Chemostratigraphic and lithostratigraphic signatures of the Anthropocene in estuarine areas from the eastern Cantabrian coast (N. Spain)

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Abstract

A range of chemostratigraphic and lithostratigraphic markers of human impacts can be recorded in four estuaries located in the eastern Cantabrian coast (northern Spain). Metal-enriched levels and stable Pb isotopic ratios in dated sediment cores allowed the recognition of an ancient local episode of Pb contamination associated with mining activities during Roman times, as well as the widespread fingerprint of the Industrial Revolution and the “Great Acceleration” of human pressure after the Second World War. Micropalaeontological data (variations in foraminiferal assemblages) provided key information to identify agricultural soils in previously reclaimed and currently regenerated salt marshes, whereas anthropogenic beachrocks offered an example of the incorporation of technofossils to the coastal sedimentary record.

Keywords: estuarine sediments, eastern Cantabrian coast, human impact, trace elements, Pb isotopic ratios, benthic foraminifera

1. Introduction

Since anatomically modern humans emerged as species about 200,000 years ago, the planet we live in has experimented significant modifications. Crutzen and Stoermer (2000) coined the term “Anthropocene” to describe the present time interval, in which many key environmental processes are driven by human activities. The Anthropocene has rapidly gained much attention not only within the scientific community, but also in popular publications (Zalasiewicz, 2013). As the definition of the term is still imprecise, a proposal to formalise it as a new geologic epoch is being developed by the Anthropocene Working Group of the International Commission on Stratigraphy, with a current target date of 2016. Nowadays we are witnessing an open debate about the convenience or not to recognize the Anthropocene as a formal chronostratigraphical unit (Gale and Hoare, 2012; Autin and Holbrook, 2012a, 2012b; Zalasiewizc et al., 2012). However, there is a general consensus that human activities have changed the world and that it is reflected not only in the climate and other atmospheric and surface processes but also in a variety of sedimentary markers (Zalasiewizc et al., 2011; Rull, 2013).

One of the main controversial tasks under discussion around the Anthropocene is its temporal definition (Smith and Zeder, 2013). The original suggestion of Crutzen considered the beginning to be at around 1780 Common Era (CE), coinciding with the invention of the steam engine and the Industrial Revolution in Europe (Crutzen, 2002). The stratigraphic evidences found in sediments from remote lakes led Wolfe et al. (2013) to support a date for the Holocene/Anthropocene boundary around 1950 CE, inmediatly following the “Great Acceleration” (Steffen et al., 2007). However, other authors advocate for an earlier beginning, tracing it back even as far as the Pleistocene/Holocene boundary (Smith and Zeder, 2013). Ruddiman and Thomson (2001), in turn, proposed to ascribe the onset of significant human impact at about

5000 yr before present (BP), whereas Certini and Scalenghe (2011) advanced the hypothesis of a Late-Holocene start at approximately 2000 yr BP.

Although the Anthropocene is commonly associated with global transformation (Foley et al., 2014), some of the human induced changes registered have a limited impact at a global scale, remaining Earth System still operating within the Holocene state (Steffen et al., 2011). In this current context of debate about the definition of the Anthropocene, high-resolution regional studies can provide key information to assess the magnitude, timing and spatial scale at which these events occurred. Estuaries and coastal areas have been focal points of human settlement throughout history (Lotze et al., 2006), and they are likely to have played a significant role in the dispersal of anatomically modern human populations from their African origins (Bulbeck, 2007). In these areas, sediment deposits appear as reliable environmental archives, allowing the historical reconstruction of environmental changes to be made (Cooper and Brush, 1993; López-González et al., 2006). This paper presents a range of stratigraphic markers of different historical human impacts recorded in four estuaries of the eastern Cantabrian coast (Pasaia, Urdaibai, Bilbao and Santoña). The chemostratigraphic signals include the occurrence of metal-enriched sediments in different estuaries and changes in Pb isotope ratios. The lithostratigraphic fingerprint comprises the modification of natural sedimentary environments via formation of agricultural soils in reclaimed salt marshes, as evidenced by micropalaeontological data, and the identification of novel strata such as anthropogenic beachrocks.

2. Regional setting

The eastern Cantabrian coast (northern Spain) is characterized by rocky elevated marine terraces and wave-cut cliffs and platforms with few, narrow and relatively small estuaries where salt marshes develop. The Pasaia estuary, located at its eastern bound (Fig. 1), is 5.5 km long and has a total surface of 100 ha (González et al., 2012). This estuary represents the tidal part of the Oiartzun river and receives the drainage from most mineralized materials of the Arditurri ores. Exploitation of these deposits can be traced back to at least Roman times, being extraction of argentiferous galena the main driving force for the development of the most important Roman settlement on this coastal area, the port of Oiasso (modern Irun) (Fig. 1). The geochemical analysis of sediments of Roman age from the port and the adjacent estuarine area supported that mining activities may have caused severe environmental impact due to high levels of Pb pollution (Irabien et al., 2012). Although these works usually required a continuous supply of wood, local palinological record did not exhibit evidences of significant deforestation (Sánchez Goñi, 1996).

The Urdaibai estuary is formed by the seaward section of the Oka river (Fig. 1), covers an area of 765 ha and occupies the flat bottom of a 12.5 km long and 1 km wide alluvial valley. Besides evidences of prehistoric human settlements, archaeological surveys have found remains of a small Roman outpost where ferrous metallurgical works developed. This estuary is one of the best preserved of the northern Spanish coast, and due to the good balance between the natural environment and human activities it constitutes the main part of the Urdaibai Biosphere Reserve declared by UNESCO in 1984.

The Bilbao estuary is formed by the tidal section of the Nervion river (Fig. 1). Nowadays it has been transformed into a tidal channel, 15 km long and 100 m wide, which flows across the Great Bilbao Metropolitan Area. During more than 150 years this estuary received huge amounts of wastes derived from the exploitation of local Fe ores, industrial activities (mainly metallurgical works) and urban areas, which significantly degraded its environmental conditions. Accordingly, estuarine sediments reached extremely high levels of metal pollution (Cearreta et al., 2000, 2002a). However, in the course of the last years there is a decreasing trend in metal concentrations, probably related to the economic recession which led to the closure of many factories and the pollution abatement measures implemented by local authorities (Leorri et al., 2008; Larreta et al., 2013).

Finally, the Santoña estuary (Fig. 1) represents the tidal part of the Asón river. It has a total surface of 2000 ha and is about 14 km long and 500 m wide. The Santoña salt marshes have an undeniable ecological value as a wintering area or residence and nesting area for birds on their N-S migrations. In 1994 the Convention of Wetlands of International Importance designed them as a Ramsar site and now they are part of a Nature Reserve that includes woodlands, meadows, cliffs, beaches and dunes.

3. Material and methods

3.1. Sampling

General information regarding the boreholes and cores studied in this work, collected in different salt marshes, are presented summarized in Figure 1 and Table 1.

3.2. Chemical analyses

Sediments were passed through a 1-mm sieve, oven dried at 45ºC and mechanically homogenized in an agate mill in order to avoid metal contamination. Elemental determinations were performed by Activation Laboratories Ltd (Actlabs, Ontario, Canada) using Inductively Coupled Plasma-Optic Emission Spectrometry (ICP-OES) after digestion with aqua regia for two hours at 95ºC. Each sample was cooled and then diluted with deionized water. Method reagent blanks, sample duplicates and certified reference materials (GXR-1, GXR-4 and GXR-6) were used for quality control purposes. Detection limits were 0.01% for Al, 3 mg kg^{-1} for As, 2 mg kg^{-1} for Pb and 1 mg kg^{-1} for Zn, Cu and Ni.

