R.C.L., Bícego, M.C. 2016. Mud depocentres on the continental shelf: a neglected sink for anthropogenic contaminants for the coastal zone. Environ. Earth Sci. 75, 1-12.

Martínez García, B.M. 2012. Cambios oceanográficos y climáticos en el sur del Golfo de Vizcaya durante el Cuaternario final, detectados por medio de foraminíferos y ostrácodos. Unpublished PhD dissertation, University of the Basque Country UPV/EHU, 433 p.

McKay, J.L., Pedersen, T.F., Mucci, A. 2007. Sedimentary redox conditions in continental margin sediments (N.E. Pacific) – Influence on the accumulation of redox-sensitive trace metals. Chem. Geol. 238, 180-196. https://doi.org/10.1016/j.chemgeo.2006.11.008

Mengual, B., Le Hir, P., Cayocca, F., Garlan, T. 2019. Bottom trawling contribution to the spatio-temporal variability of sediment fluxes on the continental shelf of the By of Biscay (France). Mar. Geol. 414, 77-91. https://doi.org/10.1016/j.margeo.2019.05.009

Michel Rodríguez, M. 2006. El Pino radiata en la historia forestal vasca: Análisis de un proceso de forestalismo intensivo. Munibe Sup. 23, 10-11.

Mil-Homens, M., Stevens, R.L., Boer, W., Abrantes, F., Cato, I. 2006. Pollution history of heavy metals on the Portuguese shelf using 210Pb chronology. Sci. Total Environ. 367, 466-480. https://doi.org/10.1016/j.scitotenv.2006.03.042

Mojtahid, M., Durand, M., Coste, P.O., Toucanne, S., Howa, H., Nizou, J., Eynaud, F., Penaud, A. 2019. Millenial-scale Holocene hydrological changes in the northeast Atlantic: New insights from *"La Grande Vasière"* mid-shelf mud belt. Holocene 29, 467-480.

Monna, F., Lancelot. J., Coudace, I., Cundy, A., Lewis, J.T. 1997. Pb isotopic composition of airborne particulate matter from France and the United Kingdom: implications for Pb pollution sources in urban areas. Environ. Sci. Technol. 31, 2277-2286.

Montero, N., Belzunce-Segarra, M.J., Del campo, A., Garmendia, J.M., Ferrer, L., Larreta, J., González, M., Maidana, M.A., Espino, M. 2013. Integrative environmental assessment of the impact of the Pasaia harbour on the Oiartzun estuary (southern Bay of Biscay). J. Mar. Sys. 109-110, S252-S260.

Moon, D.S., Hong, G.H., Baskaran, M., Chung, C.S., Kim, S.H., Lee, H.J., Lee, S.H., Povinec, P.P. 2003. Accumulation of anthropogenic and natural radionuclides in bottom sediments of the Northwest Pacific Ocean. Deep-Sea Res Pt II 50, 2649-2673. https://doi.org/10.1016/S0967-0645(03)00140-1

Moore, P.D., Webb, J.A., Collinson, M.E. 1991. Pollen analysis. Blackwell, London. 216 pp.

Mouret, A. Anschutz, P., Lecroart, P. Chillou, G. Hyacinthe, C., Deborde, J., Jorissen, F.J., Deflandre, B., Schmidt, D., Jouanneau, J.M. 2009. Benthic geochemistry of manganese in the Bay of Biscay, and sediment accumulation rate. Geo-Mar. Lett. 29, 133-149.

Nittrouer, C.A., Austin, J.A., Field, M.E., Kravitz, J.H., Syvitski, J.P.M., Wiberg, P.L. 2007. Writing a Rosetta Stone: insights into continental-margin sedimentary processes and strata. In: Nittrouer, C.A., Austin, J.A., Field, M.E., Kravitz, J.H., Syvitski, J.P.M., Wiberg, P.L. (Eds) Continental margin sedimentation: From sediment transport to sequence stratigraphy. IAS Spec. Publ. 37, 1-48.

OSPAR. 2006. Overview of OSPAR assessments 1998-2006. Monitoring and Assessment Series, 89 pp.

Pascual, A., Cearreta, A., Rodríguez-Lázaro, J., Uriarte, A. 2004. Geology and Palaeogeography. In: Borja, A., Collins, M. (Eds), Oceanography and Marine Environment in the Basque Country. Elsevier Oceanographic Series 70, 52-73.

Pascual, A., Rodríguez-Lázaro, J., Martín-Rubio, M., Jouanneau, J.M., Weber, O. 2008. A survey of the benthic microfauna (foraminifera, Ostracoda) on the Basque shelf, southern Bay of Biscay. J. Mar. Sys. 72, 35-63. https://doi.org/10.1016/j.jmarsys.2007.05.015

Pfitzner, J., Brunskill, G., Zagorskis, I. 2004. ^{137}Cs and excess ^{210}Pb deposition àtterns in estuarine and marine sediment in the central region of the Great Barrier Reef lagoon, north-eastern Australia. J. Environ. Radioactivity 76, 81-102. https://doi.org/10.1016/j.jenvrad.2004.03.020

Qiao, S., Shi, X., Wang, G., Zhou, L., Hu, B., Hu, L., Yang, G., Liu, Y., Yao, Z., Liu, S. 2017. Sediment accumulation and budget in the Bohai Sea, Yellow Sea and East China Sea. Mar. Geol. 390, 270-281. https://doi.org/10.1016/j.margeo.2017.06.004

Ramos, A., Legorburu, I., Millán, E. 1990. Impacto ambiental por metales pesados en sedimentos superficiales de los estuarios exteriores de Guipuzcoa. Lurralde 13, 157-164.

