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Trace metals from different anthropic sources on the mid-west coast of Asturias: Concentrations, dispersion and environmental considerations

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ABSTRACT

The central coast of Asturias (Spain), which has suffered significant anthropogenic impacts during the last 150 years, has been studied using 71 sediment samples to establish a preliminary scenario of the geochemical and environmental state of sediments, relating them to their potential sources. In general, As (max 28.5 $\mu g\ g^{-1}$), Cd (max 1.1 $\mu g\ g^{-1}$), Pb (max 123.5 $\mu g\ g^{-1}$) and Zn (max 572 $\mu g\ g^{-1}$) were the elements that presented the greatest concern due to 97.2 % of the sediment samples presented Cd concentrations higher than the regional baseline, 91.5 % of the samples for Zn, 90.1 % for Pb and 78.9 % for As. Additionally, Hg presents a particular case due to the existence of a natural geological anomaly which favours the presence of high concentrations. Nevertheless, anthropic activity contributes with a significant effect on the concentration of this element in the coastal environment.

1. Introduction

Coastal environments are one of the most important ecosystems on the planet as they have a high level of biodiversity, a wide variety of biogeochemical processes, and are responsible for many ecosystem services essential for human activities (Martínez et al., 2007; Grizzetti et al., 2019). However, these ecosystems are affected by different factors coming from human activities, including the input of anomalous concentrations of pollutants that have a negative impact on environmental quality and ecosystem services (Bashir et al., 2020; Häder et al., 2020).

These areas are highly exposed to pollution as they are in the contact zone between sea and land and are therefore subject to pollutants from both sources (Wang et al., 2017; Wu et al., 2020). In addition, since a large part of the global population settles close to these areas, anthropic activities such as fishing, tourism, urbanisation, industry, mining and agriculture produce an increase in the load of pollutants (Yang et al., 2018; Al-Sulaiti et al., 2022; Dai et al., 2022). Among the different contaminants introduced into the coastal environment by anthropic activities heavy metals stand out and have become the cause of increasing global concern owing to their negative impacts on health and the environment (Li et al., 2019, 2020; Tian et al., 2020; Khoshmanesh et al., 2023). Heavy metals are a group of chemical elements characterised by their persistence in the environment, being poorly biodegraded by organisms and having a significant concentration-dependent toxicity towards living beings, as well as their ability to bioaccumulate and biomagnify through the trophic chain, extending their negative effects beyond the individual to subsequent generations (Gao et al., 2021; Martins et al., 2023).

One of the environmental compartments where heavy metal contamination has a notable effect is in sediments, due to their dual role as a sink or/and source of contamination (Covelli et al., 2008; Sharma et al., 2021). Sediments are of great environmental importance since they are a significant source of nutrients and the habitat for a wide variety of marine organisms. Contamination can alter their physical and chemical properties, affecting biodiversity and biological community succession (Shuaib et al., 2021). For this reason, recognised environmental organisations classify this group of elements as a priority in the study of coastal ecosystems (Buchman, 1999; Cly, 2001; OSPAR, 2004; between others).

Asturias is a region located in the north of Spain characterised by

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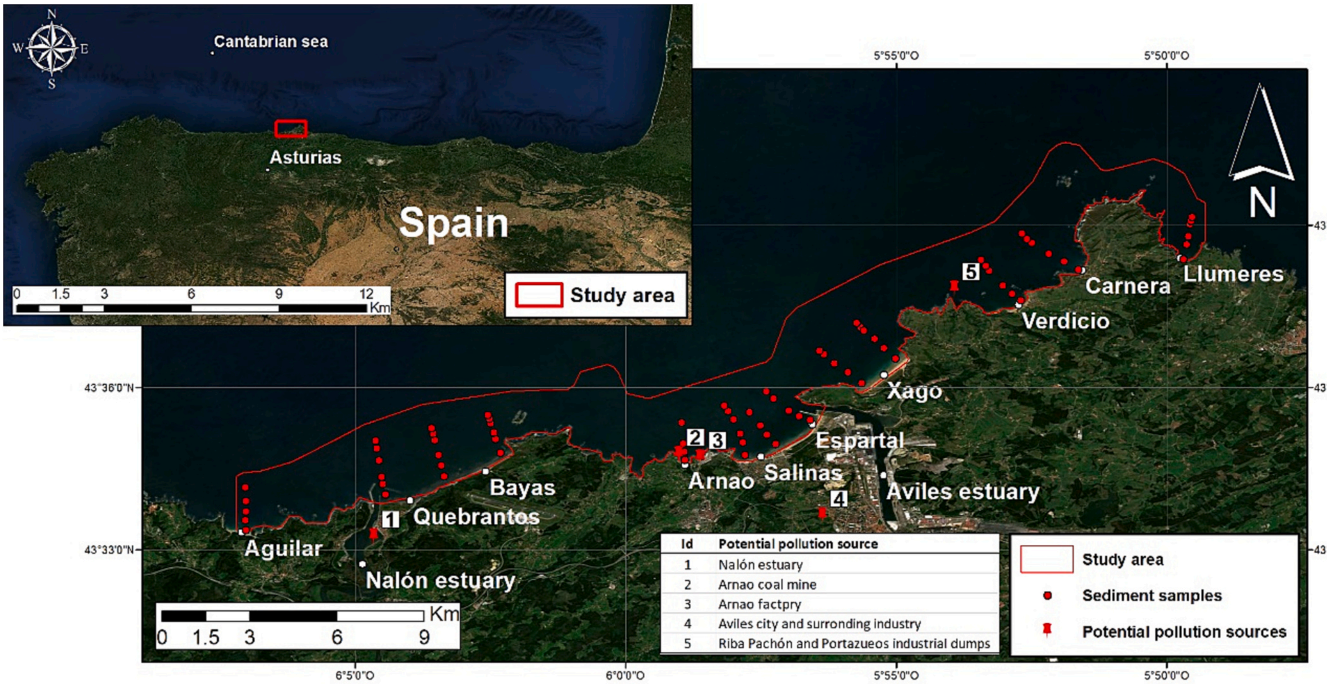