Lead isotope analyses were performed at the Geochronology and Geochemistry-SGIker facility of the Universidad del País Vasco UPV/EHU (Spain). About 0.100 gr of powdered sample was digested overnight in HNO_3 and evaporated to dryness. The residue was taken in HBr, and Pb isolated by conventional ion-exchange chromatography (AG1-X8 resin in HBr and HCl media). The recovered lead was evaporated to dryness, dissolved in 0.32N HNO_3 and diluted to a final concentration of 150-200 ppb. Lead isotope ratios were measured with a Thermo NEPTUNE multicollector ICP-MS, and the mass fractionation was internally corrected after the addition of thallium isotopic reference material NBS-997 (Walder et al., 1993). Detailed protocols were similar to those described by Chernysev et al. (2007). Accuracy of the results was confirmed by analyses of lead isotopic reference material NBS-981.

3.3. Microfaunal study

Samples analyzed for foraminiferal content were sieved through 1 mm (to remove large organic fragments) and 63 µm sieves and washed to remove silt and clay material. Tests were picked until a representative amount of more than 300 individuals for each assemblage was obtained and they were studied using a stereoscopic binocular microscope under reflected light. Abundance of foraminiferal test was calculated and normalized to 50 gr of bulk sediment.

3.4. Sediment dating

Short-lived radionuclides were analyzed at the Universitat Autònoma de Barcelona (Spain). All samples were sealed and stored at least for 21 days prior to counting in order to allow equilibration between ^{226}Ra and its short-lived daughter ^{214}Pb. The activities of ^{226}Ra and ^{137}Cs were analyzed by gamma-spectrometry using calibrated geometries in a co-axial high-purity Ge detector (EG&G Ortec). The ^{226}Ra activity was determined from ^{214}Pb through its 351 keV gamma emission. Determination of total ^{214}Pb was performed through the measurement of its daughter ^{210}Po nuclide by alpha spectrometry, following the methodology described in Sánchez-Cabeza (1998). $^{210}Pb_{xs}$ activities were determined by subtracting the ^{226}Ra activity (assumed to equal the supported ^{210}Pb activitiy) from the total ^{210}Pb activitiy.

Radiocarbon analyses were performed by Beta Analytic Inc (Miami, USA) using

Accelerator Mass Spectrometry (AMS). Conventional radiocarbon ages BP were adjusted for local reservoir correction and their conversion into calendar years was performed by Beta Analytic following Talma and Vogel (1993). Data mentioned in text and graphically represented in Figure 2 are 2σ calibrated results (95% probability).

4. Results and discussion

4.1. Roman impact: Pasaia estuary

The borehole P9 drilled in the Pasaia estuary (Fig. 1) is composed by alternating levels of gravels, sandy muds and muds covered by a thick layer of anthropogenic infilling materials (Fig. 2). Radiocarbon-derived ages from these materials are listed in Table 2. Concentrations of Pb from 7.65 to -0.85 m depth remain low and constant, ranging between 14 and 25 mg kg^{-1} (Fig. 2). These values are in good agreement with those proposed for pre-industrial materials from other estuaries of the surrounding area (Legorburu et al., 1989; Cearreta et al., 2000), similar to background data in the region (Rodríguez et al., 2006; Cearreta et al., 2013) and S. Spain (García-Alix et al., 2013) and could be used as baseline data. Above -0.85 m depth, between 3380-3100 and 930-680 cal yr BP, there is a five-fold enrichment in Pb concentrations. As the Oiartzun river drains most mineralized materials from Arditurri before flowing into the Pasaia bay (Fig. 1), this increase is likely to be related to the onset of exploitation of galena upstreams during Roman times (around 1900 cal yr BP) and the consequent release and transport of Pb-enriched particles. Vertical distribution of Pb in this borehole is fairly similar to that obtained by Irabien et al. (2012) adjacent to the ancient port of Oiasso (modern Irun, Txingudi estuary) (Fig. 1), where post-Roman sediments were polluted as a consequence of the intensive exploitation of local ores. Moreover, in both estuaries maxima contents of this metal (225 mg kg^{-1} in Pasaia and 421 mg kg^{-1} in Txingudi) appear several centuries after Roman colonization, but prior to the Industrial Revolution. Given that no significant industrial activities are documented for this historical period, these enrichments could be explained by the remobilization of previously polluted materials from unidentified waste heaps during flood events. In that case, mineral exploitation in Arditurri not only exerted a severe environmental impact at local scale in Roman times (Irabien et al., 2012), but also left a legacy of pollution for the following centuries.

Cearreta et al. (2005) performed a technical report for local authorities with the main aim to provide geological tools for the environmental interpretation of the Roman settlement of Forua (Urdaibai estuary, see Fig.1 for location). The three boreholes drilled adjacent to the archaeological excavation (FO1, FO2 and FO4) comprised grey muds with some layers of sandy and conglomeratic materials and plant and bioclastic remains, covered by a level of brown soil (1.10-1.50 m thick). Radiocarbon dating of a bivalve shell from the base of the longest borehole (FO4) indicated an age of 6210-5970 cal yr BP. Foraminiferal assemblages (unpublished data) confirmed that both sedimentary records from Pasaia and Forua represented a typical sequence of estuarine infilling, with the former reflecting more abundant inputs of fluvial materials. This could be related to the increased average water flow (4.8 $m^3 s^{-1}$) of the Oiartzun river when compared to other regional rivers with bigger catchment areas, which is likely to be a consequence of the elevated rainfall recorded in its watershed (González et al., 2012).

Contents of Pb in all sediments from Forua (n=25) remained below 35 mg kg^{-1}. Concentration maxima were slightly higher than those determined in pre-Roman sediments from Irun (Irabien et al., 2012) and Pasaia (<25 mg kg^{-1}). However, this metal showed a reasonably good correlation with Al (Pearson´s correlation coefficient, r=0.75, p<0.0001), a conservative element that has been frequently used as grain-size proxy (Cearreta et al., 2002a; Alvarez-Iglesias et al., 2007). Therefore, this apparent enrichment was more likely to reflect a granulometric effect than significant anthropogenic inputs. Previous studies have demonstrated the ubiquitous nature of the Roman Pb peak in peat-bogs, lakes and ice cores (see Renberg et al., 2001).

However, the regional relevance of its environmental impact is more arguable. As expected, and notwithstanding the relatively short distance existing between the Pasaia and Urdaibai estuaries (70 km in a straight line, see Fig. 1), no significant sign of the severe impact caused by Roman mining activities in the former was recognized in the latter.

4.2. Industrial and post-Industrial Revolution impacts

4.2.1. Metal enrichment: Axpe Norte (Urdaibai estuary)

Samples from the short core collected in Axpe Norte (Fig. 1) are mainly composed of light brown coloured mud (sand content<10%). Concentrations of metals below 22 cm depth display constant and low enough values to consider them as representative of their natural background levels (Table 3). In these bottom sediments geochemical composition is largely controlled by granulometric variations, as proven by the reasonably close linear relationship with Al exhibited by Pb ($r=0.77$), Zn ($r=0.87$), Cu ($r=0.83$), Ni ($r=0.92$) and As ($r=0.80$) ($p<0.001$). Therefore, in an attempt to provide a better perspective of the magnitude of the anthopogenic inputs and to make them easily comparable, elemental data will be represented in terms of Al-normalizad Enrichment Factor (EF) (Fig. 3). These values have been calculated as the quotient between the measured concentrations of each element and those calculated on the base of the linear regression to Al (Skowronek et al., 1994).

On the other hand, distribution of ^{210}Pb (Fig. 3) does not suggest any mixing or disruption in the sedimentation process. Values show an exponential decline with depth, pointing out that rates of deposition have been relatively constant. Therefore, ^{210}Pb-derived chronology has been calculated using the simple model proposed by Robbins (1978), where sediment accumulation rate is given by the slope of the least square fit for the natural log of the $^{210}Pb_{xs}$ activity plotted against depth. Results indicate that the uppermost 18 cm have been deposited over the last 100 years. The downcore profile of ^{137}Cs shows a clear activity subsurface maximum at about 7 cm depth, declining with depth to negligible values at 15 cm. The ascription of this peak to 1963 CE, maximum in atmospheric fallout from nuclear weapons testing, is in reasonably good agreement with the ^{210}Pb-derived chronological estimates presented in Figure 3. Although global dispersion and fallout of ^{137}Cs occurred from 1954 CE onwards, in this core it has been detected in older sediments (at 14 cm depth, dated 1923 CE). The mobility of this radionuclide in salt marsh sediments has been previously reported by other authors such as Milan et al. (1995) and Leorri et al. (2010).