Reille, M. 1992. Pollen et spores d'Europe et d'Afrique du Nord. Laboratoire de Botanique Historique et Palynologie, Marseille. 520 pp.

Rey, J.J., Mendialdea, T. 1989. Los sedimentos cuaternarios superficiales del margen continental español. Publicaciones Especiales del Instituto Español de Oceanografía, 3, 29 pp.

Ridgway, J., Shimmield, G. 2002. Estuaries as repositories of historical contamination and their impact on shelf seas. Estuar. Coast. Shelf Sci. 55, 903-928. https://doi.org/10.1006/ecss.2002.103

Robbins, J.A. 1978. Geochemical and geophysical applications of radioactive lead isotopes. In: Nriagu. J.O. (Ed), Biochemistry of Lead. Elsevier, Amsterdam, 85–393.

Robles-López, S., Fernández Martín-Consuegra, A., Pérez-Díaz, S., Alba-Sánchez, F., Abel-Schaad, D., López-Sáez, J.A. 2018. The dialectic between deciduous and coniferous forests in central Iberia: A palaeoenvironmental perspective during the late Holocene in the Gredos range. Quat. Int. 470, 148-165. https://doi.org/10.1016/j.quaint.2017.05.012

Rodriguez, J.G., Tueros, I., Borja, A., Belzunce, M.J., Franco, J., Solaun, O., Valencia, V., Zuazo, A. 2006. Maximum likelihood mixture estimation to determine metal background values in estuarine and coastal sediments within the European Water Framework Directive. Sci. Total Environ. 370, 278-293. https://doi.org/10.1016/j.scitotenv.2006.08.035

Rodriguez-Iruretagoiena, A., Elejoste, N., Gredilla, A., Fdez-Ortiz de Vallejuelo, S., Arana, G., Madariaga, J.M., de Diego, A. 2016. Occurrence and geographical distribution of metals and metalloids in sediments of the Nerbioi-Ibaizabal estuary (Bilbao, Basque Country). Mar. Chem. 185, 82-90. https://doi.org/10.1016/j.scitotenv.2006.08.035

Sáez-Muñoz, M., Ortiz, J., Martorell, S.; Gómez-Arozamena, J., Cearreta, A. 2020. Sequential determination of uranium and plutonium in soil and sediment samples by borate salts fusión. J. Radioanal. Nucl. Chem. 323. https://doi.org/10.1007/s10967-020-07028-5

Schmidt, S., Tronczynski, J., Guiot, N. Lefevre, I. 2005. Dating of sediments in the Biscay bay: implication for pollution chronology. Radioprotection 40, 655-660.

Silverberg, N., Nguyen, H.V., Delibrias, G., Koide, M., Sundby, B., Yokohama, Y., Chesselet, R. 1986. Radionuclide profile, sedimentation rates, and bioturbation in modern sediments of the Laurentian Though, Gulf of St. Lawrence. Oceanol. Acta 9, 285-290.

Tribovillard, N., Algeo, T.J., Lyons, T., Ribolleau, A. 2006. Trace metals as paleoredox and paleoproductivity proxies: An update. Chem. Geol. 232, 12-32. https://doi.org/10.1016/j.chemgeo.2006.02.012

Tueros, I., Borja, A., Larreta, J., Germán Rodríguez, J. Valencia, V., Millán, E. 2009. Integrating long-term water and sediment pollution data in assessing chemical status within the European Water Framework Directive. Mar. Pollut. Bull. 58, 1389-1400. https://doi.org/10.1016/j.marpolbul.2009.04.014

Uriarte, A., Collins, M. Cearreta, A., Bald, J., Evans, G. 2004. Sediment supply, transport and deposition: contemporary and Late Quaternary evolution. In: Borja, A., Collins, M. (Eds), Oceanography and Marine Environment in the Basque Country, Elsevier Oceanographic Series 70, 97-131.

Valette-Silver, N.J. 1993. The use of sediment cores to reconstruct historical trends in contamination of estuarine and coastal sediments. Estuaries 16, 577-588.

Velasco, F., Pesquera, A., Herrero, J.M. 1996. Lead isotope study of Zn-Pb ore deposits associated with the Basque-Cantabrian basin and Paleozoic basement, Northern Spain. Miner. Deposita 31, 84-92.

Véron, A., Flament, P., Bertho, M. L., Alleman, L., Flegal, R., Hamelin, B. 1999. Isotopic evidence of pollutant lead sources in Northwestern France. Atmos. Environ. 33, 3377-3388. https://doi.org/10.1016/S1352-2310(98)00376-8

Viñas, L., Franco, M.A., Soriano, J.A., González, J.J., Pon, J., Albaigés, J. 2010. Sources and distribution of polycyclic aromatic hydrocarbons in sediments from the Spanish northern continental shelf. Assessment of spatial and temporal trends, Environ. Pollut. 158, 1551-1560. https://doi.org/10.1016/j.envpol.2009.12.023

FIGURE CAPTIONS

Fig. 1. a) Simplified map of the Bay of Biscay with the main continental margins (modified from Martínez-García, 2012). b) Sedimentary map of the Basque shelf (modified from Jouanneau et al., 2008) and location of sampling sites (white dots) in the Basque Mud Patch.

Fig. 2. Distribution of $^{210}Pb_{xs}$, ^{137}Cs and $^{239/240}Pu$ (Bq kg^{-1}) with depth in core KS-04.

Fig. 3. Distribution of Al-normalised concentrations of metals with depth in core KS-04.