Fig. 1. General and detailed location of the study area showing the location of potential pollution sources to the coastline and sediment samples collected.

having one of the most naturalised coastal strips on the Iberian Peninsula. Additionally, it is the site of significant historical mining of energy resources (coal) and metals (iron, copper, lead, zinc, mercury, gold, etc.) and is also the location of associated industries which exploit these resources, such as steel and metallurgy. This has led to the existence of numerous contaminated sites in the region (Loredo et al., 1999; Álvarez-Quintana et al., 2022; Ugaz et al., 2023 among others), establishing heavy metals as the most problematic pollutants.

This contamination not only occurs in mining-industrial areas, but has also been exported to the coastal environment, where there has been significant impact mainly located in the central zone of the region (Garcia-Ordiales et al., 2019, 2020; Sanz-Prada et al., 2020, 2022a; Romero-Romero et al., 2022).

Due to its ecological importance, a detailed study of this region is necessary to evaluate the potential impact and scope of human activities and whether recovery measures are necessary. Since sediments are an environmental compartment capable of retaining contaminants in a stable manner for a long period of time thanks to their so-called "memory" (Nawrot et al., 2021) and they provide valuable information about the state of the environment (Simpson and Batley, 2016), this matrix is a target for environmental research.

Based on a study of coastal sediments, the objectives of this research were to evaluate the current state of heavy metal concentrations in coastal sediments and identify the potential impact sources through statistical and dispersion analysis, as well as carry out a first evaluation of the potential ecological risk that could serve as a basis for future research in the area or in other areas that face similar threats.

2. Materials and methods

2.1. Study area

The study covers a coastline of approximately 50 km between the Aguilar and Llumeres areas (Fig. 1). Geologically, this coastal strip is characterised by the presence of Cambrian rocks (mainly sandstones, lutite and slate) between the Aguilar and Quebrantos areas, and a mixture of Permian, Mesozoic and Tertiary rocks from the Quebrantos area to Llumeres, the main outcrop rocks being limestone, sandstone, quarzite and lutite (Aramburu et al., 1995; Vera, 2004). The direction of the prevailing marine currents and sediment transport in this area is W-E (Fernández-Nóvoa et al., 2019) and has a nearby coastal shelf area about 4 km wide with maximum depths close to 40 m.

Regarding the coastal platform, the majority is made up of sandy bottoms which favour the formation of numerous sandbanks scattered along the coast. In addition, this area stands out for being the coastal strip subjected to the highest anthropic pressures in the entire coast of the region. From west to east, between the areas of Aguilar and Los Quebrantos, the first potential source of pollution contribution is located in the middle part of the Austurias coastline and comes from the mouth of the Nalón River. The Nalón River basin has been one of the most important historical mining areas in Spain, being the largest coal extraction district in the country, and second in terms of mercury extraction.

As a consequence, several studies have demonstrated the influence of these anthropic activities both in the watershed (Ordóñez et al., 2011, 2013, 2014; Méndez-Fernández et al., 2015 between others) and in the estuary (Garcia-Ordiales et al., 2018, 2019, 2020; Pavoni et al., 2021; between others), as well as in the nearby coastal area (Sanz-Prada et al., 2020, 2022a; Romero-Romero et al., 2022).

Further east, in the Arnao area, the first coal mine in Spain and the first underwater mine in Europe are located, which were operational between the 16th and the beginning of the 20th centuries. To the east and very close to Arnao, there is a zinc factory which dumped significant amounts (quantity unknown) of industrial waste on the nearby Dolar beach (Lopez-Pelaez, 2021).

Following the coastal strip to the east is the city of Avilés, which is characterised by the presence of large steel, metallurgical, chemical and fertiliser manufacturing industrial complexes that have had a significant impact on its urban area (Gallego et al., 2002; Ordóñez et al., 2003, 2015) as well as on the coastal and marine environment (Sierra et al., 2014; Baragaño et al., 2022; Mangas-Suarez et al., 2022). After Avilés, between the Xagó and Verdicio areas, there are the Portazuelos and Riba Pachon beaches, which served as dumps for steel waste between 1962 and 1972 (Lopez-Pelaez, 2021). Finally, in the Llumeres area, there is an iron mine that was in operation from the mid-19th to the mid-20th century.

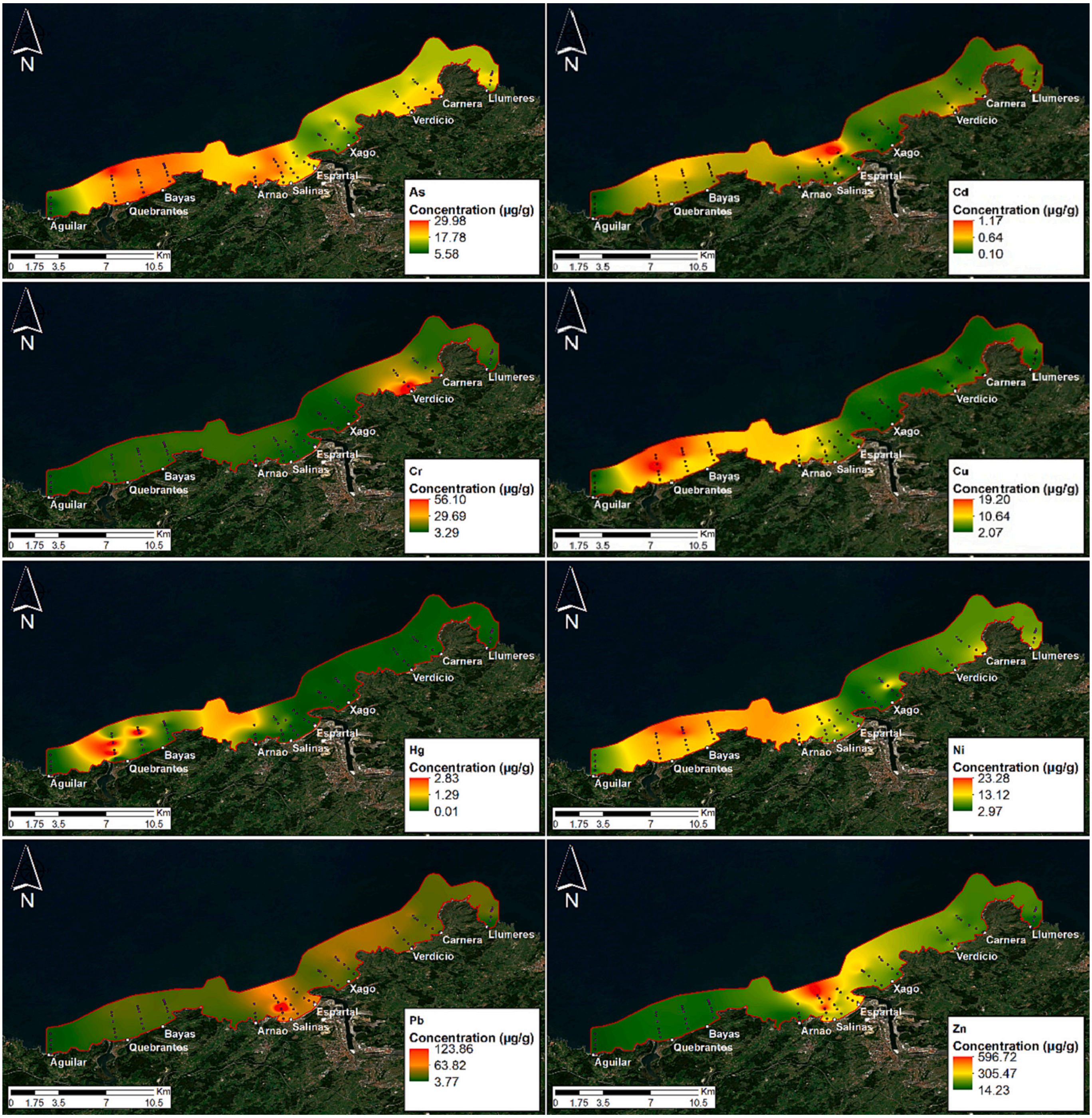

Fig. 2. General dispersion maps of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn concentrations in the study area. Note that in the areas without samples (Ex: Bayas-Arnao,Xagó-Verdicio, Carnera-Llumeres), the interpolation carried out may have considerable uncertainty, but that it is nevertheless consistent with the general coastal dynamics and with the description of sources and expected dispersion of contamination from them explained in the text.

As described in the previous paragraphs about the study area, the existing potential contamination in the studied coastal strip is a historical contamination of >100 years caused from the inexistence or lightness of existing environmental laws. Today, contributions from existing sources are very limited and their impact on the coast is significantly less than the historical sources described in this work.

A total of 71 sediment samples of approximately 3 kg were collected along the study area, as shown in Fig. 1. The samples were collected at different bathymetric levels between 0 m.a.s.l to −25 m.a.s.l by boat using an AISI 316 stainless Steel Van Veen grab. Afterwards, samples were homogenised and stored in the field at a temperature below 4 °C in order to preserve them.

Each sample was dried in an oven at 35 °C for 24 h to avoid the loss of contaminants and then divided into representative subsamples using a rifle-type channel divider with a removable hopper. For granulometric analyses, an aliquot of each sample was treated with a 3 % (v/v) H_2O_2 solution for 48 h to remove most of the organic matter (Garcia-Ordiales et al., 2018).

Subsequently, samples were wet sieved to eliminate the fraction larger than 2 mm and analysed with a Fritsch ANALYSETTE MicroTec Plus 22 granulometric laser according to the procedure set out by the manufacturer. The grain size data were synthesised according to the

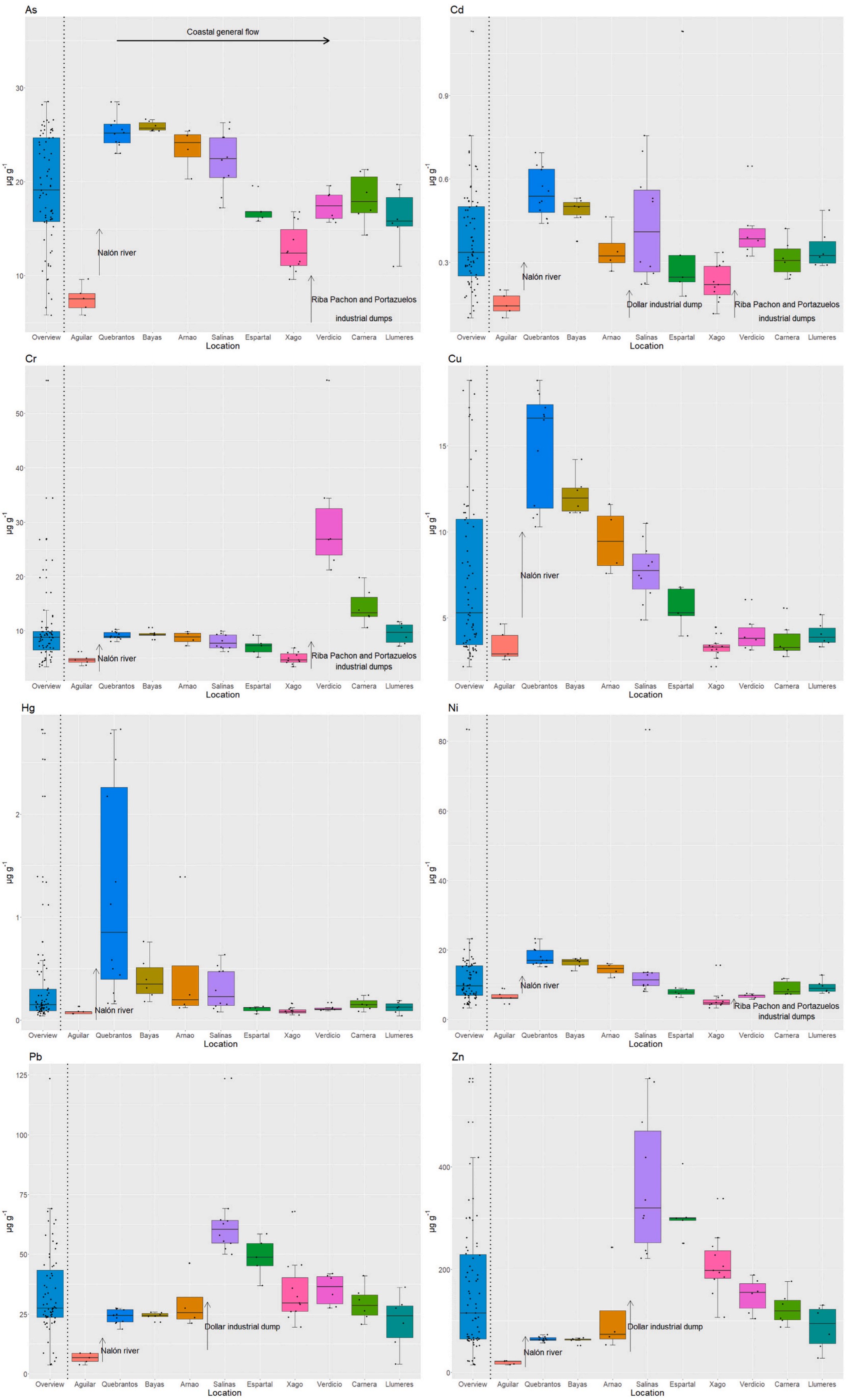

Fig. 3. General boxplot diagrams in the different sampled areas of the concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. The vertical arrows represent locations of potential sources of contribution of each element to the coastal sediments.

Spanish maritime regulations in the sand-fine fractions (silt + clay). For the chemical analyses, 30 g representative of a sample smaller than 2 mm were pulverised by means of an agate ball mill to a size <63 μm and digested in a microwave using the pseudototal aqua regia method (HCl + HNO_3), filtered and analysed by mass spectroscopy inductively coupled plasma (HP 7700 Agilent Technologies ICP-MS) in the Global ALS Geochemical laboratory (Seville, Spain). The accuracy and precision of the results were verified by comparison with an analysis of the standard reference materials RTC-CRM026–050 (Sandy Marl 9), CRM042–056 (Sandy Marl Marl 2), OREAS 503c (Rock), and MRGeo08 (Rock). Quality control samples were prepared with standard solutions (Merck and Icus 3058 Custom Standard, Ultra-scientific), blank analysis, and random sample duplicates.

2.2. General results

In general, the sediments from the platform have an average gravel size content of 2.9 % by weight, with 50 % of the samples having a gravel content of <0.6 %. The sandy fraction is predominant, with contents that vary between 33.4 % and 100 %, with the general D50 of 241.1 μm, which corresponds to a medium sand size according to Folk and Ward (1957). Finally, the fine sizes of silts and clays (<63 μm) are the least predominant with an average content of 1.7 % by weight and with 50 % of the total samples with a content of <1.1 %.

Regarding heavy metals and metalloids, As concentrations ranged from 5.8 to 28.5 μg g^{-1}, Cd from 0.1 to 1.13 μg g^{-1}, Cr from 3.4 to 56.1 μg g^{-1}, Cu between 2.2 and 18.8 μg g^{-1}, Hg between 0.04 and 2.82 μg g^{-1}, Ni between 3.3 and 23.2 μg g^{-1}, Pb between 3.8 and 123.5 μg g^{-1} and Zn between 14.5 and 572 μg g^{-1}. In Fig. 2, the dispersion maps of the element concentrations are shown. Likewise, in Fig. 3, the distribution of the heavy metals and metalloid concentrations are presented by means of boxplot diagrams.