Concentrations of Pb began increasing in the second half of the 19th century, whereas Zn and Cu showed a departure from baseline values since 1900 CE (Fig. 3). Lead appears to be the most ubiquitous metal contaminant emitted into the atmosphere from the northern hemisphere (Valette-Silver, 1993). In Europe, the integrated record of ombrotrophic bogs suggests that human control of Pb in airborne particles spans the last 2300 years (Dunlap et al., 1999). The onset of metal enrichment in these sediments is in good agreement with the local history of industrial development, in which metallurgical activities were one of the main driving forces for the economic growth. The first iron and steel industry was established in the nearby Bilbao estuary (about 20 km in a straight line, see Fig. 1) as early as 1854 CE, while the beginning of the industrialization of the main town in the Urdaibai estuary (Gernika) occurred later in time, in the 1910s. From 1900 CE onwards the chemostratigraphic fingerprints of Pb, Zn and Cu exhibited a fairly similar evolution (Fig. 3). Raising concentrations were found up to the early 1920s, followed by a time interval with steady levels. Between 1923 and 1948 CE contents of Pb mantained a 2.5-fold increase when compared to baseline values, while Zn and Cu reached lower values (EFs<1.7). From an historical perspective, the first half of the 20th century was marked by the two World Wars and the Spanish Civil War (1936-1939 CE) which favoured the regular operation of the local weapons industry. Since 1950 CE, inmediately following the onset of the “Great Acceleration” (Steffen et al., 2007), enhancing trends accelerated substantially and new contaminants such as Ni and As entered the estuary. Total concentrations of Pb increased three times in less than 25 years, reaching maximum values in 1973 CE, coinciding with maxima emmisions of this metal to the atmosphere in Europe (Pacyna et al., 2007). When the Axpe Norte isotope data are plotted as ^{207}Pb/^{206}Pb versus ^{206}Pb/^{208}Pb (Fig. 4, upper panel), a trend towards isotopically depleted values can be observed as Pb concentrations increase. This dramatic shift reflects the addition of anthropogenic sources less radiogenic than the background component. Samples deposited after 1950 CE appeared together within the field associated with both Spanish (Díaz-Somoano et al., 2007) and British coals (Farmer et al., 1999), which have been the main fossil fuels used by the local iron and steel industry. This shift is coeval with an increase of concentrations of total Pb (Fig. 4, lower panel), where higher concentrations correlate with less radiogenic signatures until concentrations of total Pb reach ca. 70 mg kg^{-1} and the isotopic signal is mainly dominated by anthropogenic sources with values between 0.847 and 0.850 (^{207}Pb/^{206}Pb). As stated previously by Leorri et al. (2014) on the basis of Pb isotopic ratios and high molecular weight PAH isomer ratios in another dated sediment core from this estuary, throughout the 19th century there is a clear switch from wood to coal, with the latter becoming dominant during the 20th century.

From the mid-1990s to the Present contents of all the analyzed elements except Ni increased again, with Pb reaching the highest enrichment (EF=4.9, see Fig. 3). Leaded gasoline has been considered the most prevalent source of atmospheric Pb over Europe from the 1950s onwards (Dunlap et al., 1999). Since 1987 CE Spanish authorities have undertaken institutional measures to reduce progressively the content of Pb in gasolines, leading to its complete phaseout in 2001 CE. Therefore, it should be reasonable to expect a decrease in Pb during the last years, as observed in other estuaries worldwide (Seen et al., 2004; Lima et al., 2005; Vane et al., 2011). Far from it, sediments from this core exhibit increasing Pb levels during the last decade, supporting a relatively low contribution of leaded gasoline to pollution. In fact, in a previous work developed in this estuary (Leorri et al., 2014) it was calculated to be between 13% and 24% by 1973 CE, when maxima concentrations of Pb appeared.

Metal pollution from the Industrial Revolution onwards appears as a widespread anthropogenic impact across the northern Spanish coast, as almost all the estuaries studied in this area exhibit enhanced metal concentrations in topmost samples (see references below). Furthermore, the chronological trends determined in Axpe Norte bear a striking resemblance with those recorded in most coastal areas across the industrialized countries (Gearing et al., 1991; Hornberger et al., 1999; Valette-Silver, 1993). Notwithstanding that a similar historical evolution has been observed in the nearby Plentzia estuary (Cearreta et al., 2002a), at regional scale changes seem to be diachronous. Events such as the later industrialization of the Galician estuaries (Rubio et al., 2001; Cobelo-García and Prego, 2003) and the Santander bay (Viguri et al., 2007), the exploitation of local ores upstreams the Suances estuary (Irabien et al., 2008a), the implementation of specific industrial processes in the Ria of Vigo (Alvarez-Iglesias et al., 2007), and the existence of different sedimentation rates and/or sedimentary disruptions in the Bilbao, Urdaibai and Santoña estuaries (Cearreta et al., 2000, 2013; Leorri et al., 2013b, 2014) are likely to have caused local historical/geological records that override the temporal pattern of global-scale Pb deposition.

4.2.2. Salt marsh reclamation: Carasa (Santoña estuary)

Sediments from the short core (50 cm length) collected in the Carasa salt marsh (Fig. 1) were composed of grey dark mud below 27 cm depth and light brown mud above it (Fig. 5). Historical aerial photography provided evidence of human impact (agricultural occupation) in the recent past and at least until the late 1950s (Fig. 6).

The abundance of benthic foraminifera was high in the upper 41 cm and low in the rest of the core. In total, 6230 foraminiferal tests were obtained in the 28 samples analyzed. Foraminiferal results are expressed as percentage or as number of foraminiferal tests per 50 g of dry sediment for standardization. Eleven different foraminiferal species were found in this core, but only *Jadammina macrescens* (Brady, 19870) and *Trochammina inflata* (Montagu, 1808) were dominant throughout (Fig. 5). Three depth intervals (DIs) are distinguished in terms of presence, abundance and dominance of foraminiferal species (Fig. 5). The lowermost 9 cm (DI 3) are represented by very low numbers of foraminiferal tests (average foraminiferal density/50 g is 40 tests). Species number (average 3 species) is very low. This lower interval could represent the anthropogenic deposit introduced during agricultural occupation of this area. The following 18 cm (DI 2) are characterized by low and upwards-increasing numbers of foraminiferal tests (average foraminiferal density/50 g is 230 tests), dominated by *J. macrescens* (average 70%) and *T. inflata* (average 28%). Species number (average 3 species) is very low. This intermediate interval would represent a transitional environment between the agricultural horizon below and the regenerated salt marsh above. According to aerial photography (Fig. 6), the regeneration process took around 10-15 years, since areas that appeared cultivated in the late 1950s were already undistinguishable from other surrounding salt marsh areas in the early 1970s, as stated by Rivas and Cendrero (1991). Therefore, sedimentation rates during the regeneration process would be around 14 mm yr^{-1}. The last 23 cm (DI 1) show high numbers of foraminiferal tests (average foraminiferal density/50 g is 3416 tests), dominated by *J. macrescens* (average 67%) and *T. inflata* (average 27%). *Haplophragmoides wilberti* (Andersen, 1953) (average 4%) and *Arenoparrella mexicana* (Kornfeld, 1931) (average 2%) appear as secondary forms. Species number (average 5 species) is low but slightly higher than in the previous intervals. This upper interval represents the modern regenerated salt marsh environment. Compared to the previous transitional period, estimated sedimentation rate is significantly lower (6 mm

yr^{-1}), similar to regional values calculated by Cearreta et al. (2013). Analogous episodes of land-use changes in salt marshes have been documented also in the Plentzia (Cearreta et al., 2002b) and Urdaibai estuaries (Leorri et al., 2013b).