Fig. 4. a) Dispersion plot of concentrations of Pb versus $^{208}Pb/^{207}Pb$ ratios in samples from core KS-04. b) Dispersion plot for $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{207}Pb$ ratios. Full circles represent sediments from the BMP (this work): grey circles indicate samples deposited before 1880 CE and black ones those deposited later. Full triangles and empty circles are used for pre-industrial samples from Basque (Leorri et al., 2014) and French estuaries (Elbaz-Poulichet et al., 1984; Monna et al., 1997) respectively. Squares represent galenas from the Arditurri district (Velasco et al., 1996). Empty inverted triangles indicate Spanish coals (Alvarez-Iglesias et al., 2007; Díaz-Somoano et al., 2007), whereas diamonds were used for metallurgical emissions from Northwestern France (Véron et al., 1999). Full inverted triangles represent leaded gasolines used in France and the United Kingdom (Monna et al., 1997) and in Spain (Alvarez-Iglesias et al., 2007).

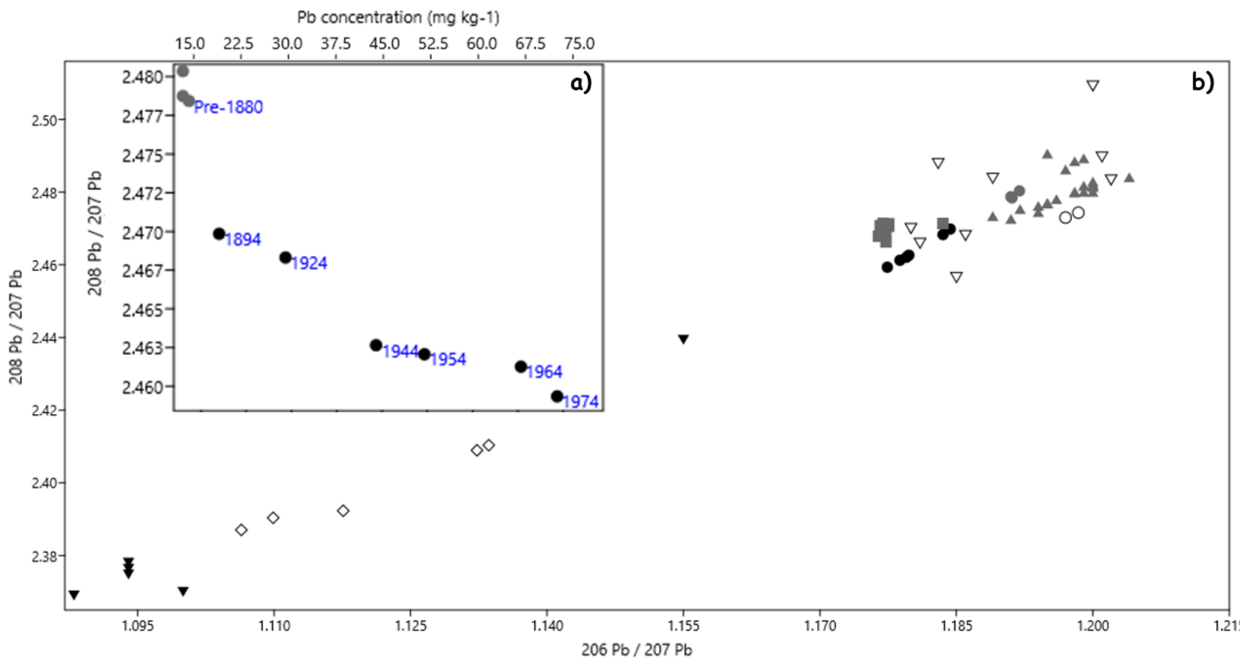
Fig. 5. Distribution of Al-normalised concentrations of metals with depth in cores KI-03 and KI-06.

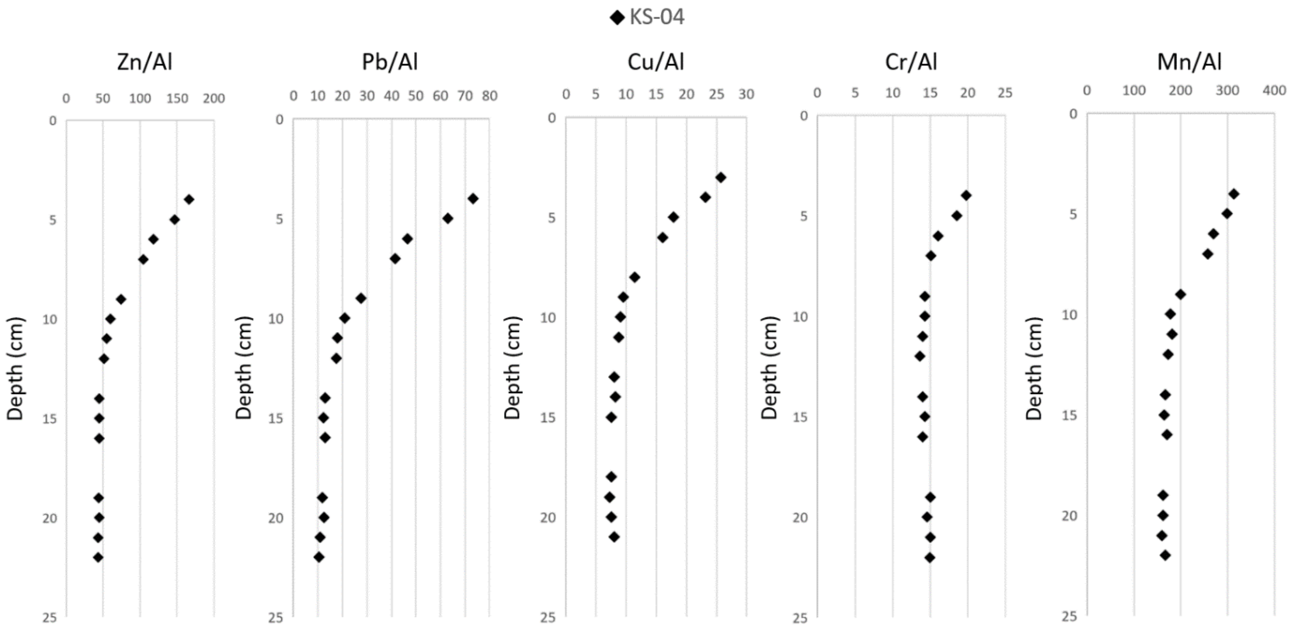
Fig. 6. Relative abundance (%) of dominant foraminiferal species with depth in cores KI-03 (above) and KI-06 (below).

