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Anthropocene footprint in the Nalón estuarine sediments (northern Spain)

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ABSTRACT

Four boreholes drilled at depths ranging from 9 to 27 m and retrieved from the Nalón estuary (Asturias, northern Spain) were investigated to assess the impact of the historical human footprint on the sedimentary sequence. Analytical measurements of grain size, geochemical composition (major and trace elements), and stable Pb isotopic ratios were performed. Two different sections of the sedimentary profile were identified throughout the sedimentary sequence using Pb isotopic ratios and then corroborated with grain size characteristics and As, Hg, Pb and Zn concentrations. The upper sediment layer of the boreholes (variable depth ranging between 3 and 9 m) exhibited an increase in $^{208}\text{Pb}/^{206}\text{Pb}$ ratios and a decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, whereas, in the deepest layers, these ratios remained unchanged. These variations reflected the anthropogenic input of Pb into estuarine sediments, which can be attributed to mining activities when compared to Pb isotopic ratios from coal mined in the region. The anthropogenic input can be also noted on the basis of the variability of the trace element concentrations with depth. The enrichment factors of As (max 7.5), Hg (max 45.4), Pb (max 10.3), and Zn (max 8.6), calculated using local geochemical background values helped distinguish the impact of intense anthropogenic activities, which can be attributed to mining exploitation in the Nalón River drainage basin. Despite the closure of several of these mines during the second half of the 20th century, geochemical characteristics have revealed the ongoing input of As, Hg, Pb, and Zn into the coastal zone. Thus, the legacy of contamination from these elements, mainly from leaching slags and tailing dams, is still being recorded in estuarine sediments and requires careful scrutiny on the part of local authorities in terms of its possible effects on the aquatic biota.

1. Introduction

Estuaries are transitional environments positioned at the boundaries between continental and marine systems where a large variety of anthropogenic activities have been developed (Essink, 1999; Cooper, 2003). Most estuaries have been identified as potential contamination sources; this includes ports and their management as well as industrial, urban, and recreational settlements (Van Rijn, 2005; Spearman et al., 2014). In addition, some estuaries have been modified, thus resulting in changes to their morpho-dynamic and sedimentary distribution (Flor et al., 2006; Monge-Ganuzas et al., 2013; Flor-Blanco et al., 2013; López-Peláez, 2015; Flor-Blanco and Flor, 2019).

Estuaries also act as nurseries for many forms of aquatic life, while their intertidal and saltmarsh areas are important ecological niches for the nesting and breeding of several migratory and resident bird species (Burton, 2020). Estuaries are also major areas of interaction between

fluvial waters and seawater, occurring through tidal currents and leading to variations in the physical and chemical properties of the aquatic compartment, including grain size and the composition of suspended particulate matter, water flow dynamics, salinity, pH, Eh, and the organic fraction (Yuan et al., 2014). These variations play an important role in the transport, deposition, and resuspension of sediment particles in the estuarine water column, influencing the spatial distribution, transformation, and eventual bioaccumulation of the associated dissolved and particulate contaminants (Liu et al., 2020). Estuarine sediments consist of mineral and organic components and are mainly derived from river catchments, but also from the sea or are produced in situ (Pan et al., 2019). In uncontaminated estuaries, the sediment geochemistry is mainly influenced by the geological characteristics of the bedrock caused by active weathering processes along the river catchment (Pandey et al., 2019); however, potentially toxic trace elements can be introduced into the estuarine environment by

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various anthropogenic sources (He et al., 2019). Contaminants are then stored in estuarine sediments, which can also function as secondary sources of contamination within the aquatic environment, depending on natural events (e.g., wave action, tidal currents, bioturbation and storm surge); or human activities (e.g., dredging, shipping and trawling) (Ciszewski and Grygar, 2016; Grygar and Popelka, 2016). The long-term input and deposition of sediments into the estuarine environment creates excellent historical records that aid in the reconstruction of sedimentary sequences from the past decades and centuries (Covelli et al., 2006; Yang et al., 2012; Gao and Chen, 2012; Shylesh Chandran et al., 2019). The anthropogenic footprint of these sediments is thus quite useful for obtaining regional and local geochemical backgrounds and assessing the degree of contamination (Galuszka, 2007). Several cases of anthropogenic contamination in estuarine environments have been detected in the Iberian Peninsula. Among them, the most distinctive are the Odiel and Tinto estuaries, which have been affected by natural and mining contamination since Tartessian and Roman times (Borrego et al., 2005; Carro et al., 2019) along with the Guadiana and Guadalquivir estuaries (González-Ortegón et al., 2019) in Southern Spain. Another example is the Tagus estuary in Portugal, which is contaminated by Yttrium and rare earth elements (Brito et al., 2018). In the neighbouring estuaries of the north of Spain, such as Galicia, Lorenzo et al. (2007) analysed heavy metals in the sedimentary sequence. In the Asturias region, however, few studies have investigated the link between human activities and the sediment contamination of trace elements (Flor and Flor-Blanco, 2005; Sierra et al., 2014; Flor-Blanco and Flor, 2019), which has most recently been detected in the Nalón River estuary (García-Ordiales et al., 2015, 2019a, 2019b).

The Nalón River estuary is the point at which the main hydrogeological system of northern Spain flows into the coastal area of the Cantabrian Sea. This wide drainage basin has been affected by anthropogenic contamination due to long-term mining activities which have taken place in the region since 1850 (García-Ordiales et al. 2019). The presence of a large number of decommissioned mines results in a great number of streams that discharge potentially toxic trace elements into the NRE. Previous studies have investigated several aspects of the Nalón River drainage basin, such as metal(oid) concentrations upstream of the estuary, as well as the fluvial geomorphology of the estuary itself (Ceñal and Flor, 1993; Flor et al., 1998; Silva et al., 2014; Ordoñez et al., 2014; López-Peláez, 2015). The distribution and accumulation of contaminants, specifically potentially toxic elements, has not yet been thoroughly explored in this environment. The main objective of this study involves the historical reconstruction of estuary sedimentary sequences, the identification of contamination related to metal(oid)s and coal mining using isotopic ratios, and the assessment of their enrichment as a consequence of anthropogenic sources with respect to local geochemical baseline levels.

2. Study area

The NRE belongs to the continental shelf of the Cantabrian coastline (northern Spain) (Fig. 1). At the basin level, the hydrographic system flows through Paleozoic bedrock from the Cambrian to the Upper Carboniferous periods. The western sector of the basin is characterised by the presence of low-grade metamorphic silico-clastic rocks interbedded with a calcareous series of grey limestones and dolomites, whereas, in the eastern section, calcareous and siliciclastic series predominate (Julivert et al., 1972). Specifically, the Asturian cliff coast is represented by up to 12 different levels of *rasa* (Flor and Flor-Blanco, 2005), while the Nalón estuary is embayed by lithological control, mainly paleozoic siliciclastic materials in the external sector and mixed deposits (calcareous and siliciclastic facies) upstream from the estuary (Flor-Blanco and Flor, 2019).