Human occupation of estuarine areas represents one of the main geomorphological impacts on the whole eastern Cantabrian coast (Rivas and Cendrero, 1991). Significant salt marsh reclamation for agricultural and disease-erradication purposes started at the beginning of the 18th century, being particularly intense from the Industrial Revolution century onwards. The Bilbao estuary was originally the most extensive transitional environment of this coast, but since the 19th century the intense land reclamation carried out for the development of the Great Bilbao Metropolitan Area reduced it to a simple tidal channel (Cearreta et al., 2000). The Pasaia estuary has lost more than 50% of its original wetlands (González et al., 2012), which have been mainly occupied by port facilities. Although the Urdaibai and Santoña estuaries exhibit a better degree of environmental preservation, they have also undegone significant reduction of their original tidal areas, losing about 30% (Rivas and Cendrero, 1991) and 15% (Irabien et al., 2008b) respectively. In total, more than 50% of the original wetlands of this coast have been converted to other (mainly anthropogenic) uses (Rivas and Cendrero, 1991). However, some reclaimed salt marshes for agricultural purposes were abandoned over the last decades, mainly since the 1950s, as a consequence of the engagement of the population to the flourishing local industry and the subsequent declining of farming activities. The lack of dyke maintenance provoked its partial break-down and the entrance of tidal estuarine water, allowing their rapid regeneration. This process is of great interest for environmental management in the current scenario of sea-level rise, given that rapid salt marsh restoration would represent a valid adaptation measure (Cearreta et al., 2013). Surprisingly, anthropogenic impacts such as land-clearance in the surrounding area may contribute to this process, providing abundant detrital material to assist in salt marsh evolution (Leorri et al., 2013a).

On the other hand, contents of trace elements in the agricultural horizon are low and fairly homogeneous (Table 3), probably as a consequence of the frequent remobilization of the soil during ploughing. However, sediments deposited during the regeneration process, from the late 1950s onwards, exhibit enhanced values of most analyzed elements. Concentrations of Pb, Zn and As are fairly similar to those determined in anthopogenically-affected sediments from the Axpe Norte salt marsh in the Urdaibai estuary (Table 3), pointing out the widespread effect of human activities.

4.2.3. Anthropogenic beachrock: Tunelboca and Gorrondatxe (Bilbao estuary)

Recent strata composed mostly by materials of anthropogenic origin appeared adjacent to the mouth of the Bilbao estuary (Fig. 1), lying discordantly over Eocene materials (Fig. 7A). They form a main outcrop of about 1 km long and 50-100 m wide and two little occurrences of about 100-150 m long and 20-50 m wide (Arrieta et al., 2011). Although Knox (1973) originally interpreted these sediments as mainly volcanic, later studies (García-Garmilla, 1990; Arrieta et al., 2011) proved without further doubts their anthopogenic provenance. They comprise sand to gravel-sized fragments of slags, with minor amounts of local detrital particles, bioclasts and other artificial products such as brick pieces, glasses and plastic materials (Fig. 7B), which seem to have been cemented by carbonates and iron oxides in a marine-phreatic context (Arrieta et al., 2011). The origin of a significant part of these materials is related to the local iron and steel industry. Since 1854 CE, when the first foundry began to work over reclaimed salt marshes on the middle reaches of the Bilbao estuary, the development of the Great Bilbao Metropolitan Area has been linked to the input of industrial and urban wastes to the environment (Leorri et al., 2008). Moreover, open-sea disposal of slags ad steel mill powder has been a standard practice for a long time. Azpiri (1983) calculated that the most important local foundry (“Altos Hornos de Vizcaya”) spilled into the sea, at few km to the north of the coast, more than 25 million tonnes of slags and rubble since its founding in 1902 CE until 1966 CE. This practice concluded in 1980s and, since then, these deposits formed during the 1940-1980 decades are being eroded by the tides and waves. The geophysical study of the marine dumping areas showed that most of the slag heaps have been dispersed and mixed with the original seabed sediments (Borja et al., 2008), confirming their potential as a suitable source for the materials currently cemented in the beachrocks.

These beachrocks offer a good example to illustrate the possible incorporation of technofossils (see definition in Zalasiewicz et al., 2014) to the coastal sedimentary record. Their artificial nature can help to document the chronological setting. In fact, the detailed study of some brick fragments allowed Astibia (2012) to determine their industrial provenance and their approximate date of manufacture. However, it is worth mentioning that in the current context of sea-level rise shingle beaches from this coast are expected to undergo significant shoreline retreat in the near future (Chust et al., 2010), in which these deposits could be eroded, at least partially. In that case, they could act as a potential secondary source of contaminants to the coastal environment.

5. Conclusions

The chemostratigraphic record of human influence in salt marshes from the eastern Cantabrian coast can be traced back to Roman times**.** Although Pb pollution derived from Roman mining activities could have represented a serious environmental impact at local scale, it does not seem to have caused a significant perturbation on a wider scale. On the contrary, the occurrence of metal enriched sediments from the Industrial Revolution onwards is a recurrent observation along this coast and other industrialized areas of the world. Lead concentrations and stable Pb isotope ratios provide practically usuable signals of anthopogenic change, but they seem to be diachronous even at this regional scale. In turn, artificial radioactive isotopes such as ^{137}Cs, produced as a result of atmospheric nuclear weapons testing mainly during the

1950s, offer a globally distributed signal. Unfortunately, the potential mobility of this radionuclide in the sediment profile can difficult its use as a chronomarker.

Changes in land use for agricultural purposes of the estuarine domains are marked by changes in the microfossil content of the sedimentary record. The study of the foraminiferal assemblage variations has indicated that, surprisingly, the “Great Acceleration” of human pressure after the 1950s brought along an unexpected positive environmental impact on this coast: the abandonment and rapid regeneration of previously reclaimed salt marshes.

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Appendix A. Supplementary data

Supporting Information (SI). Figure S1 represents the measured ^{210}Pb$_{XS}$ and ^{137}Cs together with modelled ^{210}Pb$_{XS}$ data versus mass depth profile for the Axpe Norte salt marsh core (Urdaibai estuary). Supplementary data to this article can be found online at http://dx.doi.org/XXXXXXX.

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Figure captions

Fig. 1. Geographic location of the studied estuaries in the eastern Cantabrian coast. Dots represent boreholes and cores, while empty circles represent places mentioned in the text.

Fig. 2. Vertical distribution of Pb concentrations and radiocarbon-derived ages (2σ calibrated BP results) in the Pasaia borehole. Depths are referred to Local Ordnance Datum LOD (lowest tide at the Bilbao Port on 27th September 1878).

Fig. 3. Core photograph and vertical distribution of Al-normalized Enrichment Factors (EF) calculated for Pb, Zn, Cu, Ni and As, and total ^{210}Pb and ^{137}Cs concentrations in the Axpe Norte salt marsh core (Urdaibai estuary). See Figure S1 for the fit between modeled (simple model) and measured $^{210}\mathrm{Pb}_{XS}$ concentrations.

Fig. 4. Upper panel: Plot of the Axpe Norte salt marsh ^{207}Pb/^{206}Pb versus ^{206}Pb/^{208}Pb and other relevant Pb isotope values. White circles represent samples from other nearby cores considered unimpacted. Black circles represent samples from Axpe Norte deposited prior to 1950 CE. Black triangles (with associated ages) represent samples younger than 1950 CE bracketed by isotope ratios in coals 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; Alvárez-Iglesias et al., 2012). Background values (number 1) are from Greenland Ice Holocene samples (Rosman et al., 1997) and the Basque Region (Monna et al., 1997). Norwegian peat bog sediments from 1800 to 1950 CE are indicated by number 2, whereas samples from 1960 to later than 1980 CE are indicated by number 3 (Dunlap et al., 1999). References of local galenas are included as Reocin and Bizkaia (ca 120 km and 55 km respectively from Axpe Norte) (Velasco et al., 1996).

Lower panel: Plot of the Axpe Norte salt marsh total Pb concentrations (mg kg^{-1}) versus ^{207}Pb/^{206}Pb isotopic ratio.

Fig. 5. Core photograph, main foraminiferal species (1*: A. mexicana*; 2: *H. wilberti*; 3: *J. macrescens*; 4: *T. inflata*) and foraminiferal density/50 g of bulk dry sediment in the Carasa salt marsh core. Black dots in the foraminiferal profile represent samples with less than 100 tests.