Fig. 7. Palynological diagram of cores KI-03 (above) and KI-06 (below) including the relative abundance of the most representative pollen taxa and NPPs. Black dots indicate the presence of *Eucaliptus* in the upper samples.

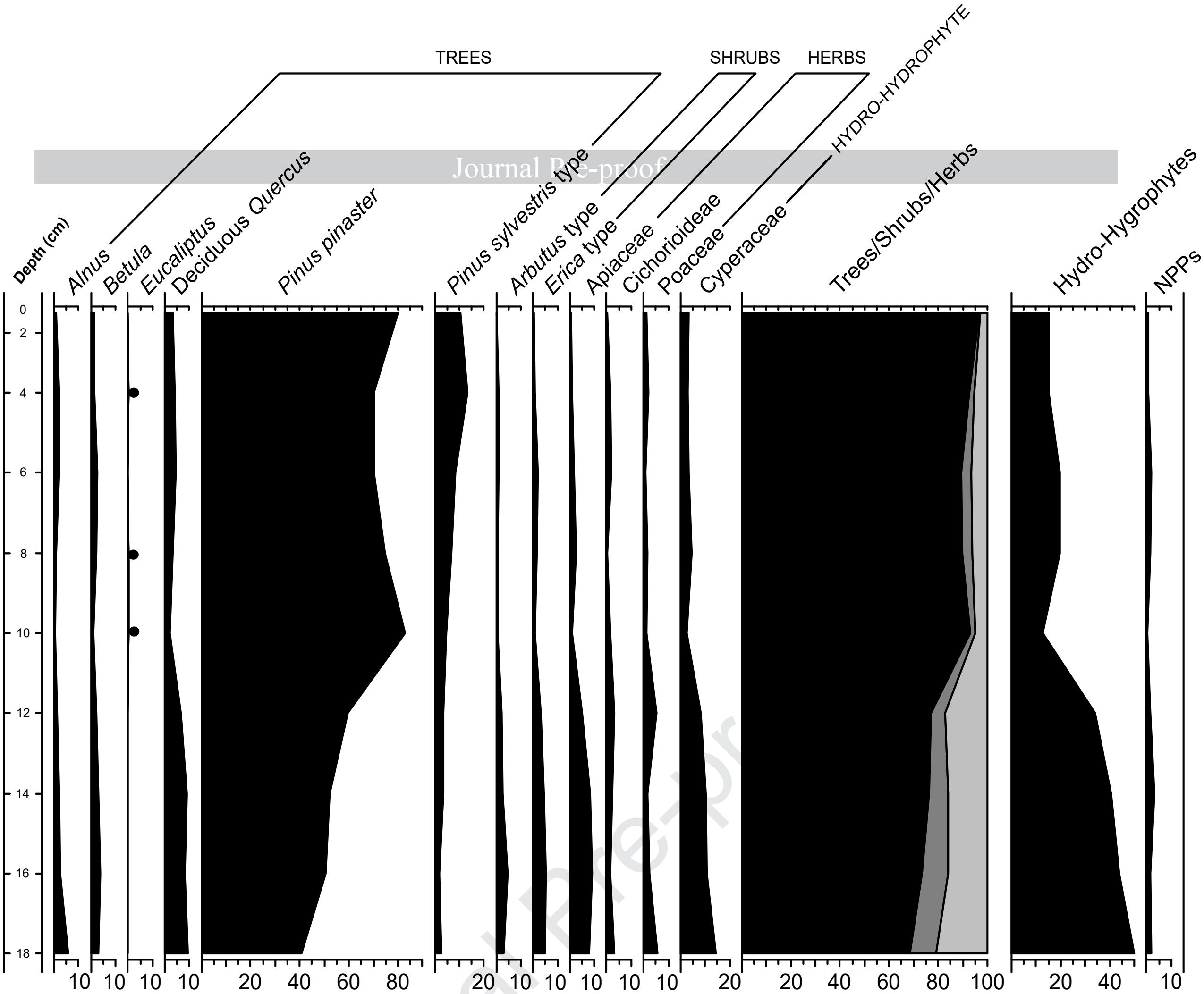
Table 1. Ranges of metal concentrations in the analysed cores, regional pre-industrial values for coastal areas proposed by different authors, mean contents determined in downcore samples (n=12) and Sediment Quality Guidelines used in this work (all in mg kg^{-1}).