According to Fig. 2, the highest concentrations of As, Cu, Hg and Ni were located in the western part of the study area, decreasing in the W-E direction concurring with the direction of the prevailing marine currents in the Cantabrian Sea (Fernández-Nóvoa et al., 2019). In the case of Cd, Pb and Zn, their highest concentrations appeared in the central zone, while the highest concentrations of Cr were found in the Eastern zone. Considering both Fig. 2 and Fig. 3, there are increases in the concentrations of all the studied elements between the Aguilar and Los Quebrantos areas, which corresponds to the mouth of the Nalón River. The Nalón basin has historically been one of the largest mining districts in Spain for nearly 150 years and as a consequence of this activity, recent studies in the estuary have reported significant contamination by heavy metals in current sediments (Garcia-Ordiales et al., 2018), as well as in historical estuary sediments (Garcia-Ordiales et al., 2015, 2019, 2020). It is for this reason that the increase in contaminant concentrations is associated with the contributions of sediments from this river. Hence, among these general enrichments, concentrations of As, Cu, Hg and Ni stand out being the first transects to the east of its mouth where contributions are less diluted that ones with the highest concentrations of these elements. The geochemical association between As and Hg due to mercury mining has been widely studied in the Nalón River estuary (Garcia-Ordiales et al., 2018, 2019; Pavoni et al., 2021) and in the nearby coastal area (Sanz-Prada et al., 2020), attributing the enrichment in coastal sediments of both elements to historical mining activities. Aditionallity Romero-Romero et al. (2022) studied the Hg concentration in the food chain of the Avilés Canyon which is located northwest of the estuary. For this reason, the influence of the contributions of this estuary is also noticeable to a lesser extent in the western part of it,and consequently the extension of the remarkable concentrations slightly to the west of the estuary. In the case of Cu and Ni, the enrichment is attributed to a geological anomaly of the materials from the geographical basin (IGME, 2012), since different studies on the estuary and the mining areas have not been able to establish a correlation between these elements and mining activities (Ordóñez et al., 2014; Garcia-Ordiales et al., 2015, 2020). Regarding Cd, Pb and Zn, as shown in Fig. 2 and Fig. 3, there is a significant increase in their concentrations between the Arnao and Salinas areas, which subsequently decrease in the direction of the prevailing currents. This increase has previously been reported in the study of sediments from several beaches by Sanz-Prada et al. (2020), attributing the enrichment to industrial activities and their waste in the area. Moreover, a detailed study in this area has made it possible to identify Dolar beach as the potential source of pollutant contributions to the coastal environment. According to Lopez-Pelaez (2021), this beach served as a landfill for industrial waste from a nearby zinc factory, which formed a rocky beach that has gradually been dismantled by the waves. The Cd-Pb-Zn association, similar to the one identified in this study, has previously been reported in other studies around the area and also attributed to the Zinc industry (Sierra et al., 2014; Mangas-Suarez et al., 2022; Baragaño et al., 2022).

To verify these potential sources, analyses on 3 sediment samples from this beach were carried out, showing average concentrations of 1.3 μg g^{-1} of Cd, 87 μg g^{-1} of Pb and 513 μg g^{-1} of Zn, being consistent with the results obtained in coastal sediments and therefore reaffirming this origin. Additionality, checking the sediments transects in this area, the first located to the east of this potential source was the one that presented the highest concentrations of the elements coincident with the prevailing marine sediments transport. Another potential source of these three elements could be the Avilés estuary, in which significant concentrations have been reported. However, Mangas-Suarez et al. (2022) reported that the estuary does not export pollution to the coast, thus Dolar beach appears to be the most plausible origin of these elements in coastal sediments. Important to remark that Cd presents the highest concentrations in the deepest samples of Salinas and Espartal, suggesting a local enrichment in this area linked to the natural coastal environment together to anthropic contributions from the coast.

Finally, there was an enrichment in Cr concentrations in the areas between the Xagó and Verdicio areas (Fig. 2 and Fig. 3) due to Cr concentrations detected in sediments from Verdicio (mean 31.4 μg g^{-1}) which are 6 times higher than Cr concentrations detected in sediments from Xagó (mean 4.9 μg g^{-1}). Furthermore, it should be noted that in this area there is also an increase in the concentrations of As, Cd and Ni. In this case, the most probable sources are the natural dismantling by waves of the materials that form both Portazuelos and Riba Pachon beaches, which, between 1962 and 1972, served as a dump for steel waste, dumping a total of 1,820,000 mt during that period (Lopez-Pelaez, 2021). Steel residues have significant concentrations of these four elements in their composition, Cr being the predominant one in this type of residue (Piatak et al., 2021). Samples from these beaches reported a mean concentration of 476 μg g^{-1} of Cr, 193 μg g^{-1} of Ni and 35 μg g^{-1} of As. These data are consistent with the results obtained in coastal sediments and with the enrichment of the Verdicio sediments transect because it is the area to the east closest to the source and consequently, the anomalous concentrations identified in the sediments in this area can be attributed to this potential source.