Fig. 6. Geographic location of the Carasa core (dot) in different historical aerial photographs (1946, 1956, 1972 and 2002 CE).

Fig. 7. A. General view of the Tunelboca beachrock at the mouth of the Bilbao estuary. Altitude of the cliffs is 40 m; B. Detail of the Gorrondatxe beachrock lying discordantly over Eocene materials and including diverse technofossils. Thickness of the Anthropocene deposit is 1.60 m.

Figure
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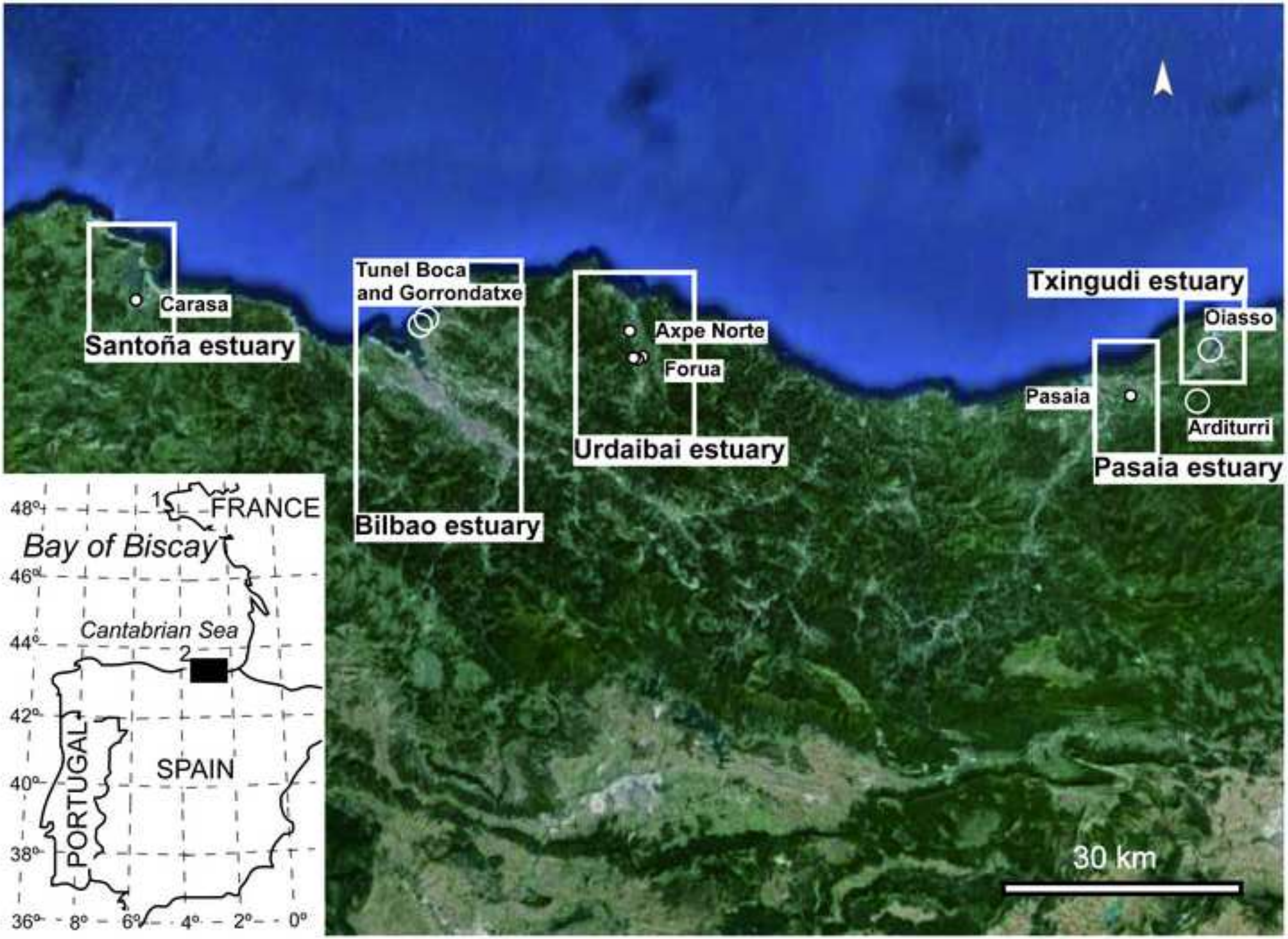

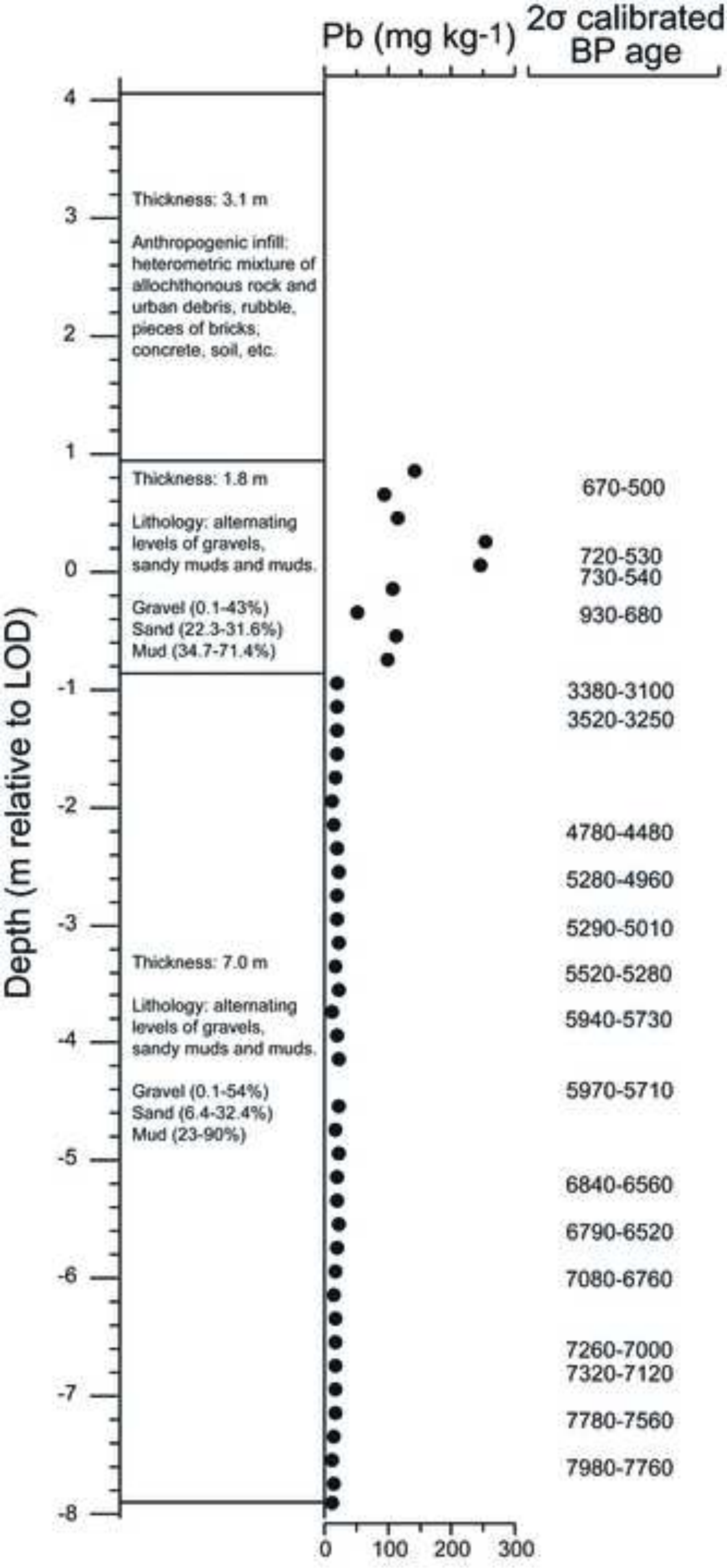
Pb (mg kg-1)
2σ calibrated BP age
Depth (m relative to LOD)
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
Thickness: 3.1 m
Anthropogenic infill: heterometric mixture of allochthonous rock and urban debris, rubble, pieces of bricks, concrete, soil, etc.
Thickness: 1.8 m
Lithology: alternating levels of gravels, sandy muds and muds.
Gravel (0.1-43%)
Sand (22.3-31.6%)
Mud (34.7-71.4%)
Thickness: 7.0 m
Lithology: alternating levels of gravels, sandy muds and muds.
Gravel (0.1-54%)
Sand (6.4-32.4%)
Mud (23-90%)
0
100
200
300
670-500
720-530
730-540
930-680
3380-3100
3520-3250
4780-4480
5280-4960
5290-5010
5520-5280
5940-5730
5970-5710
6840-6560
6790-6520
7080-6760
7260-7000
7320-7120
7780-7560
7980-7760