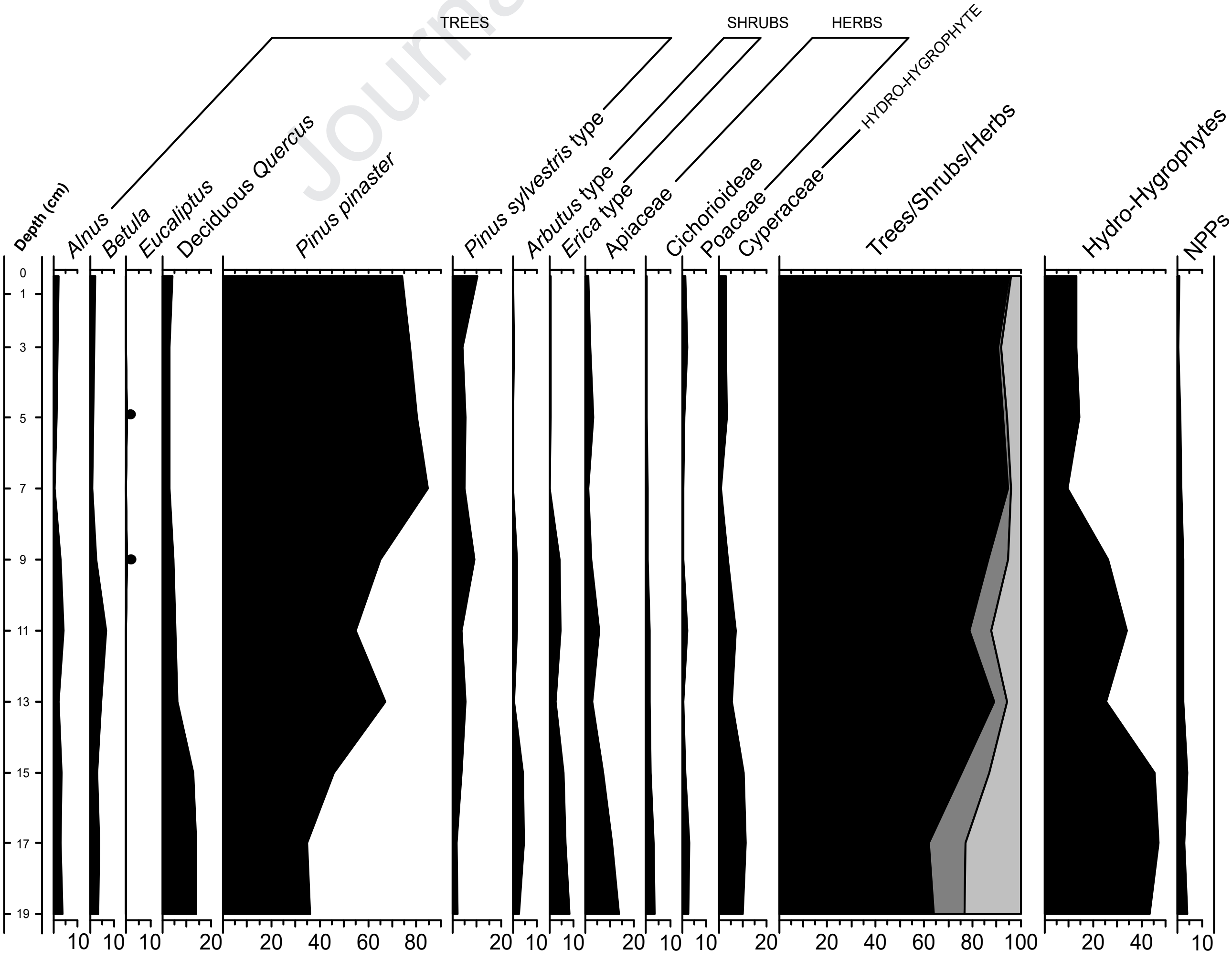
	Mn	**Pb**	**Zn**	**Cu**	**Cr**
KS-04	145-323	9-74	30-168	7-26	13-20
KI-03	162-303	15-95	49-163	10-24	16-22
KI-06	167-349	10-89	51-175	10-27	17-27
Background values					
Cearreta et al. (2002)	400	23	60	18	76
Legorburu et al. (1989)	289	15.8	56.1	20.9	25.6
Rodríguez et al. (2006)	240	31	174	33	26
OSPAR (2006)	-	25	90	20	60
Downcore samples (this work)	154	14	52	9	16
Sediment Quality Guidelines					
ERL (Long et al., 1995)		46.7	150	34	81
ERM (Long et al., 1995)		218	410	270	370