Since the mid-19th century, mining activities in the basin have seen a dramatic increase in the discovery of significant mercury and coal

deposits. All mining runoffs were directly poured into the fluvial channel, causing contamination of the estuary (García-Ordiales et al., 2018). The NRE is over 6 km long; in its uppermost section, the main estuarine channel retains its natural river banks and meanders, but in the lower section, in which the two ports (San Esteban de Pravia and San Juan de la Arena) were constructed, the natural morphology and sedimentation dynamics of the estuary have been altered (Flor-Blanco et al., 2015). The estuary channel is > 2 m deep and is affected by an annual meso-tidal range between 1.0 and 4.2 m. In general, the tides tend to reach over 2 m for > 70% of the year (Flor et al., 1998). The mercury mines have been closed since the 1970s, and coal mining has seen a major decrease over the last 40 years, however, the estuarine environment is still under pressure from the impact of decommissioned tailings and mining waste (Loredo et al., 2003; Ordóñez et al., 2013).

3. Materials and methods

3.1. Sampling operations

Four boreholes were collected from the estuary in 2014 using a rotary drilling method with a core recovery. The boreholes, labelled from S-1 to S-4 (Fig. 1) according to water flow direction, were drilled as follows: S1 (15 m) in the uppermost section of the estuary, S2 (9 m) in the middle section, and S3 (24 m) and S4 (27 m) in the lower section. The boreholes can be considered representative of the various sediment depositional areas. The two boreholes in the lower estuary, S3 and S4, were relatively close to each other as they were collected near the sector that is most active in terms of sediment accumulation. In addition, the same sector has been partially affected by dredging since 1960 to maintain its navigability, whereas jetties and piers were built in 1946. The boreholes were photographed and described macroscopically for lithology, colour variability (Color, 1975), sedimentary structure, and macrofossil content. Subsampling for grain size and geochemical analysis was performed by recovering a total of 87 samples of 5 cm thickness, which were selected from each borehole based on the characteristics of the sedimentary sequence, which was previously examined to identify significant textural variability (19 samples for S-1, 16 for S-2, 28 for S-3, and 24 for S-4). The collected samples were air-dried at room temperature for several days, sieved through a 2-mm-sieve to discard gravel and shelly fractions, and then split into representative aliquots designed for each analysis.

3.2. Grain size, chemical, and isotope analyses

Organic and inorganic carbon (carbonates) content was determined using loss on ignition (LOI) analysis, according to the method and recommendations reported by Wang et al. (2011). For grain size determination, the samples were first treated with a hydrogen peroxide (H₂O₂) solution (3% v/v) during a 48-hour period to remove organic matter. Grain size distribution was measured using a Fritsch Analysette 22 laser diffraction particle analyser, and the contents of the three main components (sand, silt, and clay) were assessed according to Shepard (1954). Samples for major and trace element analysis were air-dried and crushed in a planetary agate ball mill. Representative aliquots of 1 g samples were mineralised in a closed microwave system with 5 mL *aqua regia* and 1.5 mL HF. The extracts were then analysed with an inductively coupled plasma atomic emission spectrometer (ICP-OES) model Thermo Scientific™ iCAP™ 7600, and an inductively coupled plasma mass spectrometer (ICP-MS) model Thermo Scientific Element II at the Bureau Veritas Lab (Vancouver, Canada). The calibration curves were obtained using standard solutions (Merck) prepared by dilution (1000 mg L⁻¹), and the quality was verified by measuring blank samples, quality control samples prepared with standard solutions (Merck and Icus 3058 Custom Standard, Ultra-scientific), and the lab internal-certified reference materials OREAS25A and OREAS45. The precision of the measurements as relative standard deviations reported by the

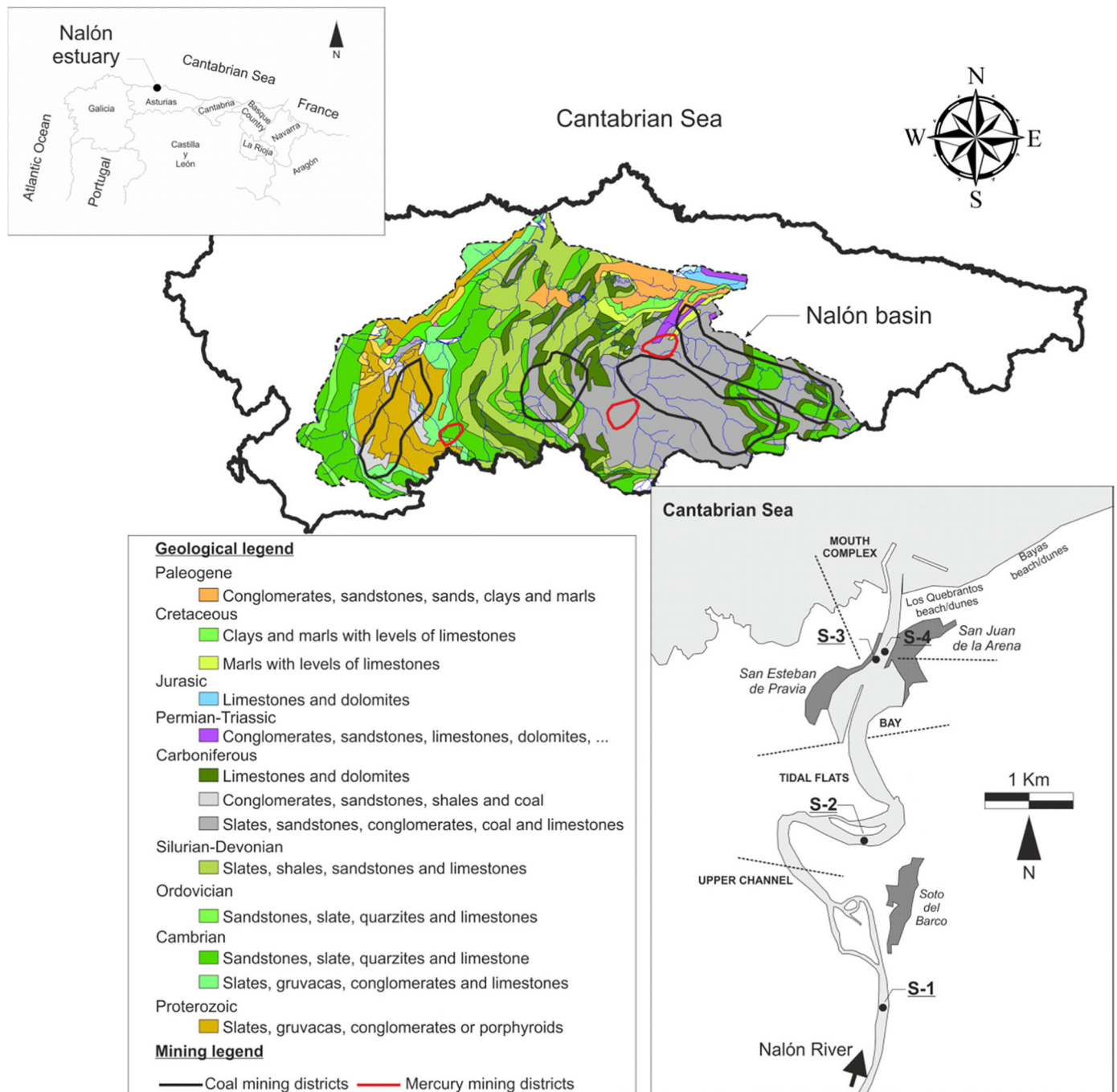


Fig. 1. Study area and borehole locations.

laboratory ranged from 1.85% for Pb to 9.61% for Cr. In addition, in selected samples, the Pb to isotope ratio measurements were carried out using an inductively coupled sector field plasma mass spectrometer (ICP-SFMS) from the Als Global Lab (Sevilla, Spain). In summary, samples for Pb isotope analysis were pre-treated following the method of De Muynck et al. (2008), which has proven effective in eliminating the matrix of the samples without giving rise to an isotopic fractionation and thus leading to erroneous measurements. After the pre-treatment, the samples were passed through a selective resin PbSpect (Triskem International, Bruz, France) in a Bio-Rad propylene column, and the matrix was eliminated with the addition of 0.14 M HNO_3 . The lead trapped in the resin was elutriated with a solution of 0.05 M $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, which was evaporated to dryness at 110 °C. The residue was dissolved with *aqua regia* on a hot plate at 110 °C for 24 h to

remove potential organic content from the $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The solution was evaporated at 110 °C for 2 h and the final content was dissolved with 0.42 M HNO_3 , and certified reference material NIST SRM-997 (Thallium Isotopic Standard) was added (Encinar et al., 2001). Analysis was validated using lab internal-certified reference materials OREAS 905, MRGeo08, and OREAS 920, and the measurement precision as relative standard deviations reported by the laboratory were < 2% for the different Pb isotopes.