Figure

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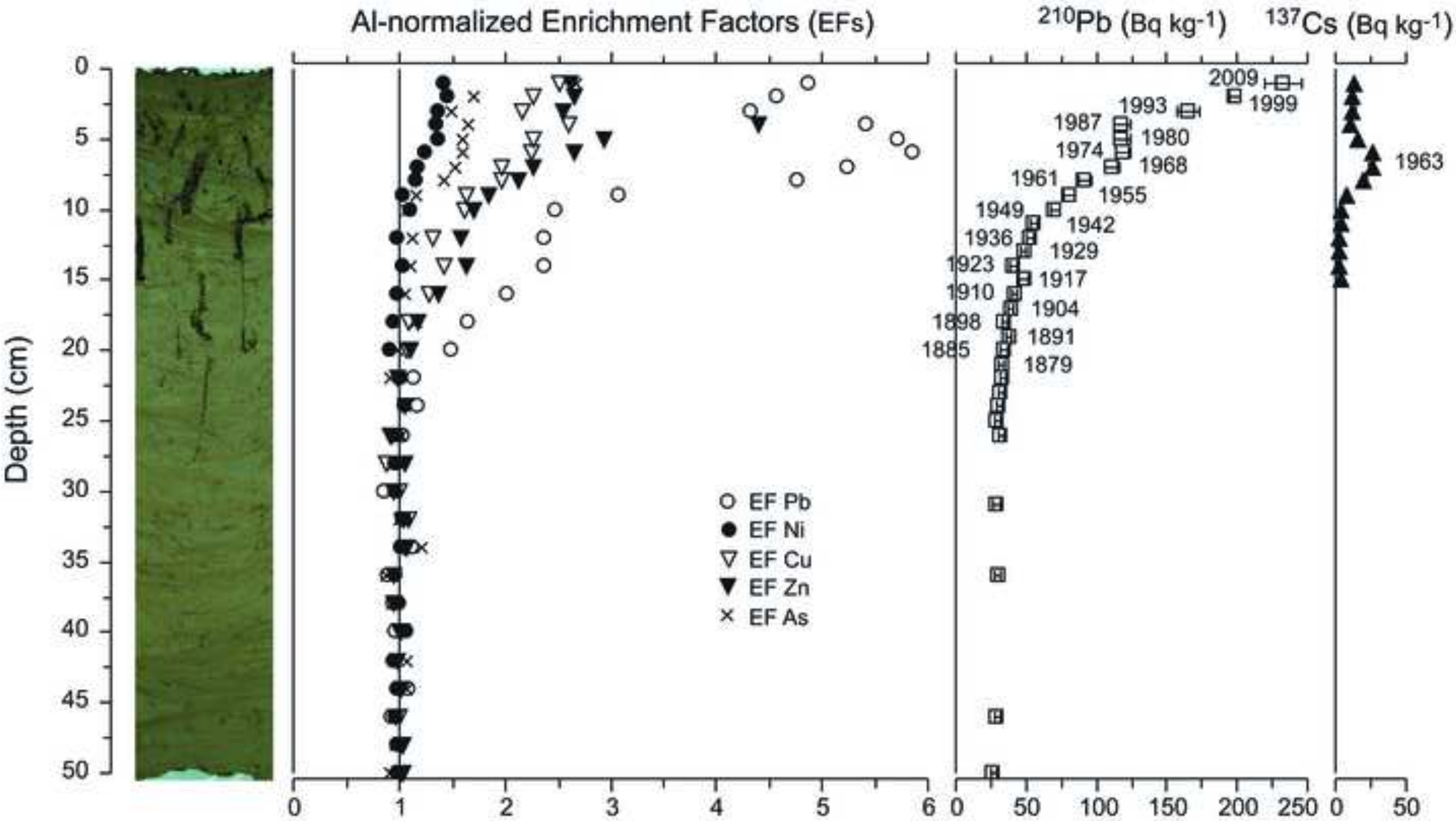
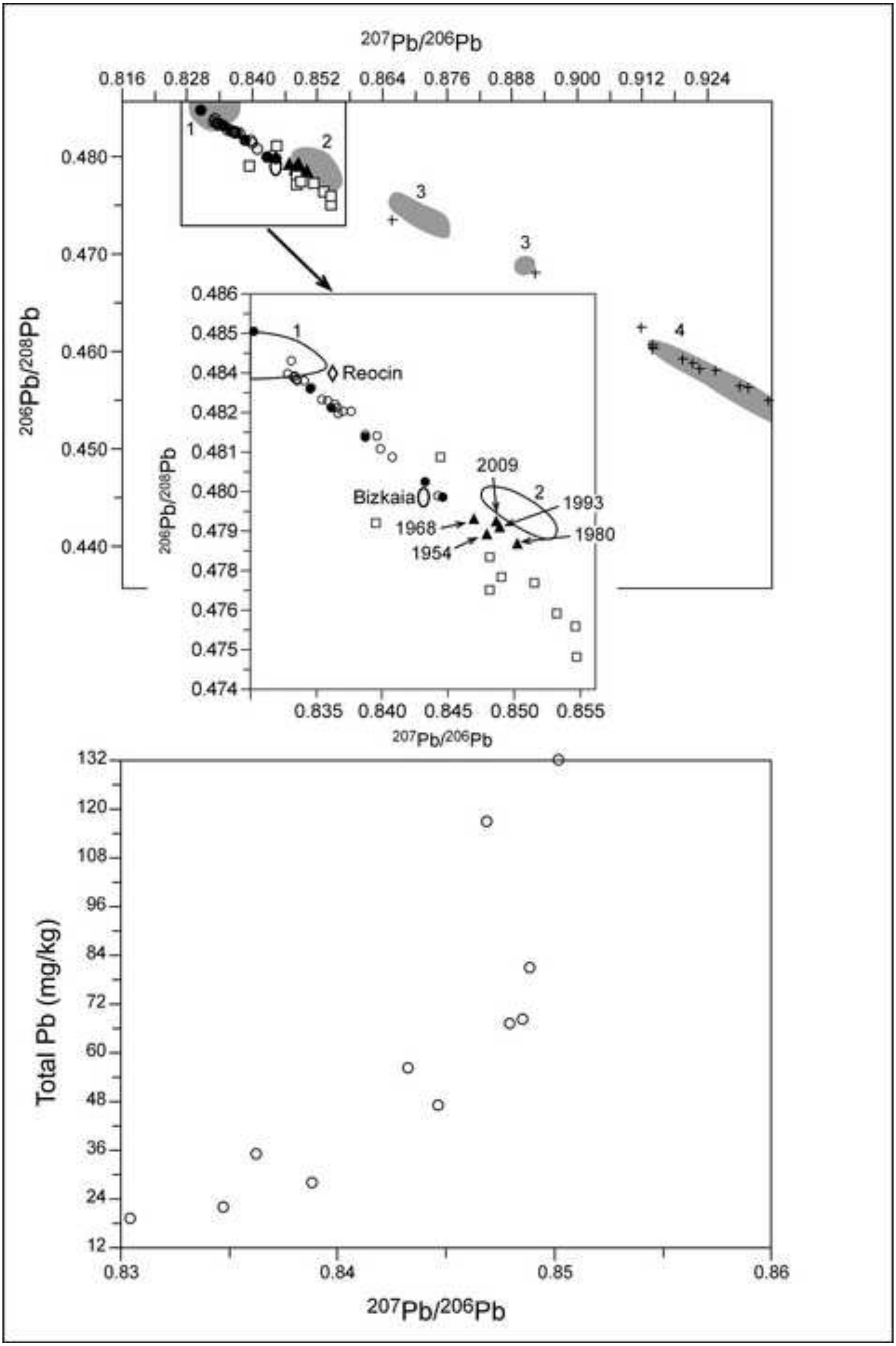
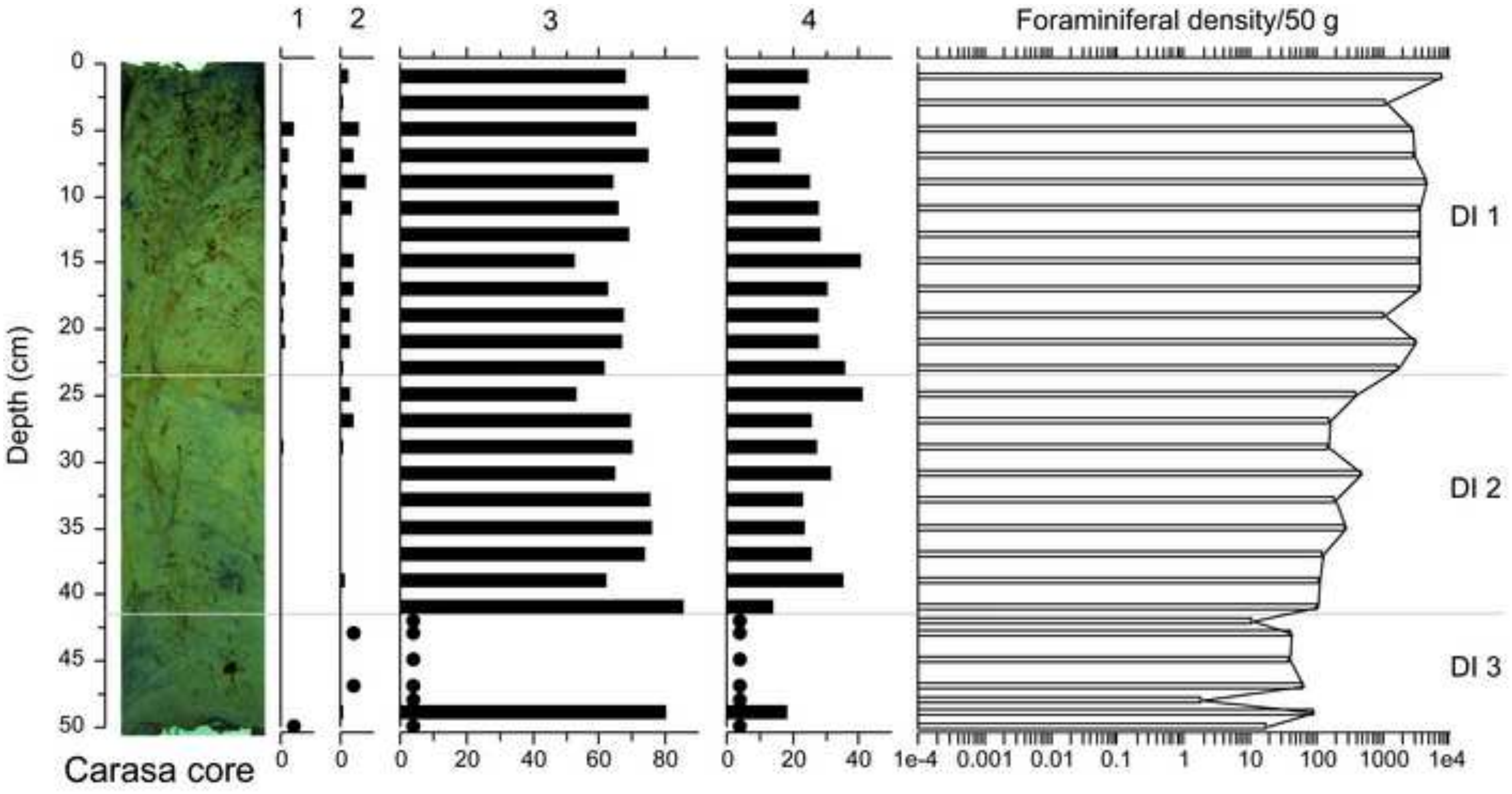



$^{207}Pb/^{206}Pb$
0.816
0.828
0.840
0.852
0.864
0.876
0.888
0.900
0.912
0.924
$^{206}Pb/^{208}Pb$
0.480
0.470
0.460
0.450
0.440
1
2
3
3
4
0.486
0.485
0.484
0.482
0.481
0.480
0.479
0.478
0.476
0.475
0.474
1
Reocin
Bizkaia
2009
2
1993
1968
1954
1980
0.835
0.840
0.845
0.850
0.855
$^{207}Pb/^{206}Pb$
132
120
108
96
84
72
60
48
36
24
12
Total Pb (mg/kg)
0.83
0.84
0.85
0.86
$^{207}Pb/^{206}Pb$


1
2
3
4
Foraminiferal density/50 g
Depth (cm)
0
5
10
15
20
25
30
35
40
45
50
Carasa core
0
0
0
20
40
60
80
0
20
40
1e-4
0.001
0.01
0.1
1
10
100
1000
1e4
DI 1
DI 2
DI 3

Figure

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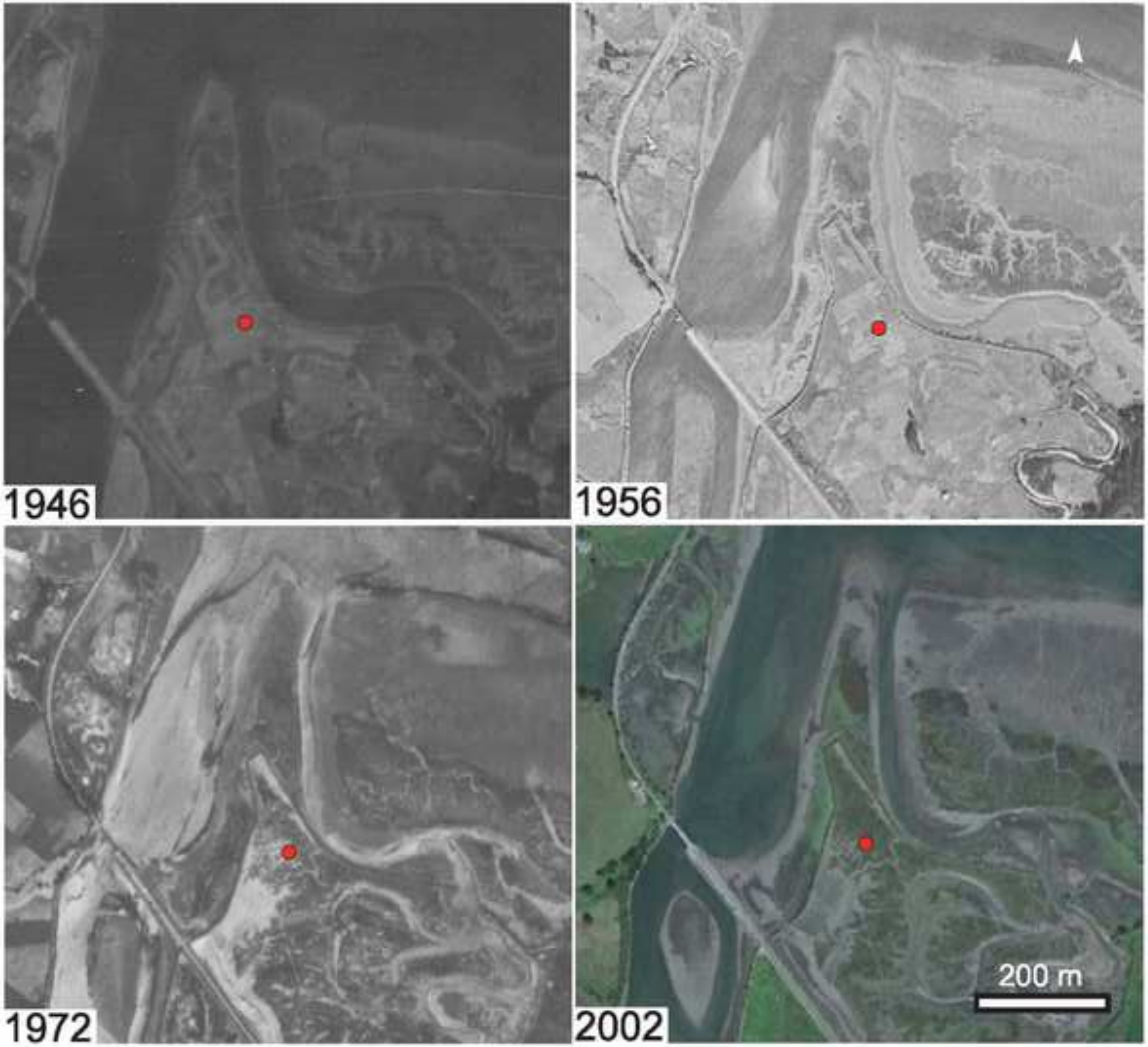