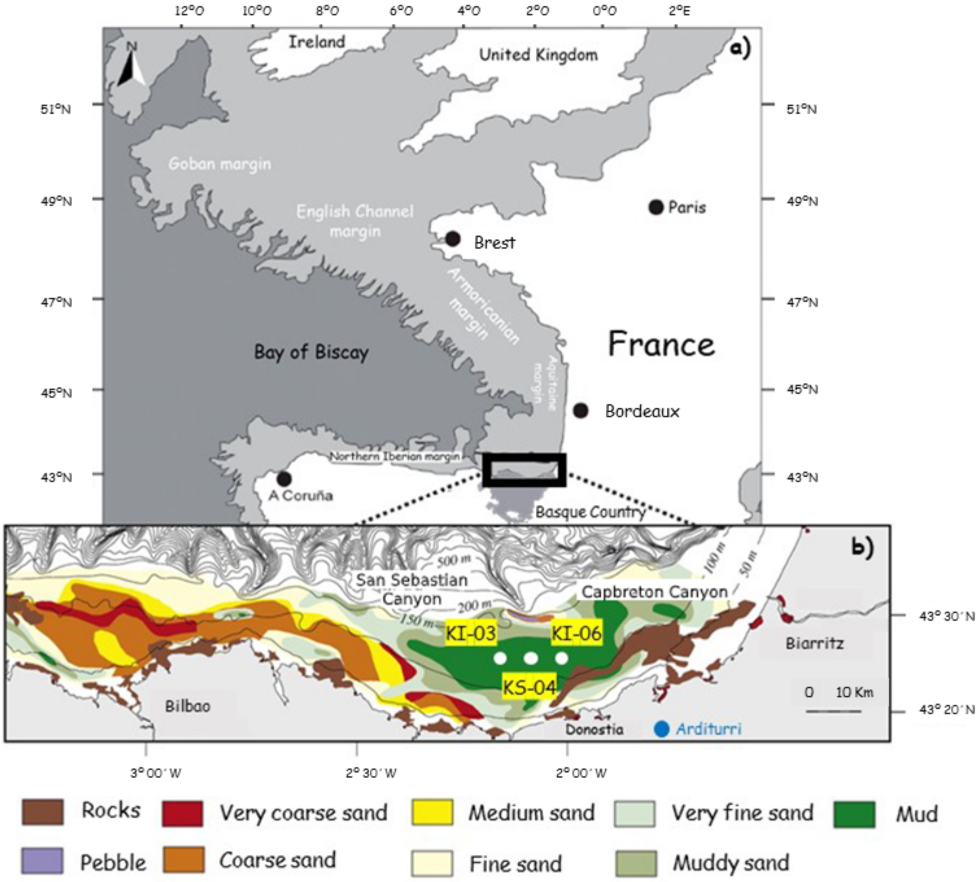

Pb concentration (mg kg-1)
15.0 22.5 30.0 37.5 45.0 52.5 60.0 67.5 75.0
208 Pb / 207 Pb
2.480 2.477 2.475 2.472 2.470 2.467 2.465 2.463 2.460
a)
Pre-1880
1894
1924
1944
1954
1964
1974
b)
208 Pb / 207 Pb
2.50 2.48 2.46 2.44 2.42 2.40 2.38
1.095 1.110 1.125 1.140 1.155 1.170 1.185 1.200 1.215
206 Pb / 207 Pb

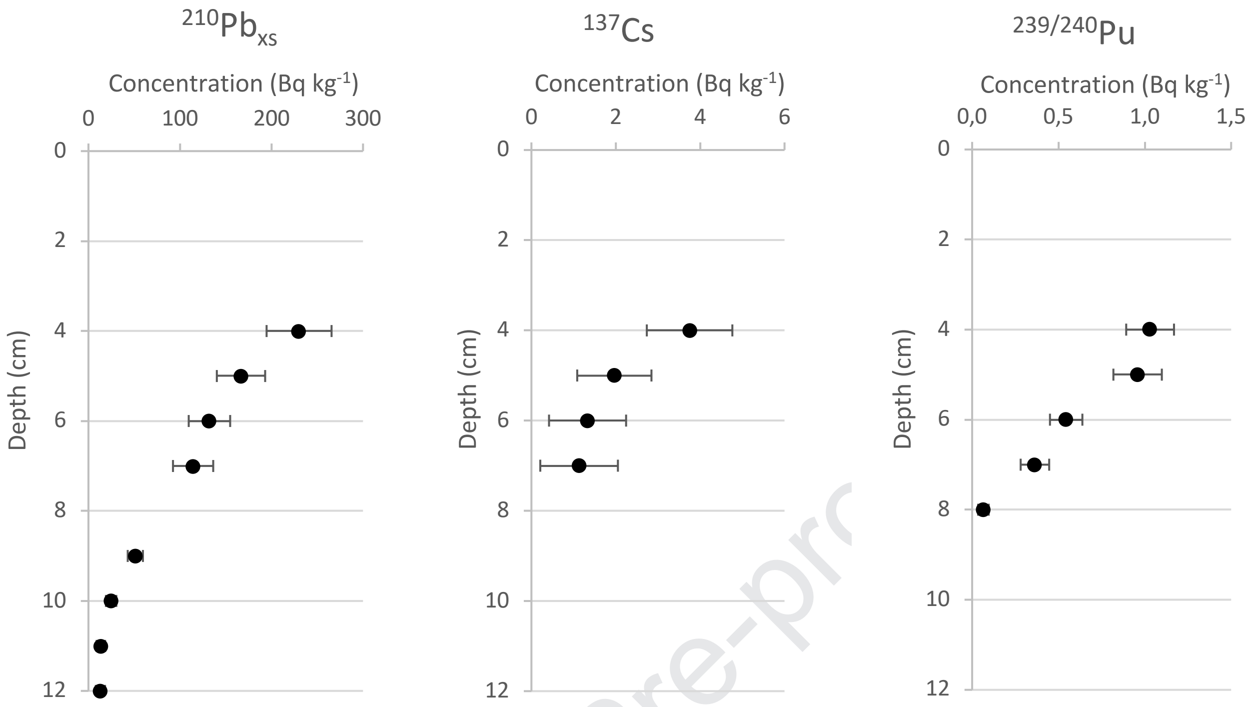


KS-04
Zn/Al
Pb/Al
Cu/Al
Cr/Al
Mn/Al
Depth (cm)