2.3. Multivariate analysis

The Kaiser-Meyer-Olkin (KMO) test was used to study the relevance of the variables for carrying out the factor analysis. The test evaluates the adequacy of the sampling for each variable in the model, as well as the entire model itself, evaluating the proportion of variance between variables, which may be caused by several factors. The results of this analysis showed a KMO for the metals and metalloids together with the granulometric sizes of 0.600, which is indicative of a medium fit and a KMO without taking into account the granulometric sizes of 0.791, indicative of a good fit. Therefore, only the concentrations of metals and metalloids were considered for the multivariate analysis, discarding the granulometric sizes as they were not significant for the model. The multivariate analysis consisted of a principal component analysis (PCA) with auto-scaled values, followed by varimax rotation using the

Table 1
Factor matrix obtained by principal components analysis (PCA).

	PC1	PC2	PC3
As	**0.44**	0.14	0.07
Cd	**0.40**	0.15	0.28
Cr	0.03	0.07	**0.91**
Cu	**0.49**	−0.07	−0.13
Hg	**0.39**	−0.10	−0.15
Ni	**0.49**	−0.11	−0.10
Pb	0.04	**0.67**	−0.11
Zn	−0.04	**0.68**	−0.13
Proportion of variance	46.30	24.90	14.00
Cumulative proportion	46.30	71.20	85.20

Euclidean distance and Ward's clustering method. The results of this analysis obtained three factors that explained 85.2 % of the variance (Table 1).

The first factor explained 46.3 % of the variance, and grouped As, Cd, Cu, Hg and Ni, relating them to the dispersion of sediments with both anthropic and natural concentrations, with the Nalón River as the source of input.

The second factor explained 24.9 % of the total variance, Pb and Zn being the elements with the highest weight. In this case, the factor is attributed to sources of anthropic origin such as the contributions of materials from old industrial dumps related to Zn industries in which Pb and Zn are characteristic elements.

Finally, the third factor explained 14 % of the total variance, presenting Cr as the only element with a significant weight. As in the previous case, this factor is related to anthropogenic sources such as the contributions of materials from old industrial dumps, which in this case are related to steel industries due to Cr being a predominant element in the slags.

With the matrix of factorial weights from the previous PCA analysis, a cluster analysis was carried out (Fig. 4) and it resulted in two main geochemical groups of samples, allowing for group 2 to be subdivided into 3 subgroups.

In detail, cluster 1 combined the sediment samples strongly influenced by the contributions of the Nalón River. This set of samples presents the highest concentrations of As, Cd, Cu, Hg and Ni and the highest number of samples are located in the areas near the mouth of the Nalón, which includes the Quebrantos and Bayas zones. Likewise, this cluster also groups one sample from the Arnao area, highlighting the broad influence that the contributions of the river have on the coastal environment.

Cluster 2 includes the rest of the samples from the study area. Within this cluster, Subgroup 2.1, which is the one that presents the greatest similarity with cluster 1, groups the samples from the areas of Salinas, Espartal and part of Xagó. This set is characterised by high concentrations of Pb and Zn compared to the rest of analysed samples, as a consequence of industrial anthropic contributions, but also by significant concentrations of Cd, As and Hg. This suggests a mixture of two anthropic sources, the most considerable one being the nearby industrial anthropogenic inputs, but also having the contribution from the Nalón River influencing both the geochemistry of the sediments in this area.

Moreover, Subgroup 2.2 includes samples from two geographically separated areas such as the Aguilar and Xagó areas. This set of samples has the lowest concentrations of the studied elements, and therefore the least anthropised and most naturalised areas of the coastal strip. Finally, Subgroup 2.3 groups the samples from the Verdicio, Carnera and Llumeres areas, to the east of the Portazuelos and Riba Pachon beaches. These samples are characterised mainly by their high Cr content compared to the rest of the samples because of the industrial anthropogenic contributions from the now disused steel waste dumps.

2.4. Preliminary environmental considerations

To evaluate the effect that anthropic contributions may have on the sediments, the geochemical base values (BL) for sediments of the Asturian coast determined by Sanz-Prada et al. (2022b) were compared.

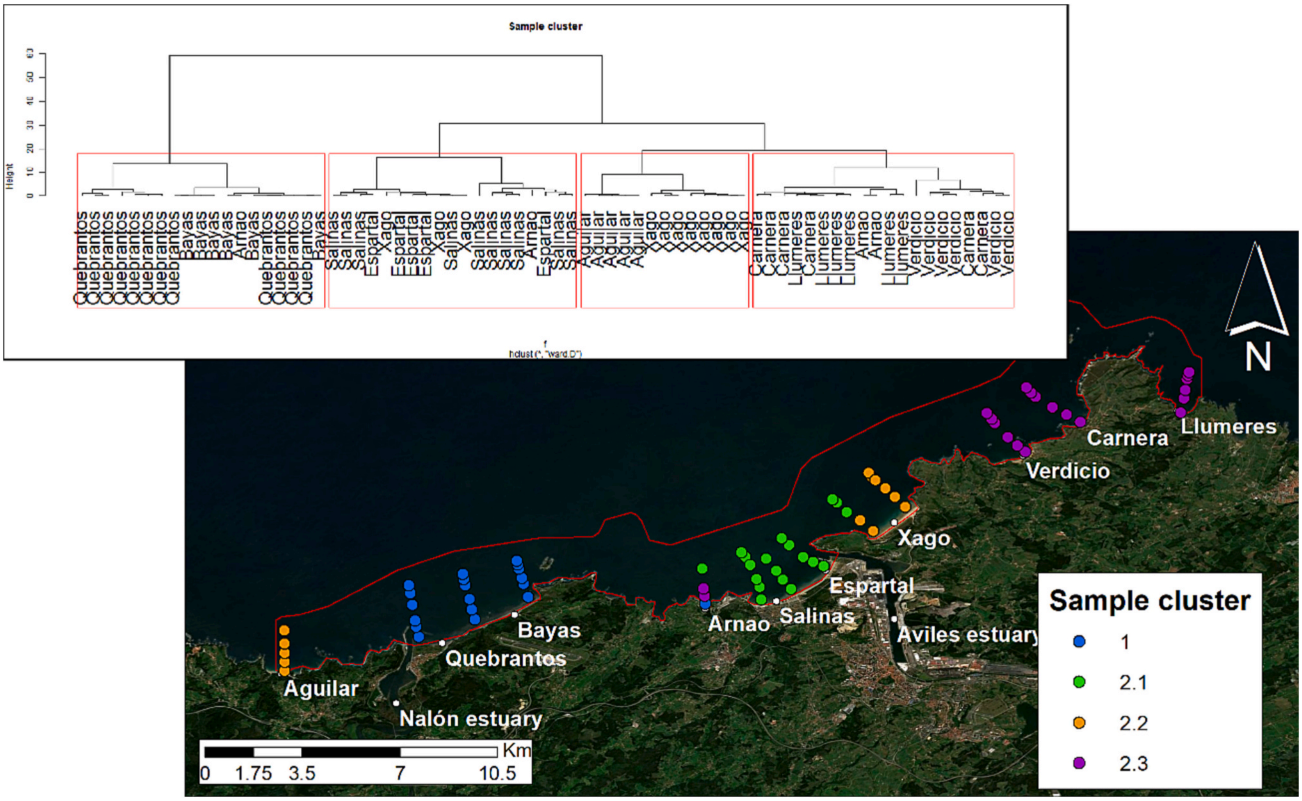

Fig. 4. Cluster hierarchy analysis results and geographical representation of the cluster results.

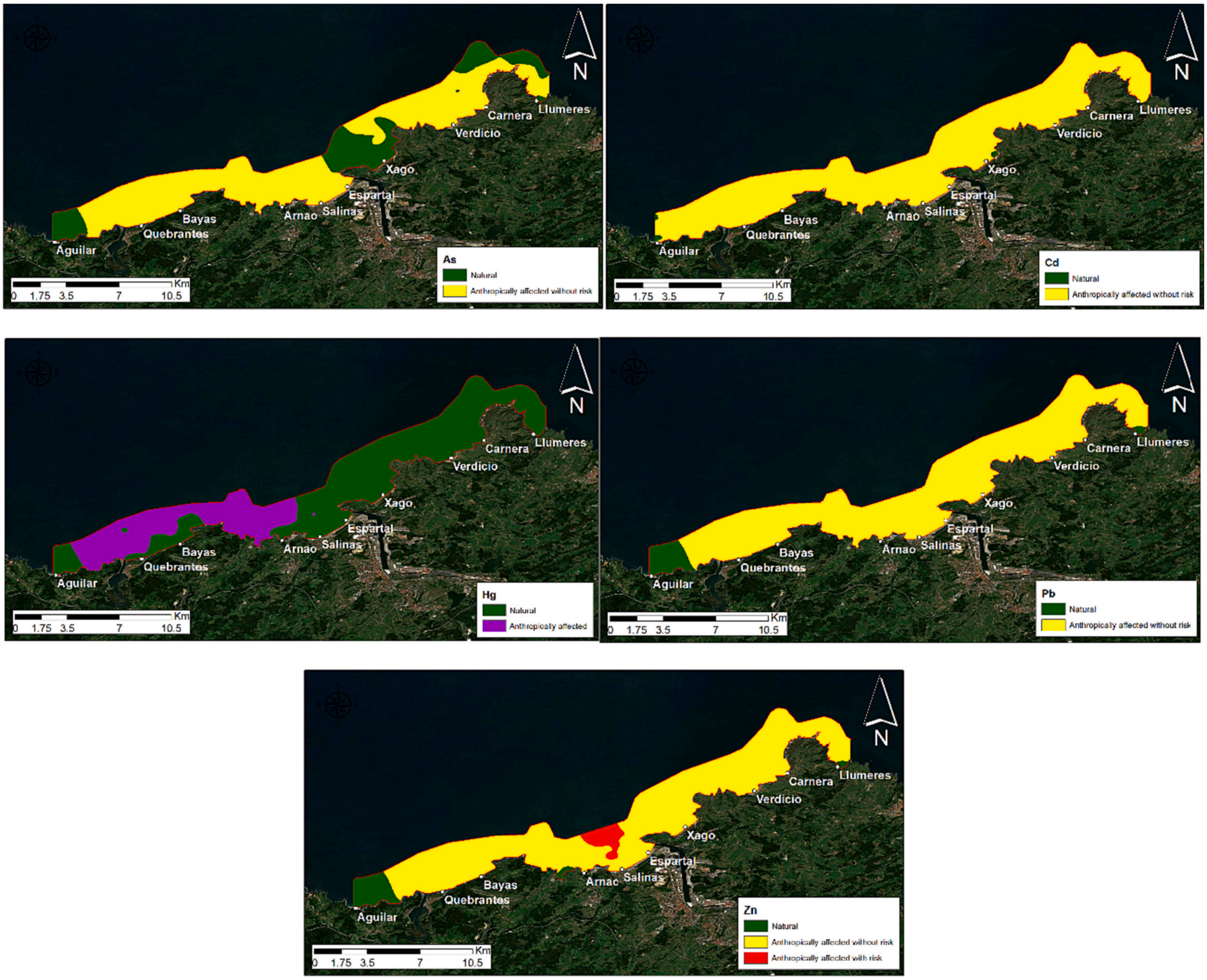

Fig. 5. Dispersion maps classified according to the non-affectation or anthropic condition, as well as based on the existence of no environmental risk or potential environmental risk. In the case of mercury, the assessment is different due to the high existing geochemical baseline of the region. Concentrations of Cu, Cr and Ni have not been represented, as they are considered natural.

These levels allow for the identification of pristine zones from other areas affected by unnatural contributions that have modified the natural geochemical partition of the studied elements. In addition, to evaluate the potential risk for the biota, the Apparent Effect Thresholds (AET) of the USA National Oceanic and Atmospheric Administration (NOAA) were used as a reference. The AET value for each element is based on empirical relationships between sediment concentrations and the results of toxicity bioassays or impacts observed in the benthic community. Thus, this threshold is potentially more sensitive than other thresholds such as the Effects Range-Median (ERM).It is important to highlightthat the values determined by Sanz-Prada et al. (2022b) were estimated through the study of corers from four regions of the Asturian coast, therefore the values identified by them are generics and that in the case of some element would be overestimate or underestimate it as a consequence of the rocky outcrops in different parts of the coastline, since they are not totally particular to our study area. However, it is considered that the combination of these values with those of NOAA allow a first environmental consideration of the existing impact to be made, quite realistic.

Analysing the sediments based on the BLs established by Sanz-Prada et al. (2022b) (Fig. 5), it stands out that 97.2 % of the sediment samples presented Cd concentrations higher than the BL (0.12 μg g^{-1}), 91.5 % of the samples for Zn (BL = 47 μg g^{-1}), 90.1 % for Pb (BL = 14 μg g^{-1}), 78.9 % for As (BL = 14.7 μg g^{-1}), 22.5 % for Cu (BL = 11 μg g^{-1}) and 12.7 % for Hg (BL = 0.6 μg g^{-1}). Among the previously analysed elements, note the levels of As, Pb and Zn, as the percentage of samples with concentrations above the BL always exceeded 50 % of the dataset. This allows us to identify an important non-natural contribution of these elements towards the coastal environment. For Cu and Ni, 99 % of the samples presented concentrations below their respective BL, considering both geochemical natural elements.

Comparing the concentrations with the AET threshold value, it should be noted that only for Zn, 5.6 % of the samples presented concentrations susceptible to generate adverse effects on the biota. For the rest of the elements, their concentrations were below the AET threshold. However, special mention should be made in the case of Hg, since the estimated BL for the region in coastal sediments (0.6 μg g^{-1}) is twelve times higher than the BC (0.05 μg g^{-1}) for natural areas established by OSPAR for Region IV – the Bay of Biscay and the Iberian Coast. This high BL also exceeds the AET (0.41 μg g^{-1}) established by NOAA, therefore it does not make sense to base a risk assessment on this. Nevertheless, these high concentrations of Hg cannot be ignored. Since there is a natural geochemical anomaly of this element, it can be hypothesised that the organisms that inhabit this area have strengthened their self-protection mechanisms to avoid adverse effects derived from the high environmental concentration of this element. An example of this hypothesis are the studies reported by Romero-Romero et al. (2022) and Sanz-Prada et al. (2022c), in which both ichthyofauna (different species) and mussels (*Mytilus galloprovincialis*) showed the use of selenium as a protector against Hg-induced toxicity. It is for this reason that despite the high concentrations of Hg identified, it can be asserted that there is a low risk for biota owing to these self-protection mechanisms.

3. Conclusions

Due to the historical and current mining-industrial activities in Asturias, the coastal sediments of the central-eastern coastal strip have suffered a significant impact due to the presence of anthropic concentrations of heavy metals. The existence of different sources along the coastal area has resulted in a wide dispersion, as well as a cross-mixture of pollutants that cause a rise in the potential risks for the biota and the environment. The pollutants with the largest dispersion and environmental risk were As, Pb and Zn, influencing most of the study area. Others, such as Hg, may present an environmental risk but due to the existence of natural geochemical enrichment, it cannot be reliably confirmed. For this reason, future research on the area should focus on studying in more detail the transfers of these contaminants on the sediment biota in order to obtain more precise models to assess the risk derived from the presence of contaminants in the sediment.

CRediT authorship contribution statement

- Conceptualization: M Mangas; E. Garcoa-Ordiales
- Methodology: M. Mangas, E, Navarro, J.I. Barquero
- Data curation: J.I. Barquero, E. Navarro,
- Validation: M. Mangas, N, Roqueñi, E. García-Ordiales;
- Writing—original draft preparation: M. Mangas, E. García-Ordiales;
- Writing—review and editing: E. García-Ordiales, N. roqueñí
- Supervision: E. García-Ordiales.

All authors have read and agreed to the published version of the manuscript.

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Declaration of competing interest

All the authors who have participated in the research and production of this manuscript have no conflict of interest.

Data availability

Data will be made available on request.

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