Figure

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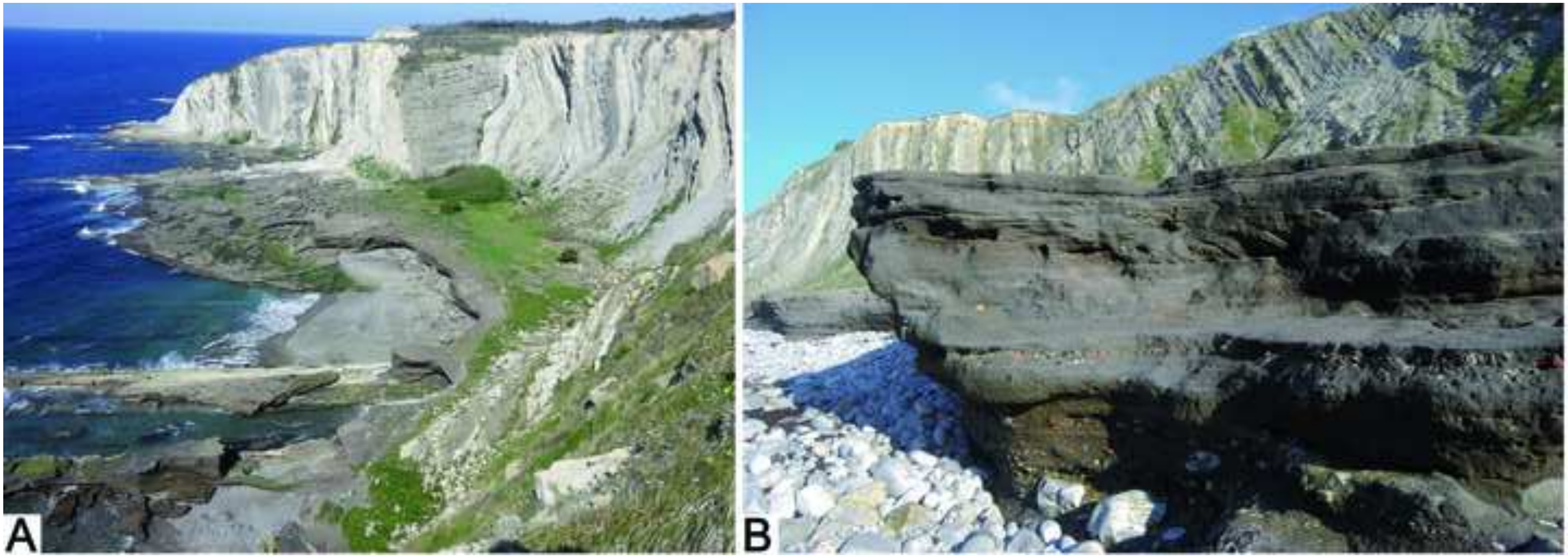

Table

Table 1. General information regarding the studied boreholes and cores.

Core	Estuary	Year	Coordinates	Height* (cm)	Length (cm)	Extraction devices	Sampling interval (cm)
P9	Pasaia	2007	X587839/Y4796700	405	120	Rotary percussion drill	30
FO1	Urdaibai	2003	X526417/Y4797809	376	387	Eijkelkamp auger	25
FO2	Urdaibai	2003	X526485/Y4797831	280	551	Eijkelkamp auger	25
FO3	Urdaibai	2003	X526426/Y4797815	377	580	Eijkelkamp auger	25
Axpe Norte	Urdaibai	2008	X525313/Y4803260	398	50	PVC tube	1
Carasa	Santoña	2010	X462590/Y4803949	307	50	PVC tube	1

* Above Local Ordnance Datum (LOD)

Table 2. Radiocarbon dates from the P9 (Pasaia estuary) and FO4 (Urdaibai estuary) boreholes.

Sample	Publication code	Altitude (m)	Material	Method	Conventional C-14 age BP*	δ^{13}C (‰)	Calendar calibrated age BP	2σ calibrated BP
P9-560	Beta-280534	0.65	shells	AMS	1000±60	-9.0	600	670-500
P9-500	Beta-280533	0.05	shells	AMS	1060±60	+1.0	640	720-530
P9-490	Beta-279117	-0.05	shells	AMS	1080±60	+1.3	650	730-540
P9-455	Beta-280532	-0.40	shells	AMS	1270±60	0.0	800	930-680
P9-390	Beta-279116	-1.05	shells	AMS	3380±60	-0.9	3250	3380-3100
P9-365	Beta-280531	-1.30	shells	AMS	3500±60	-2.5	3380	3520-3250
P9-630	Beta-310162	-2.25	shells	AMS	4440±50	+0.4	4600	4780-4480
P9-670	Beta-310168	-2.65	shells	AMS	4840±50	-1.2	5190, 5140, 5130	5280-4960
P9-710	Beta-310161	-3.05	shells	AMS	4860±50	-0.6	5210	5290-5010
P9-750	Beta-310164	-3.45	shells	AMS	5040±50	-0.4	5420	5520-5280
P9-790	Beta-310158	-3.85	shells	AMS	5480±50	+1.2	5880	5940-5730
P9-850	Beta-310640	-4.45	shells	AMS	5480±50	+0.5	5880	5970-5710
P9-930	Beta-310159	-5.25	shells	AMS	6250±60	+0.5	6700	6840-6560
P9-970	Beta-310165	-5.65	shells	AMS	6220±60	+0.9	6660	6790-6520
P9-1010	Beta-310166	-6.05	shells	AMS	6430±60	-0.1	6910	7080-6760
P9-1070	Beta-310167	-6.65	shells	AMS	6630±60	-0.3	7150	7260-7000
P9-1090	Beta-310160	-6.85	shells	AMS	6690±60	+0.8	7230	7320-7120
P9-1130	Beta-310163	-7.25	shells	AMS	7200±60	-2.0	7650	7780-7560
P9-1170	Beta-310157	-7.65	shells	AMS	7420±60	+0.1	7900	7980-7760
SFO4-1	Beta-200607	-1.80	shells	AMS	5700±50	-2.8	5710	5810-5570

*adjusted for local reservoir correction

Table

Table 3. Ranges of trace element concentrations in sediment cores from the Axpe Norte and Carasa salt marshes (all values in mg kg^{-1}).

	Pb	Zn	Cu	Ni	As
AXPE NORTE salt marsh (Urdaibai estuary)					
Above 22 cm depth	32-132	83-315	18-44	22-36	32-51
Below 22 cm depth (background values)	18-28	71-94	17-20	23-28	24-44
CARASA salt marsh (Santoña estuary)					
Above 41 cm depth (salt marsh sediments)	43-157	130-371	10-18	15-19	16-55
Below 41 cm depth (agricultural soil)	33-42	96-102	9-11	16-19	16-23