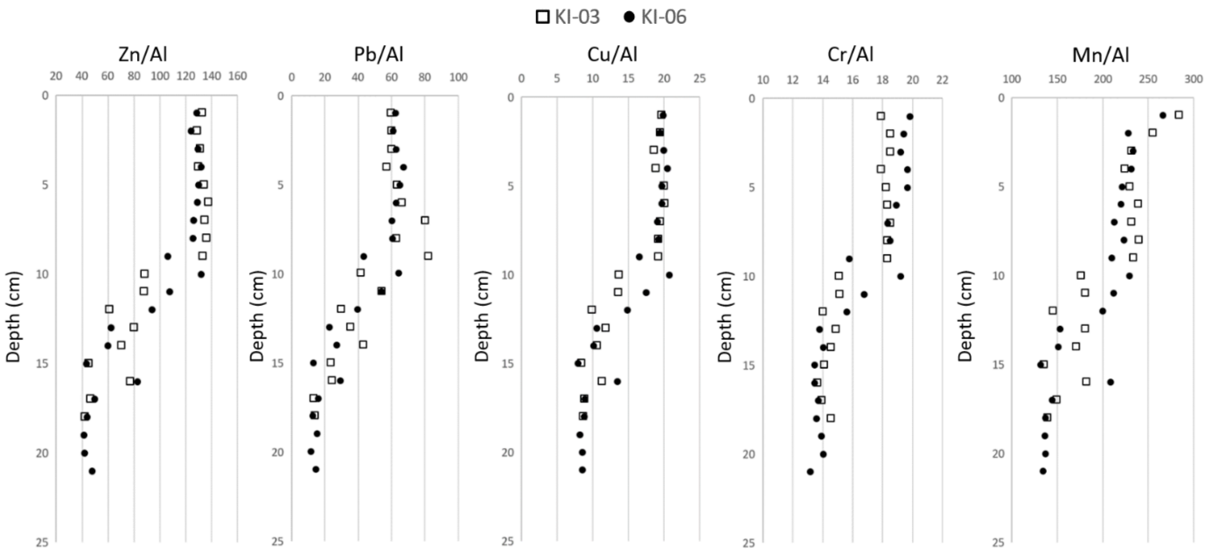

TREES
SHRUBS
HERBS
HYDRO-HYDROPHYTE
Depth (cm)
Alnus
Betula
Eucaliptus
Deciduous Quercus
Pinus pinaster
Pinus sylvestris type
Arbutus type
Erica type
Apiaceae
Cichorioideae
Poaceae
Cyperaceae
Trees/Shrubs/Herbs
Hydro-Hygrophytes
NPPs

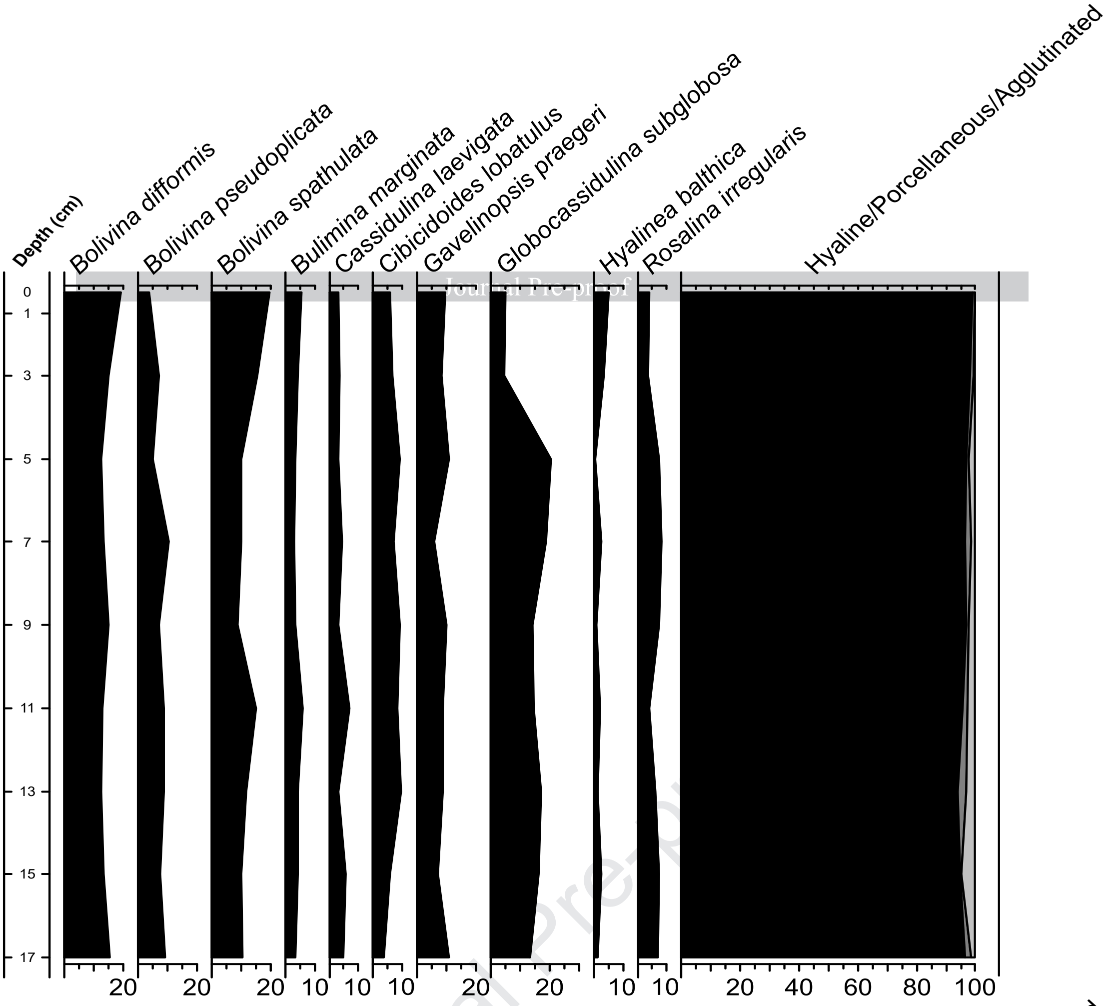

TREES
SHRUBS
HERBS
HYDRO-HYGROPHYTE
Depth (cm)
Alnus
Betula
Eucaliptus
Deciduous Quercus
Pinus pinaster
Pinus sylvestris type
Arbutus type
Erica type
Apiaceae
Cichorioideae
Poaceae
Cyperaceae
Trees/Shrubs/Herbs
Hydro-Hygrophytes
NPPs