3.3. Normalisation procedure and enrichment factor (EF)

Before any estimation of the enrichment degree, normalisation to a reference element is necessary to compensate for grain size and mineralogical effects on metal(oid) variability in the samples (Covelli and

Table 1

Geo chemical Baseline Functions (GBF) between metal(oid)s and Al. SEE indicates the standard error of the Y estimation.

Equation GBF	SEE	r, P
As = 0.0268 + 2.834 Al	0.813	0.863, < 0.001
Cr = -1.081 + 5.515 Al	0.777	0.956, < 0.001
Cu = -1.948 + 7.517 Al	1.149	0.961, < 0.001
Hg = 0.001364 + 0.008517 Al	0.002	0.912, < 0.001
Ni = 0.3810 + 10.28 Al	0.792	0.985, < 0.001
Pb = 0.3335 + 1.698 Al	0.325	0.938, < 0.001
Zn = -1.086 + 10.88 Al	4.166	0.875, < 0.001

Fontolan, 1997). In this study, the compensation of these effects was done using the geochemical baseline functions (GBF) which allows one to predict the value of a trace element through a normalising element. The baseline concentration of each element was calculated using the GBF, obtained according to the method described by Jiang et al. (2013). In brief, the first step consists of plotting the distribution histogram of the elemental concentrations to identify and remove outliers. In the second step, the cumulative distribution function (CDF) of each elemental concentration is plotted to identify the bend, splitting the dataset into a natural or geogenic background concentration set and an anthropogenically affected concentration set which was then removed from the original dataset. In the third step, the relationships among the trace elements (As, Cr, Cu, Hg, Ni, Pb, and Zn) and the best grain size proxy were linearly fitted. Aluminium was selected as a normalising element based on previous studies (e.g. Loring, 1991; Colizza et al., 1996; Covelli et al., 2006). Data points outside the 95% confidence interval were removed, and the remaining dataset was again linearly fitted to produce the geochemical baseline functions. The results of this process for each element are found in Table 1. The degree of enrichment (or enrichment factor EF) can be given by the ratio between the measured concentration and the predicted meta(oid) value determined through the linear GBF (Covelli et al., 2006). In the present study, based on the work of Abraham and Parker (2008), the established limits for the EF were 2 and 5. Within the range $2 \leq EF < 5$, samples were classified as moderately enriched; for EF values ≥ 5 , samples were considered to be severely enriched.

4. Results and discussion

4.1. Sedimentological characteristics of the boreholes

A visual description of all the boreholes (Fig. 2) revealed that the sediment profiles mainly consisted of sand and mud (silt and clay), with a low percentage of gravel (avg. 15.3%). In general, three main layers could be distinguished: an uppermost, very thick, dark layer composed of sand and mud (between 3 and 9 m); one transitional layer of variable thickness made of gravel (between 0.5 and 1.5 m); and a lower, very thick, brown layer again composed of sand and mud.

In the uppermost section of the borehole profiles (between the surface, and 3 m for S-1 and S-2; between the borehole top, and 9 m for S-3 and S-4), sediments exhibited a very dark black colour, which gradually changed to light brown at greater depths. Primary quartzite materials and a large amount of black sands and slates due to coal and by-products, were also found in this section. According to Ceñal and Flor (1993), who identified the rocky fragments as carbonaceous slates, this material could be related to the historical coal mining development in the riverine drainage basin, which has begun to significantly increase since 1850 (Fig. 3). According to this historical evidence, the uppermost section may represent the last 150–160 years of the estuarine environment. Similar to that which occurred in the Nalón estuary, Pirrie et al. (1997, 2002) reported an increase in the natural sedimentation rate in the Fall and Fowey estuaries as a consequence of mining contributions to the rivers.

In the middle section of the boreholes, identified as a transitional layer, the gravel bed was composed of riverine boulders, which likely represent a period of intense river floods that supplied coarse material added from the drainage basin.

Finally, in the third section, the bottom primary quartzite materials without slate could be observed. The absence of dark sandy deposits in this part of the sedimentary sequence and the light brown colour of the sediments suggest that the materials were derived from the erosion of bedrock that occurred prior to coal extraction as well as sediments related to estuarine dynamics. López-Peláez (2015) and Flor-Blanco et al. (2015) interpreted this section as the mouth of the estuary and its inlet before the construction of the jetties that favoured beach/dune (spit) progradation to the north.

The basal section of the boreholes, below the gravel bed, represents a different stage of the Holocene evolution in the estuarine mouth. This anomalous and notable sedimentation in the Nalón River mouth may be explained according to previous studies regarding the evolution of the Holocene (Millán and Valcarlos, 2010) and the infilling of the inner estuaries in the last century, with average rates of 1 cm yr^{-1} in seven estuaries of the north of Spain (Bruschi et al., 2013). The bioclasts of bivalves, such as mussels or clams, were abundant in boreholes S-3 and S-4, located in the “marine” section of the estuary but were undetectable in boreholes S-1 and S-2, in which freshwater conditions were dominant and did not favour the presence of bivalves. Strata with shell debris appeared below the black and gravel layers, suggesting the estuarine environment developed greater macrofauna biological activity prior to anthropogenic inputs.

4.2. Variability of major and trace elements in the sedimentary sequence

As seen in Fig. 4, in all four boreholes, the profiles of the major elements, Al, Fe, and Ti, reveal a general decreasing trend with depth similar to that observed for the silty-clayey fraction, while Si is seen to positively increase with the sandy component rich in quartz. Furthermore, boreholes S-3 and S-4, from the lower part of the estuary, show significant variations with depth for the above-mentioned elements, whereas this variability is more restricted in boreholes S-1 and S-2.

In boreholes S-3 and S-4, Ca content varied from 0.9% to 8.2%, while Mg content varied from 0.2% to 1.6%, from the top to bottom sections, respectively. These trends and peaks are associated with the significant presence of shelly fragments in the sediment. As a consequence, in the lower part of the estuary, the carbonate component of the sediments can be considered more attributable to a bioclastic origin than a mineralogical origin (Ceñal and Flor, 1993). In the upper part of the estuary, Ca and Mg profiles in boreholes S-1 and S-2 showed a slight decrease with depth, because neither was affected by the accumulation of shelly fragments due to the major influence of the riverine waters.

For the four boreholes, LOI was high in the upper section and gradually decreased in the basal section. Based on the organic matter and carbonate contents, LOI values were seen to be primarily dependent on organic matter. For the layers in which LOI reaches its maximum (23.5%), organic reach pockets were detected, which could be considered the probable cause of the highest LOI values. Sulphur and LOI profiles displayed a positive trend in the S-1, S-2 and S-3 profiles, with the sulphur source primarily related to organic matter. In the deep section of the S-4 profile, there were anomalous, sulphur-rich sediment layers which presented a strong relationship with elements that can be commonly found in the form of sulphides, such as As, Hg, Fe, or Pb. This result suggests that a contribution of sulphide-rich materials may have been the cause of these changes.

Concerning the trace elements (Fig. 5), metal(oid)s (As, Cr, Hg, Ni, Pb and Zn) exhibited high concentration values in the first 3 m of boreholes S-1 and S-2, and the first 7 m of boreholes S-3 and S-4. This can be explained by “modern” sediments comprising these shallower beds, which have been affected by anthropogenic activities that may have altered the natural geochemical abundance of the metal(oid)s in

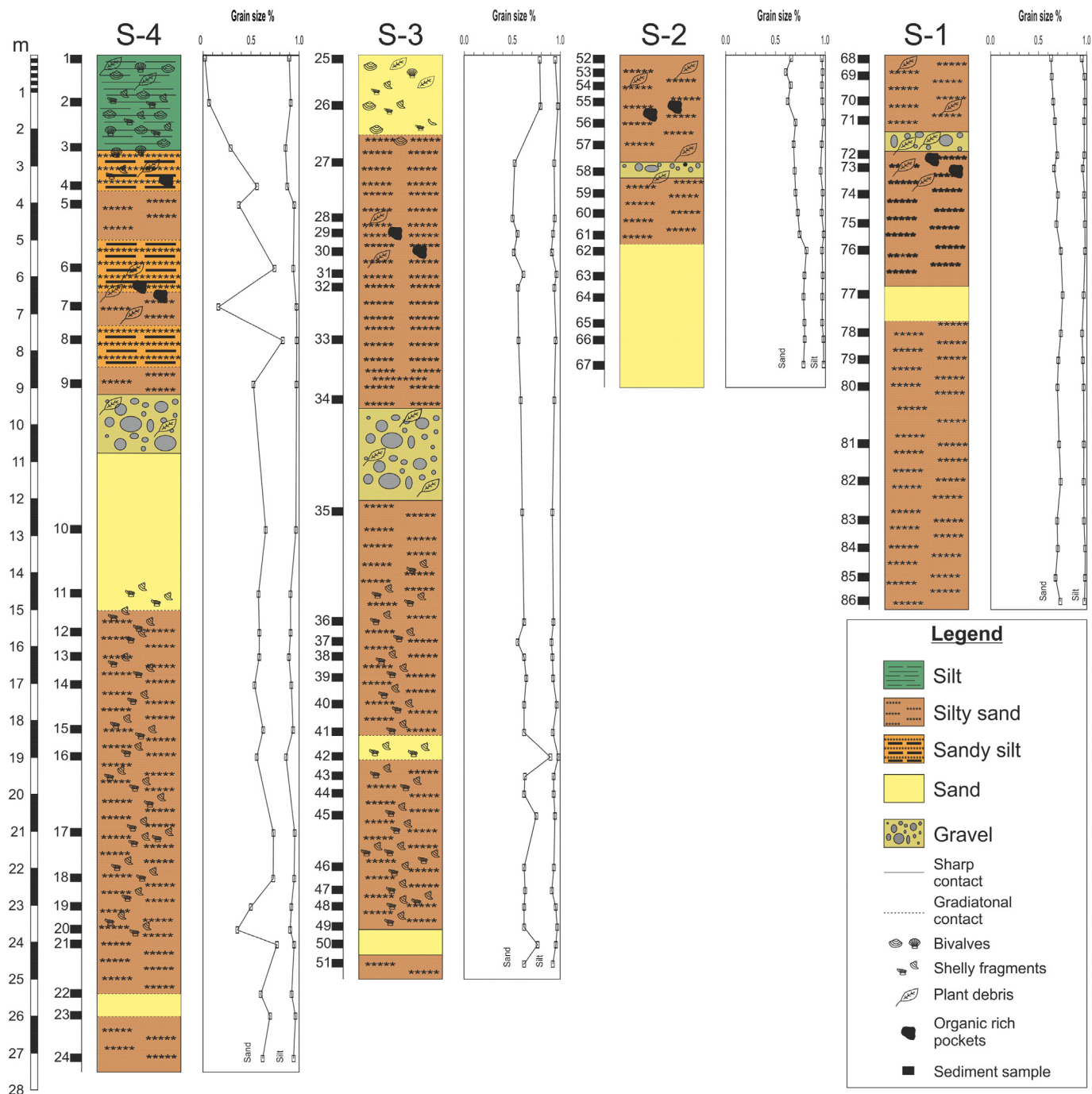


Fig. 2. Borehole logs of S-1, S-2, S-3, and S-4 showing the sedimentary sequence.

the sediment. These recent sediments are of special interest in boreholes S-3 and S-4, since this area is subject to dredging activities implemented to maintain the navigability of the estuary. In this case, based on the concentrations detected and according to the Spanish Guidelines for dredged materials (CEDEX, 2015), these “modern” sediments were classified as Level A, which corresponds to minimally contaminated sediments. Despite our results not exhibiting high concentration levels of trace metal(oid)s with respect to the national regulations, a previous study conducted by Garcia-Ordiales et al. (2019) indicated that recent sediments with similar concentrations may exhibit toxicity for aquatic organisms. Consequently, the uppermost section of the sedimentary sequence in the lower estuarine area, represented by boreholes S-3 and S-4, should be carefully handled with particular deference to dredging activities.

4.3. Variability and sources of stable Pb isotopic ratios in the sedimentary sequence

Differences in the isotopic ratios and concentrations of Pb are commonly used to suggest sources of anthropogenic Pb (Eades et al., 2002; Gao et al., 2018; Gamo, 2020) and have been useful to identify periods in which mining has altered the natural geochemical partition of sediments (Mil-Homens et al., 2017). In the Nalón River estuary, the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotopic ratios, together with the Pb/Al profiles (Fig. 6), varied considerably with depth, demonstrating the non-geogenic sources of Pb over time. Considering these variations, two well differentiated phases could be distinguished in all the boreholes related to the sediment layers described in Section 4.1.

To thoroughly identify potential contamination sources, the $^{206}\text{Pb}/$

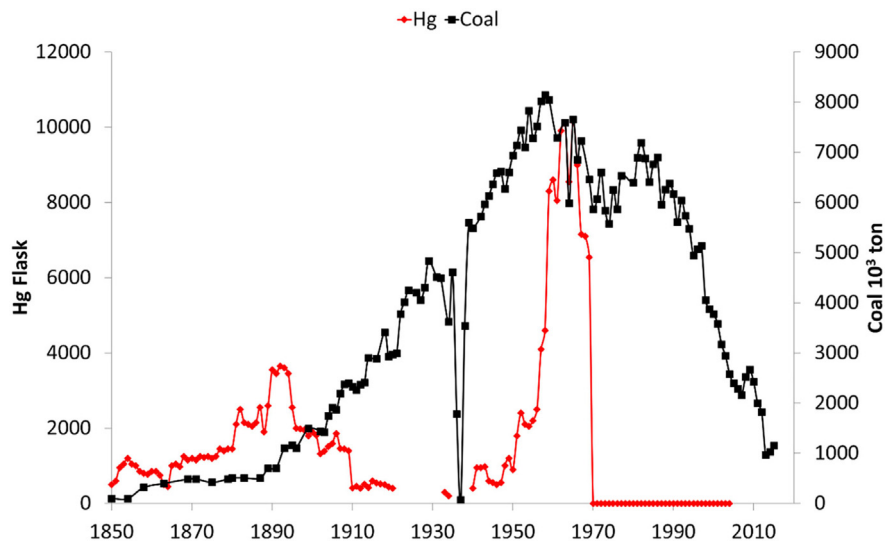


Fig. 3. Historical coal and Hg production in Asturias. Mercury is reported with the flask unit which occupies a volume of approximately 2.547 l and 34 kg.

^{207}Pb and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of the borehole sediment samples were compared to source-specific materials, such as coal samples from the area (Díaz-Somoano et al., 2007), European leaded gasolines (Monna et al., 1995, 1997; Hansmann and Köppel, 2000), aerosols from Spain (Bollhöfer and Rosman, 2001) and soils from NW Spain (Kylander et al., 2005). As shown in Fig. 7, samples from the deepest layers did not exhibit a cluster with any of the considered anthropogenic sources and appeared to resemble soils from NW Spain (Kylander et al., 2005). Conversely, samples from the uppermost sections of the boreholes were grouped with the isotopic signatures of regionally mined coal, as reported by Díaz-Somoano et al. (2007). Asturias has been the largest producer of coal in Spain and the most important coal mines are located in the Nalón River basin (Cienfuegos and Loredó, 2010). Coal has continuously been mined since the mid-19th century (Fig. 3) and residual materials from this activity are transported by the Nalón River (Fernández Valcárcel, 1992). This historical information is in agreement with the isotopic signatures found in this study and the dark colour of the sedimentary profiles. Both the isotopic signatures and the dark colour are representative of our benchmark and allow for the attribution of an approximate age of 160 years to be assigned to the dark sedimentary level identified in the four boreholes when considering that industrial coal mining began in 1850 (Anes and Ojeda, 1983). Coal mining is not the only source of anthropogenic materials in the river drainage basin, as exploitation of Hg has coexisted with coal mining for 120 years (García-Ordiales et al. 2019). In this case, the potential Pb contribution from the Hg ores, mainly cinnabar, could be considered negligible due to the rare presence of this element in Asturian ores (Ordóñez et al., 2013) and the greater magnitude of coal production (500 Mt) than Hg production (0.130 Mt) in the last 150 years. Thus, the main non-geogenic source of Pb can be attributed to coal mining.

In addition, considering the vertical profiles of the analysed elements in the black sediments, the trends of Cr, Cu, Ni, and Zn appear to be quite similar to that observed for Pb, whereas the trends of As and Hg were different. A potential secondary source other than coal mining must have contributed these elements to the estuary. The profiles of As and Hg were quite similar, and the relationship of both to their mining origins has previously been reported in sediments of the basin and estuary (Silvia, 2011; Ordóñez et al., 2013; García-Ordiales et al. 2015, 2019). To support this mining origin, a reconstruction of the geochronology of the sedimentary sequence was carried out, assuming a time period of 160 years of mining for the black sediments and a constant sedimentation rate in the estuary. Based on this analysis, in boreholes S-1, S-2 and S-3, the peak concentrations of As and Hg fell during a period approximately between 1965 and 1970 (Fig. 7), which is in agreement

with ^{210}Pb and ^{137}Cs dating and geochemical results reported by García-Ordiales et al. (2019) for the sedimentary profiles from the estuarine saltmarshes of the Nalón River mouth. As and Hg peaks could be attributed to the exploitation of Hg minerals. In the case of borehole S-4, this reconstruction did not yield the expected results (the peaks fell within the period from 1935 to 1940) despite its proximity to borehole S-3. This can be attributed to the greater variability of the concentrations of fine particles in the sediments as a consequence of dredging activities performed in this part of the channel, which did not occur in S-3. During dredging activities carried out in this area, parts of the sediments were removed, altering the natural sedimentary sequence and geochemical partitioning in the sediments.

4.4. Enrichment factor related to major periods of contamination

As shown in Fig. 8, the enrichment profiles clearly distinguished between two groups of elements. On one hand, the profiles of Cr, Cu, and Ni showed moderately enriched sediment samples but with no clear trend to identify anthropogenic periods. For this reason, variations detected in their profiles have been attributed to natural sources. This is in agreement with previous studies on the estuary (García-Ordiales et al., 2015) and in mining areas of the river basin (Méndez Pazos, 2013; Ordóñez et al., 2014b), which did not exhibit notable anomalies in this group of elements. On the other hand, the enrichment profiles for As, Hg, Pb, and Zn allow one to identify two different periods in each borehole that coincide with the two types of sedimentary material described above (dark and light). In this case, in the deepest layers of each borehole, no enrichment of these elements was detected, implying they are natural sediments unaffected by mining. However, in the most recent dark layers, these elements showed moderate to severe enrichments. Similar enrichment trends for the same elements were reported in the saltmarshes of the estuary (García-Ordiales et al. 2015, 2019), supporting the existence of two different periods of sedimentary contributions to trace metal(oid)s. In the NE coastal area of Spain, Cearreta et al. (2002) investigated the distribution and abundance of benthic foraminifera and a range of trace elements in six cores of up to 10 m in length from the Bilbao estuary to document the environmental transformation of this estuarine ecosystem and determine sediment contamination levels. The first 4 m of the sedimentary sequence was affected by moderate contamination due to anthropogenic inputs with significant enrichments (Fe EF = 3.8, Zn EF = 5.6, Pb EF = 8.0, Cu EF = 6.4 and As EF = 3.4) at the core top. Over the last 150 years, the Bilbao estuary has received waste from many sources due to the exploitation of abundant local iron ore, contributing to the early

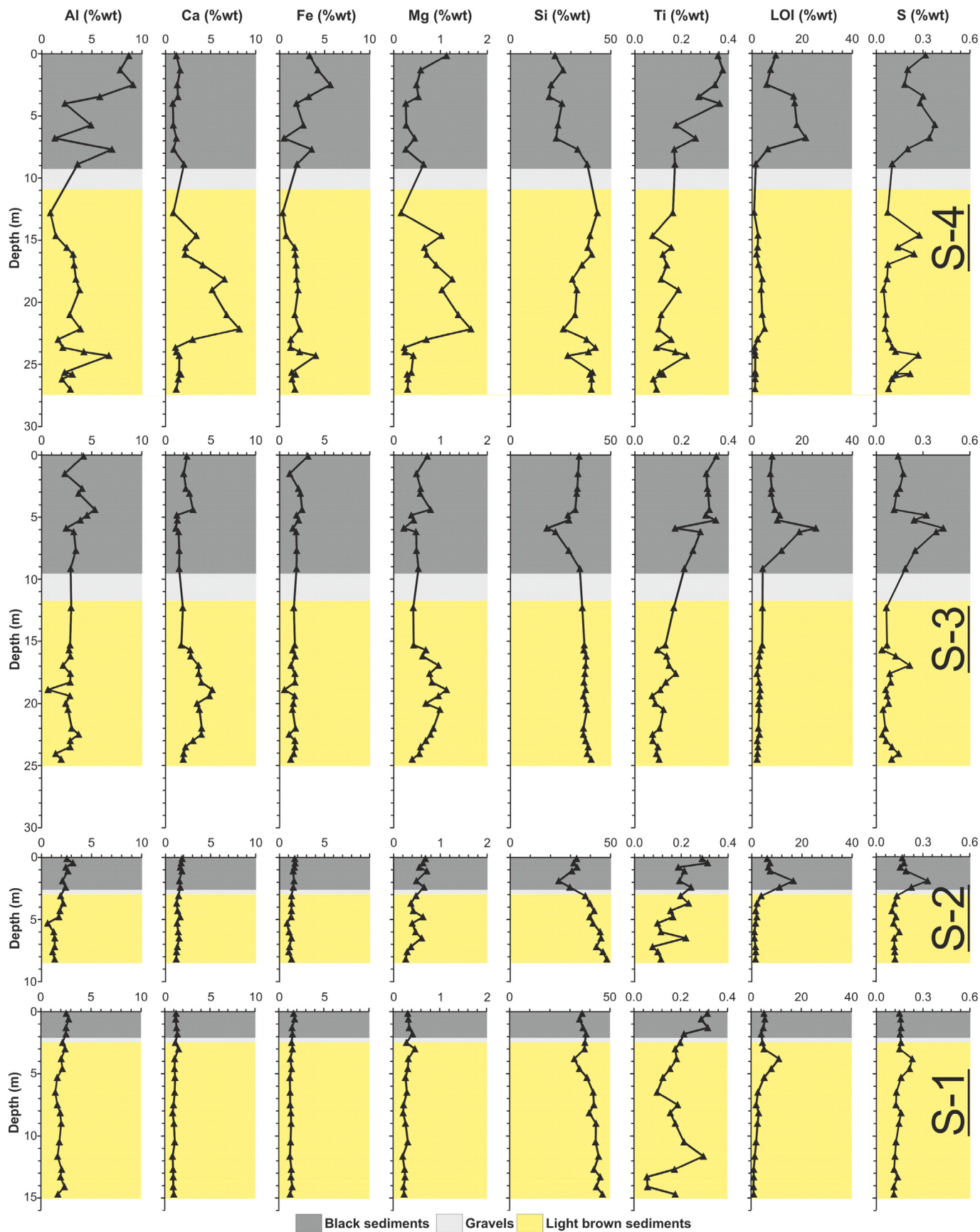


Fig. 4. Borehole logs of S-1, S-2, S-3, and S-4 showing the vertical variability of the concentrations of the major elements and organic matter (reported as LOI, Loss On Ignition).

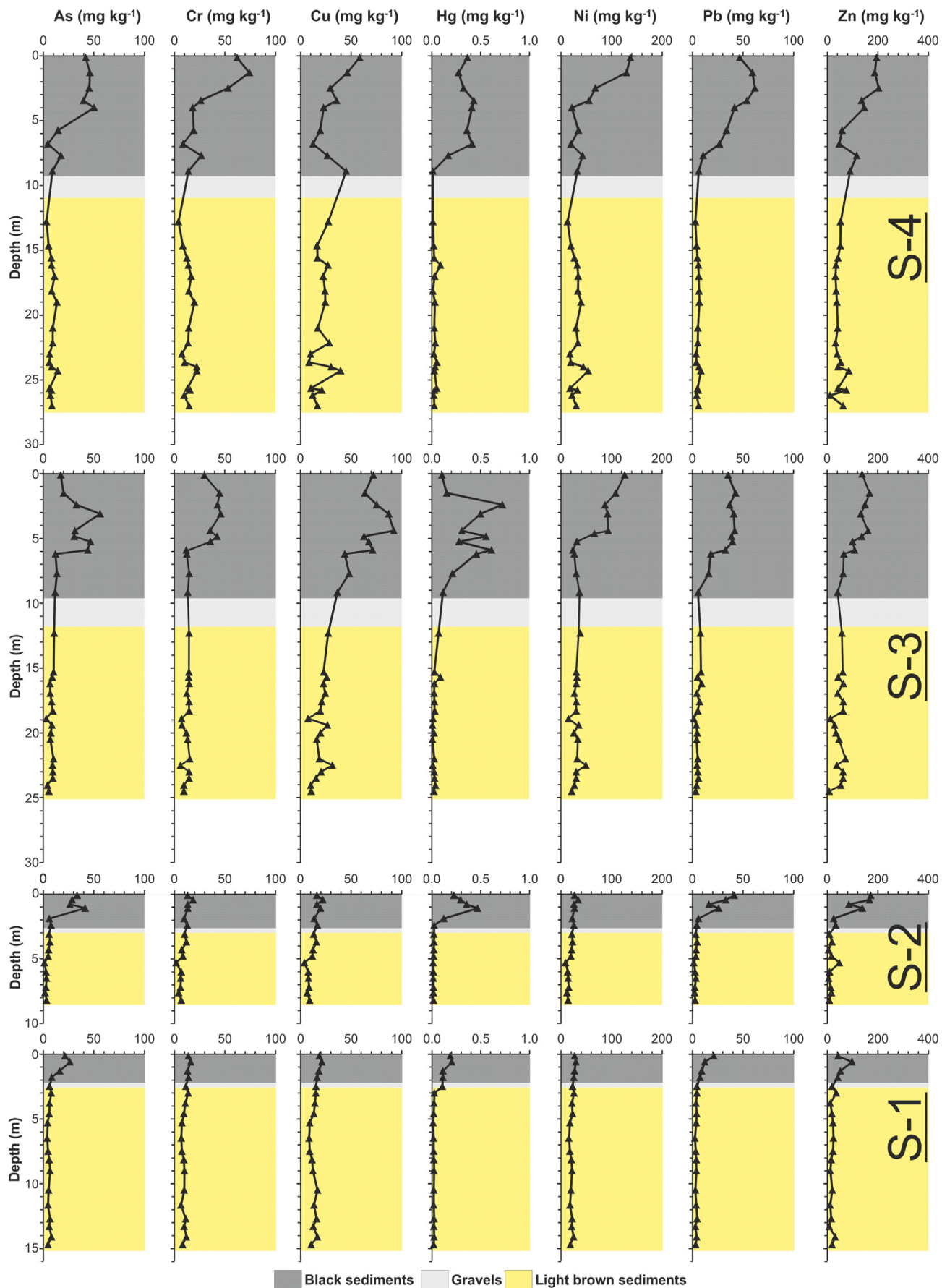


Fig. 5. Borehole logs of S-1, S-2, S-3, and S-4 showing the vertical variability of the trace element concentrations.

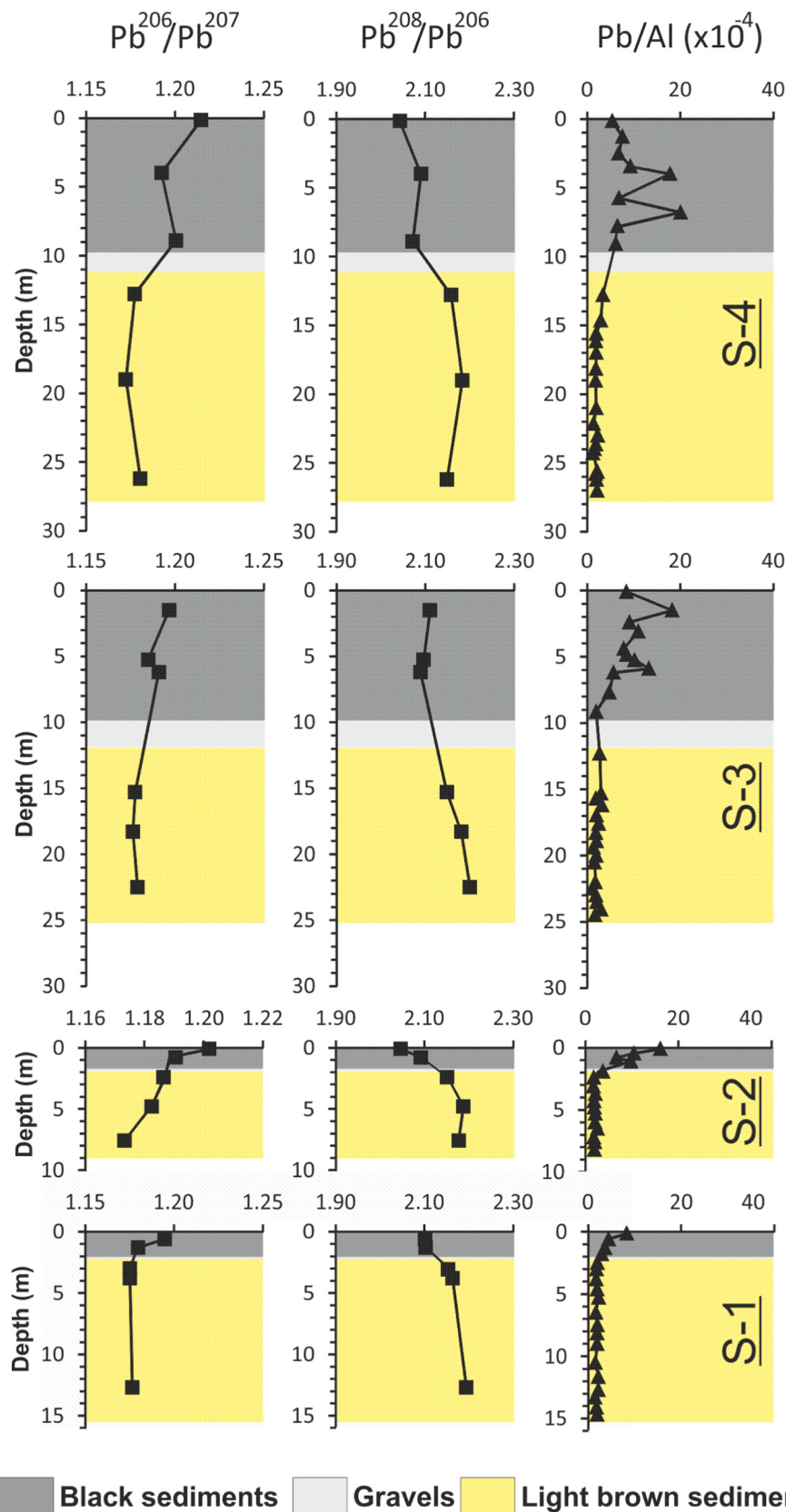


Fig. 6. Borehole logs of S-1, S-2, S-3 and S-4 showing the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotopic ratios together with the Pb/Al profiles.

industrial development of Bilbao in the mid-19th century. In the southern Bay of Biscay, an integrated geochemical–microfaunal approach was employed by [Iribien et al. \(2008\)](#) to assess the present

situation and also the last 130 years of environmental transformation in the Suances estuary. Concentrations of Zn, Pb, and Cd in both surface and core samples were remarkably higher than background values,

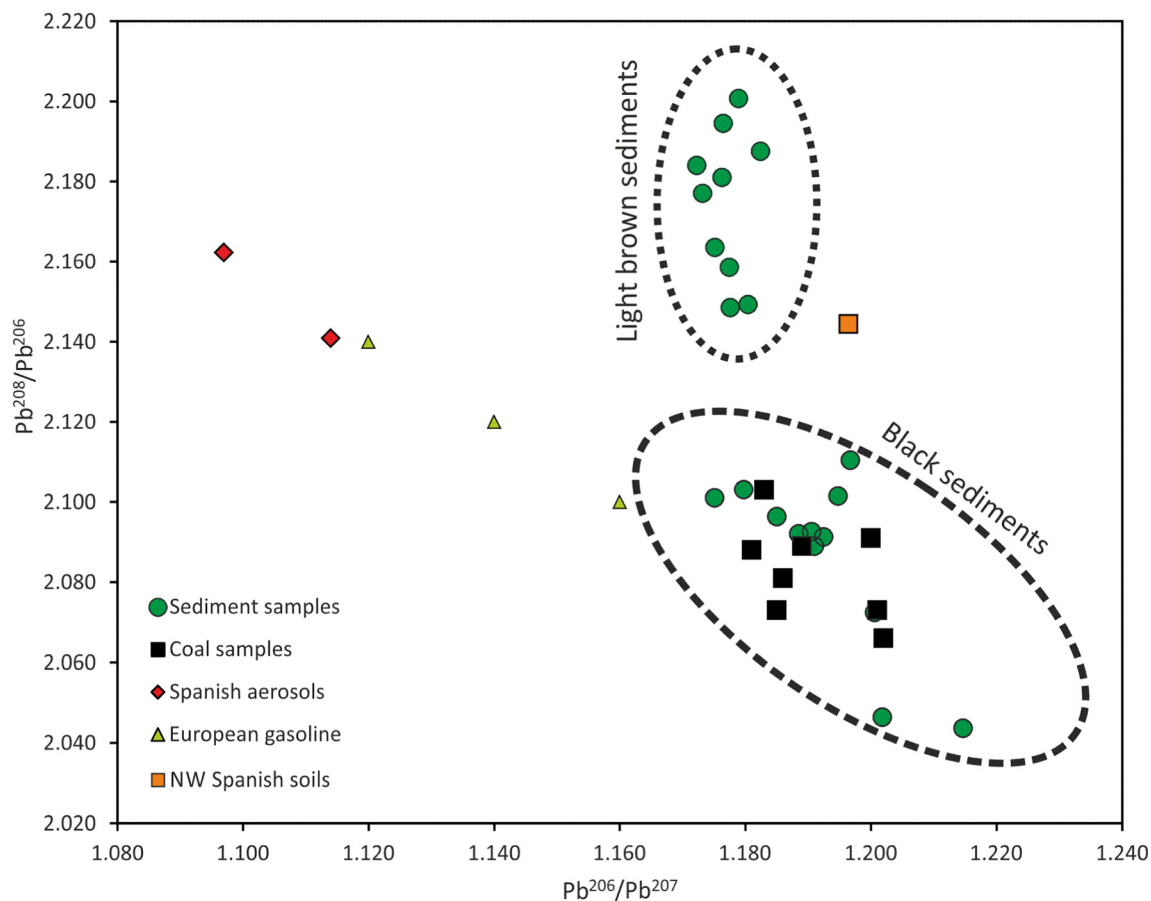


Fig. 7. Scatterplot reporting the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ sediment isotopic ratios of the boreholes together with the isotopic ratios of the potential anthropogenic and natural Pb emission sources.

resulting from the mineral exploitation of Pb–Zn deposits from the mid-19th century until 2003, whereas Hg enrichments could be related to the evolution of the chlor-alkali industry which began in 1935. In the NW Iberian Peninsula (Galicia), [Alvarez-Vazquez et al. \(2017\)](#) investigated the sedimentary records of the estuarine part of three sparsely populated and poorly industrialised rias. The results showed that the anthropogenic influence on this area is quite recent, dating back only as far as the mid-20th century. The human impact detected was due to activities such as the damming of the Eume River, lignite excavation (from the largest mine open pit in the Iberian Peninsula), bridge/road construction, vehicle emissions and river mouth urbanisation, and changes in land use.

In our study, boreholes S-3 and S-4 exhibited a higher number of enriched samples compared to S-1 and S-2. This highlights that the enrichment of the elements was related to grain size distribution in the estuary, since the greatest number of enriched samples was found in the upper sections of the sedimentary profiles in which the fine-grained component is high ([Fig. 2](#)). In addition, considering the distribution of the enriched samples with depth and in the study area, As, Hg, Pb, and Zn could be considered potential contaminants ($EF > 5$) throughout the estuary, with a higher incidence in the two boreholes located in the lower estuary. The toxicity of this group of enriched elements in the recent sediments of the estuary has previously been analysed by [García-Ordiales et al. \(2019b\)](#), reporting that the existing concentrations may affect biota based on ecotoxicological tests.

More specifically, As and Hg are similarly enriched in the analysed sedimentary levels belonging to the uppermost sections of the four boreholes. This similarity is in support of previously seen evidence that the enrichment of the two elements in recent estuarine sediments is related to a common source coming from Hg mines. Conversely, the

enrichment observed for Pb and Zn in the uppermost sections of the boreholes differs from that reported for As and Hg, thus rendering coal mining the most probable main source of the two elements in the Nalón River drainage basin.

5. Conclusions

Stratigraphic record analysis of the boreholes from the Nalón River estuary allowed us to distinguish the sedimentological and geochemical features of a very complete sedimentary sequence, providing some of the first evidence of changes to the estuarine sediments due to historical coal and Hg mining activities. These results were confirmed by geochemical relationships, using metal(oid) concentrations, mainly Hg, As, Pb and Zn, as markers of the footprint left by various mining activities.

The Geochemical Baseline Functions (GBFs) obtained from the analysed borehole samples can be used for an assessment of the anthropogenic enrichment of the estuarine and coastal sediments in the study area through the application of simple metal(oid)-Al linear relationships.

Of the entire estuary, moderate to severe contaminations of As, Hg, Pb, and Zn were detected in the uppermost sections of the boreholes, testifying to the “recent” contribution (i.e. approximately 150 years) of metal(oid)s due to mining activities. The two sources related to coal and mercury extraction activities could be distinguished on the basis of Pb isotopic composition. Moreover, highly enriched samples were detected in the lower sector of the estuary, in which fine particle sedimentation occurs. As a consequence, future operations involving sediment dredging in the estuary should carefully take the effects of a potential remobilisation of metal(oid)s from sediments to the water column and, eventually, the aquatic trophic chain into consideration.

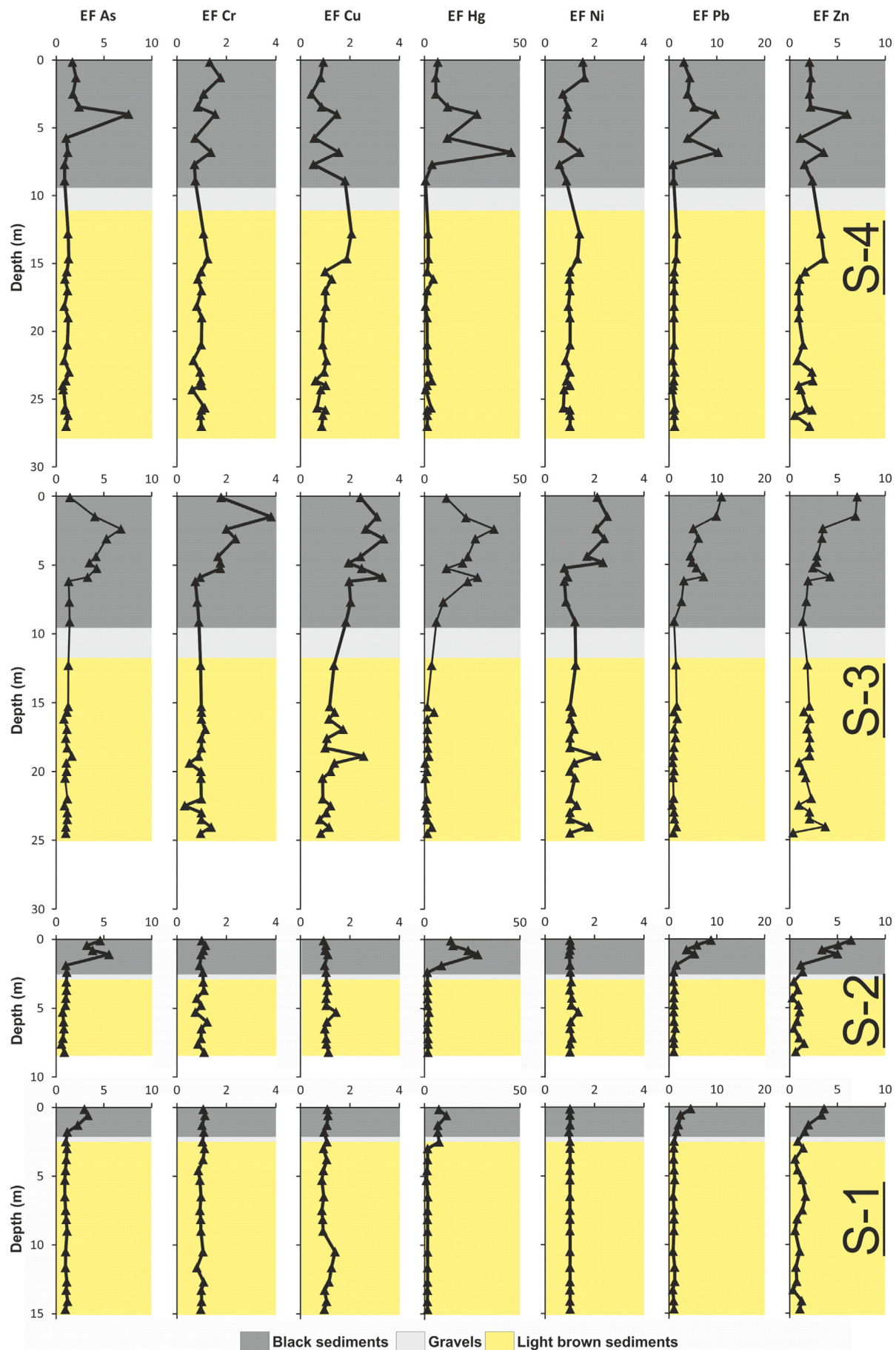


Fig. 8. Enrichment Factor (EF) profiles calculated using Geochemical Baseline Functions (GBF) and the related measured metal(oid) concentrations.

The background values obtained could be useful in the decision-making process to accurately assess the environmental impact of dredging, taking into account the environmental limits established in the regulations (CEDEX, 2015) modified by the OSPAR Commission (1998). The results obtained might assist in the integrated management of such future sediment movements and thus not damage the various habitats found within the Nalón estuary.

For the most recent sediments, trace metal(oid) profiles seemed to indicate a slow decrease in concentration but, even so, their values suggest that large amounts of these potentially toxic elements are still added to the estuary from the drainage basin of the Nalón river. Moreover, natural attenuation seemed not to be sufficiently effective in cutting the flow of trace elements to the estuary, and thus, environmental restoration measures in decommissioned mines as well as proper management of contaminated sediment in the estuary will be necessary to reduce anthropogenic pressure on this aquatic ecosystem.

Declaration of competing interest

The authors of this manuscript declare that they have no conflicts of interest in this investigation.

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