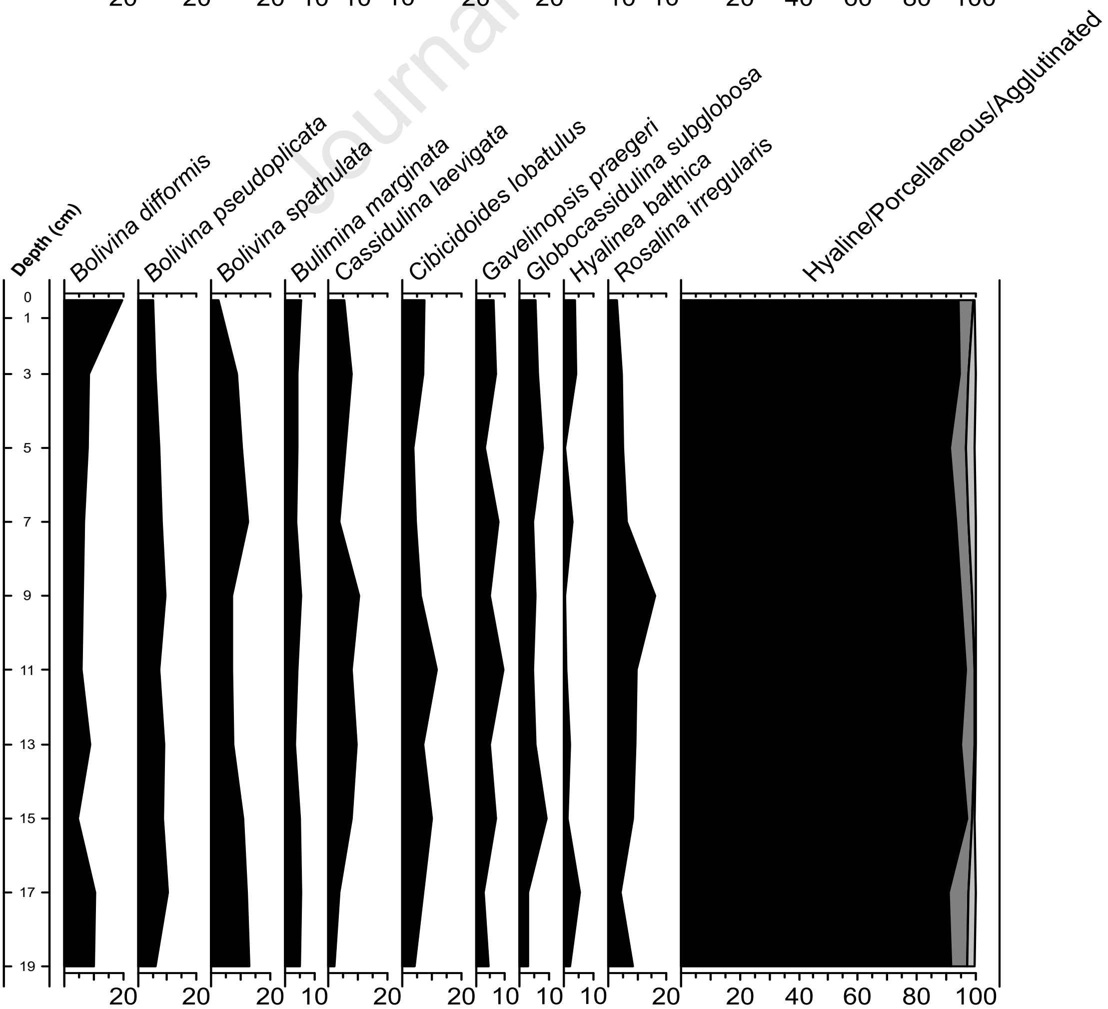

12°O
10°O
8°O
6°O
4°O
2°O
0°O
2°E
51°N
49°N
47°N
45°N
43°N
a)
Ireland
United Kingdom
Goban margin
English Channel margin
Armoricanian margin
Aquitane margin
Paris
Brest
France
Bay of Biscay
Bordeaux
Northern Iberian margin
A Coruña
Basque Country
b)
500 m
200 m
150 m
100 m
50 m
San Sebastian Canyon
Capbreton Canyon
KI-03
KI-06
KS-04
Biarritz
Bilbao
Donostia
Ardituri
0 10 Km
43° 30´ N
43° 20´ N
3° 00´ W
2° 30´ W
2° 00´ W
Rocks
Very coarse sand
Medium sand
Very fine sand
Mud
Pebble
Coarse sand
Fine sand
Muddy sand



210Pbxs
137Cs
239/240Pu
Concentration (Bq kg-1)
0
100
200
300
0
2
4
6
0,0
0,5
1,0
1,5
Depth (cm)
0
2
4
6
8
10
12


KI-03
KI-06
Zn/Al
Pb/Al
Cu/Al
Cr/Al
Mn/Al
Depth (cm)


Depth (cm)
Bolivina difformis
Bolivina pseudoplicata
Bolivina spathulata
Bulimina marginata
Cassidulina laevigata
Cibicidoides lobatulus
Gavelinopsis praegeri
Globocassidulina subglobosa
Hyalinea balthica
Rosalina irregularis
Hyaline/Porcellaneous/Agglutinated
0 1 3 5 7 9 11 13 15 17
20 20 20 10 10 10 20 20 10 10 20 40 60 80 100


Depth (cm)
Bolivina difformis
Bolivina pseudoplicata
Bolivina spathulata
Bulimina marginata
Cassidulina laevigata
Cibicidoides lobatulus
Gavelinopsis praegeri
Globocassidulina subglobosa
Hyalinea balthica
Rosalina irregularis
Hyaline/Porcellaneous/Agglutinated
0 1 3 5 7 9 11 13 15 17 19
20 20 20 10 20 20 10 10 10 20 20 40 60 80 100

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: