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Enrichment of Metals in the Sediments of an Industrially Impacted Estuary: Geochemistry, Dispersion and Environmental Considerations

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Abstract: The city of Avilés is one of the most industrialized cities in the north of Spain and, accordingly, its estuary and coastal area have been subjected to great anthropic impacts in the last 100 years. This research attempts to establish a preliminary scenario of the geochemical and environmental status of both coastal and estuarine sediments in this area. For this study, a total of 96 sediment samples were collected, processed and analyzed to quantify the granulometric distribution of the sediments, as well as their concentrations of organic carbon and main metal(oids) that may cause an environmental risk. The results show that the estuarine sediments present important concentrations of Cd, Hg, Pb and Zn that allow them to be clearly differentiated from the coastal sediments; this information, along with the sedimentology, implies that the estuary acts as a sink of pollution and not as source to the coastal area. Inside the estuary, the high levels of contamination produce a significant potential ecological risk due to contaminant transfers to other environmental compartments and to the biota. Although direct discharges of industrial effluents have been gradually eliminated, the current state of the sediment requires the implementation of measures that are more consistent than natural regeneration in order to ensure low risk levels for the ecosystem.

Keywords: sediments; heavy metals; pollution; estuary

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1. Introduction

One of the major issues in aquatic ecosystems is the metal(oids) and organic chemicals load present in sediments, which may lead to serious environmental problems [1,2]. Regarding marine environments, it is necessary to highlight estuaries due to the huge biological diversity that settles on them [3]. Moreover, estuaries are areas where fluvial waters and seawaters converge, which contributes to enabling the physical and chemical processes in aquatic compartments [4]. This has a notable impact on the water column, which conditions the spatial distribution, transformation, transfer to sediments and bioaccumulation processes of the potential contaminants present in the ecosystem [5]. Metal(oids) could enter into estuaries from both natural and anthropic sources, and many of them may be toxic even at very low concentrations [6–8]. In unpolluted areas, the metal(oid) concentrations detected in estuarine sediments are mostly derived from the lithology of the bedrocks that compose the river catchment [9,10]. Nevertheless, the strategic location of estuaries in relation to economical and industrial activities turns these areas into target zones for human settlement [11]. Even though new environmental policies have reduced anthropogenic impacts in the recent years, estuaries are still impacted by several human activities, such as agricultural and chemical fertilizers, industrial uses, and recreational occupation [12–14]. These human activities can be potential sources of contamination, since they may introduce metal(oids) into estuarine environments. After being introduced into the aquatic environment, metal(oids) from the aqueous phase can be accumulated into the sediment through physical, chemical or biological mechanisms [15,16]. Due to these mechanisms, sediments are considered as "reservoirs" of metal(oids) in estuaries, since they can act as sinks and sources of these elements depending on the natural or anthropological events that occur in the area [17]. This long persistence and bioaccumulation in sediments raises a serious threat to the biota, and also to human health [18,19].

One of the most important estuaries on the Cantabrian coast is the Aviles estuary, known not only for its environmental importance but also for the industrial and port activities developed in its surroundings. The Avilés estuary has supported direct discharges from the main Asturian metallurgical plants, and other pollutants such as fertilizers and chemicals, along with a multitude of small activities located in this important industrial area. These facilities cause not only morphological alterations, such as the construction and expansion of the docks, which has altered the marshes and dunes that surround the river, but also exponentially increased the atmospheric emissions, turning Avilés into one of the world's most polluted cities in the 1980s [20], which has affected soil and sediment quality [21,22]. These activities have developed since the 19th century with a variable intensity, leading to a significant deterioration in the environment of the area over the course of decades [23]. Fortunately, over the last few years, the main industries in the area have made significant improvements in their processes, making them more efficient from an environmental point of view. Moreover, the passage of large ships, as well as river avenues and infrastructure operations, in Avilés' harbor maintain navigation channels and docks, but entail the moving of marine sediments to the bottom of the navigable waters. These processes and operations involve the resuspension of sediments containing potential contaminants, which may give rise to several environmental risks. Although urban infrastructure and industrial developments have almost entirely altered the estuary, it still holds a very important diversity of both animal and plant species, which has earned it the designation as a Special Protection Area for birds (ZEPA) and a Place of Cultural Interest (SCI). Therefore, it is necessary to develop environmental characterizations and assessments of the Avilés estuary, not only to preserve its natural areas, but also to regulate anthropic impacts and guide future environmental management.

The aims of this study were: (i) to identify the concentrations and distributions of metal(oids) in surface sediments collected from the Aviles estuary and the nearby coastal environment; (ii) to determine the relationships between metal(oids) and other parameters so as to identify potential sources of origin; (iii) to assess the geochemical enrichment, the pollution, and the potential environmental risks that sediments may produce as a consequence of anthropic contributions. This paper seeks to establish a reference for future research in the area or in other areas facing similar threats.

2. Study Area

Aviles is a city located on the coast of Asturias (43°33′22″ N 5°55′20″ O), NW Spain, and it is characterized by a significant presence of heavy and small industry. The city is situated next to the estuary that gives it its name. The estuary includes one of the main harbors of the North of Spain, with a significant traffic of raw materials. The estuary has a longitudinal extension of approximately 9 km between its mouth and its innermost part, with an asymmetric Z shape. The nearby coastal environment is composed of three horizontal dune fields, which were designed in three main successive stages, and an active beach [24].

The main river channel that affects the Aviles estuary is produced by the confluence of two small rivers, the Tamón and the Alvares, which have small catchments, short courses and low flow regimes, together with other small coastal creeks [25]. The estuary's mouth is in the middle of the two important beaches of Xagó and Salinas (Figure 1), and it has two internal beaches called San Balandrán and Zeluán, which are listed as Special Protection Areas for birds (ZEPA). The estuary's margins have undergone significant transformations since the 19th century, with the occupation of the floodplains for agricultural use, and the subsequent industrialization of the 20th century, with the occupation of the margins for industrial, port and service use. The estuary environment consequentially came to have one of the highest concentrations of heavy industry in Spain, only surpassed by the Huelva estuary. In addition, parts of the facilities have been installed in the marsh and dune areas that surround the estuary, altering this area geomorphologically. The presence of these important industries gives rise to annual port activity equivalent to the movement of 6 million tons of raw materials, which consists of solid bulk (62%), liquid bulk (11%) and general goods (27%). Previous studies on sediments from the estuary's banks and beaches have shown that the significant presence of industry around the estuary, and a port hosting intense maritime traffic, are two of the most important factors in sedimentary contamination [26,27].

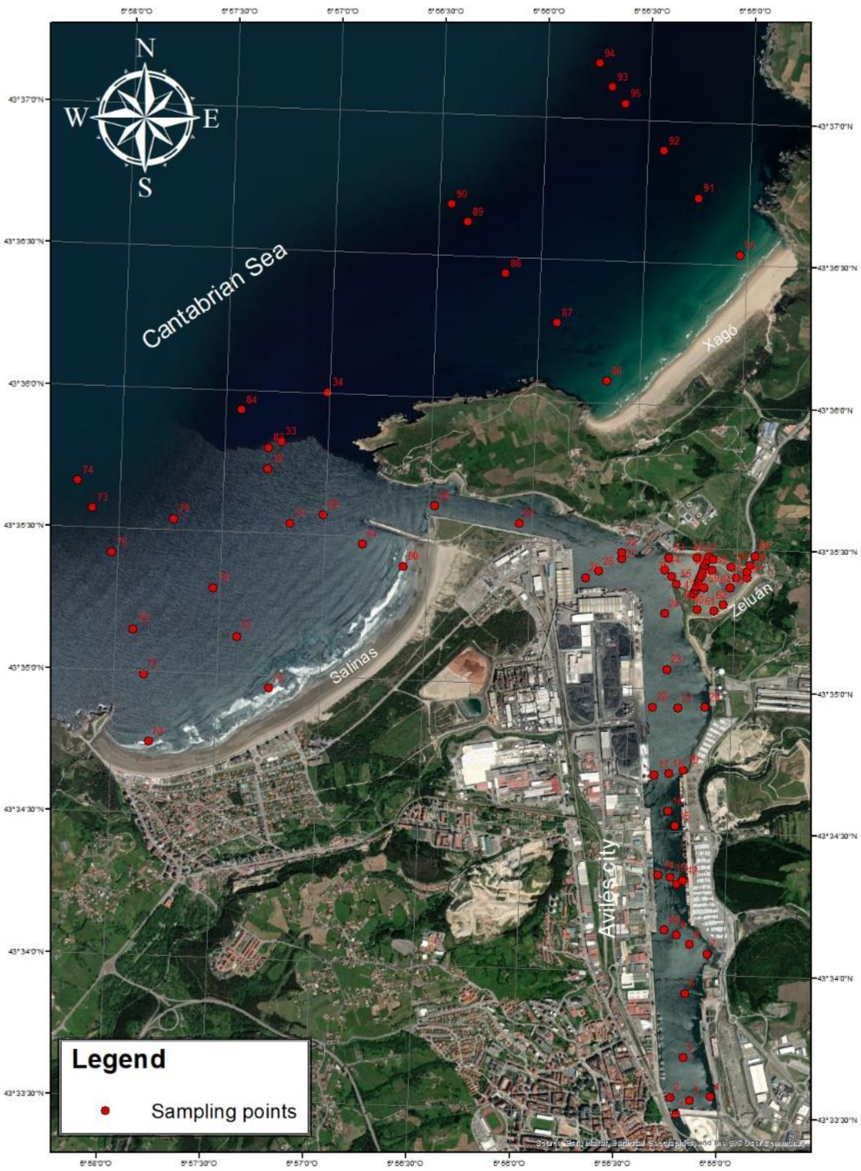

Figure 1. Study area and sampling stations.

3. Materials and Methods

3.1. Sample Collection, Preparation, and Analysis

A total of 96 sediment samples were collected from the estuary and the nearby coastal area (Figure 1). Surface sediments (0–5 cm) were collected from the submerged parts of the estuary using a stainless-steel Van Veen grab positioned on a boat. Approximately 1 kg of sediment was collected from each sampling point, homogenized in the field, stored in a double zip-lock bag, and transported to the laboratory in a portable fridge. Each sample was air-dried and divided into different representative subsamples, using a riffle-type sample splitter with a removable hopper. For grain size analysis, an aliquot of each sample was treated with a solution of 3% (v/v) H_2O_2 for 48 h to remove most of the organic matter. The sample was then wet-sieved to 2 mm and analyzed with a Fritsch ANALYSETTE MicroTec Plus 22 (Fritsch Company, Markt Einersheim, Germany). Grain size data have been synthesized according to the Spanish maritime regulations in sand-mud (silt + clay) notation. Major and trace elements were determined on 1 g representative samples, which were digested in a microwave using the pseudototal aqua regia (HCl+HNO_3) method, filtered and analyzed by inductively coupled plasma mass spectroscopy (HP 7700 Agilent Technologies ICP-MS) at the ALS Global Geochemistry laboratory (Sevilla, Spain). The accuracy and precision of the results were verified by comparison against an analysis of the Standard Reference Materials RTC-CRM026-050 (Sandy Loam 9), CRM042-056 (Sandy Loam 2), OREAS 503c (Rock) and MRGeo08 (Rock). Quality control samples were prepared with standard solutions (Merck and Icus 3058 Custom Standard, Ultra-scientific), analytical blanks and duplicates of random samples.

Total organic carbon (TOC) was measured using a Shimadzu TOC-V CSH. The TOC analysis proceeded through progressive acidification with HCl (0.1–1.0 M) at a combustion temperature of 920 °C according to the method set out by [28]. Acetanilide was used as the standard compound for calibration.

The results of the analytical analysis were treated with free statistical software R and the dispersion models were evaluated by the inverse distance weighted (IDW) method with the commercial Geographic Information System ArcGIS under the license of the University of Oviedo Subsoil and Environmental Research Team. Statistical treatments comprised normality tests such as the Anderson–Darling, Kolmogorov–Smirnov and Pearson's correlation analyses.

3.2. Evaluation of Sediment Enrichment

Pollution indices are useful tools for a comprehensive assessment of sediment enrichment and environmental risk. Many different indices have been used to assess sediment status [29–31]. In this research, the contamination factor (Cf), the pollution load index (PLI) and the environmental risk index (ERI) have been applied to study the status of the sediments.

3.3. Contamination Factor

The contamination factor (Cf) described by [32] was used as an indicator of the degree of enrichment that an element presents in the sediment. The values reported by [33] for marine sediments have been used as background values. The calculated Cf values have been classified according to the ranges proposed by [34]: Cf < 1—no enrichment; 1 ≤ Cf < 3—moderate enrichment; 3 ≤ Cf < 6—considerable enrichment; Cf ≥6—very high enrichment.

3.4. Pollution Load Index

This index has been used for the overall assessment of metal(oid) contamination degree in sediments [35–37]. The PLI values have been classified according to the ranges proposed by [34]: 0 < PLI ≤ 1, unpolluted to moderately polluted; 1 ≤ PLI < 3, moderately polluted; 3 ≤ PLI < 6, highly polluted; PLI ≥ 6, very highly polluted.

3.5. Ecological Risk Index

The ecological risk index (ERI) for sediments was used to evaluate the overall environmental risk level. This index allows for the prediction of the probability of occurrence of a negative impact on the environment by average concentrations of specific pollutants [25,38,39]. The index is based on the sedimentological-toxic factor (S_t^i) and the values determined for specific individual elements are Zn = 1, Cr = 2, Cu = 5, Pb = 5, As = 10, Cd = 30 and Hg = 40, according to [34]. The ERI values have been classified according to the ranges proposed by [18]: ERI < 150, low ecological risk; 150 $\leq$ ERI < 300, moderate ecological risk; 300 $\leq$ ERI < 600, considerable ecological risk; ERI $\geq$ 600, very high ecological risk.

4. Results and Discussion

4.1. General Characteristics of Sediments

From the granulometric distribution of the sediments of the Avilés estuary and its nearest coastal area (Figure 2), it is evident that there are two well-differentiated areas. On the one hand, in the coastal area, at the mouth of the estuary and in the Zeluán protected area, the sandy fraction is predominant in the sediments. In the inner zone of the estuary, fine fractions (silt + clay) predominate in the samples collected. This particle size distribution reveals a specific energy pattern resulting from the interactions of tidal currents, waves, and fluvial confluences in the estuary. In open areas facing currents where energy is important, sands are the predominant granulometric sizes as a result of the speed of the water column, which limits the deposition of fine particles on the bottom, causing them to remain in suspension. On the contrary, in the inner part of the estuary (where the morphology of the mouth protects against the direct force of the waves, limiting the mixing and circulation of the waters and, therefore, reducing the energy of the medium), fine-sized particles dominate, except for in the areas where rivers converge. This general distribution of predominant sizes in the different areas is indicative of the sedimentological dynamics of the estuary, which, in its innermost part, tends to act as a sink for materials from the coastal environment, and does not naturally export materials to the coastal environment. This dynamic is consistent with that reported by [40,41], where the estuary tends to receive materials from the coastal environment.

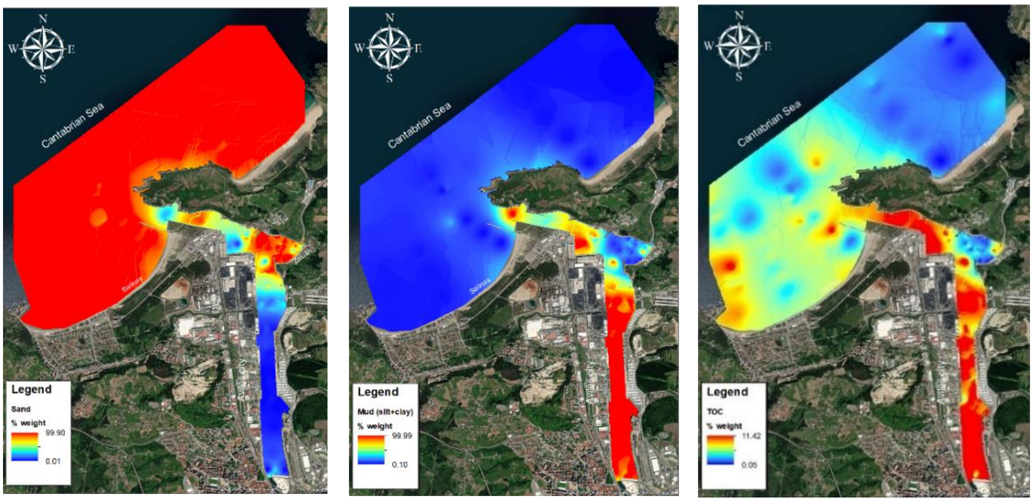

Figure 2. Spatial distribution of the sand fraction, mud (silt + clay) fraction and TOC concentrations in the surface sediments of the study area.

TOC concentrations (0.05–11.45%) are strongly correlated with the finer sizes of the sediment (r = 0.78, $p < 0.001$) because these fine fractions easily adsorb the organic compounds in bottom sediments [42,43]. Therefore, the highest concentrations of TOC were detected in the innermost part of the estuary, where the sediment is preferably composed of fine particles. On the contrary, the lowest concentrations were identified in the coastal zone and in the Zeluán area, where the coarsest component of the sediments is predominant.

4.2. Metal(Oids) in Surface Sediments

As shown in Table 1, where the statistical summary of the metal(oid) concentrations is presented, the global concentrations in the sediments of the study area ranged from 6.00

to 56.40 (average 20.87 μg g^{-1}) for As, 0.04 to 32.80 (average 6.39 μg g^{-1}) for Cd, 3.00 to 248.00 (average 29.90 μg g^{-1}) for Cr, 2.10 to 152.00 (average 34.71 μg g^{-1}) for Cu, 0.05 to 18.35 (average 2.55 μg g^{-1}) for Hg, 3.30 to 83.40 (average 11.14 μg g^{-1}) for Ni, 8.90 to 806.00 (average 187.45 μg g^{-1}) for Pb, and 49.00 to 6360.00 (average 1042.12 μg g^{-1}) for Zn.

Table 1. Statistical summary of the metal(loid) concentrations in the study area.

		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
General	Mean	20.87	6.39	29.91	34.71	2.55	11.14	187.45	1042.12
	Median	16.60	1.25	10.00	12.50	0.57	8.60	63.90	319.00
	Min	6.00	0.04	3.00	2.10	0.05	3.30	8.90	49.00
	Max	56.40	32.80	248.00	152.00	18.35	83.40	806.00	6360.00
	DVST	13.69	9.21	45.88	39.48	3.81	9.43	223.22	1291.89
Coastal	Mean	17.85	0.25	11.71	6.15	0.18	10.48	48.52	289.52
	Median	16.60	0.10	7.00	4.80	0.12	7.90	47.40	263.00
	Min	8.30	0.04	3.00	2.10	0.05	3.30	19.50	98.00
	Max	42.30	1.61	143.00	23.70	0.63	83.40	123.50	1070.00
	DVST	6.71	0.31	24.99	4.35	0.15	14.11	19.77	181.43
Estuary	Mean	22.12	9.23	38.23	47.90	3.65	11.36	251.31	1387.55
	Median	13.80	3.89	16.00	38.20	1.42	10.00	147.00	761.00
	Min	6.00	0.19	5.00	3.60	0.11	3.70	8.90	49.00
	Max	56.40	32.80	248.00	152.00	18.35	25.70	806.00	6360.00
	DVST	15.80	9.92	50.85	41.50	4.18	6.36	244.73	1432.70

In the case of the elements analyzed, their general average concentrations were, in decreasing order, Zn > Pb > Cu > Cr > As > Ni > Cd > Hg. Comparing between the port area and the adjacent coastal area, all the elements analyzed, except for As, showed higher concentrations within the port area.

On the other hand, Figure 3 shows the spatial distribution maps of metal(oid) concentrations in the sediments of the studied area. In general, the highest concentrations of metal(oids) in the sediments correspond to the middle-inner part of the estuary, while in the coastal area, only As, as shown in Table 1, was present at remarkable concentrations. In the cases of Cr and Ni, their presence in the coastal area has been attributed to a very local anomaly due to the lack of spatial continuity. In addition to the spatial distribution maps, Figure S1 of the Supplementary Material shows the Pearson correlation matrix of the different metal(oids) analyzed, together with the granulometric sizes and the TOC. According to this, all the metal(oids) presented significant correlations ($p < 0.05$) with the sizes of the sediments and the concentrations of TOC in them. This is because both finer sediments and organic matter are widely recognized as important metal(oid) sinks due to their electronegativity, which allows them to trap metal(oid) cations mainly by adsorption mechanisms [42,44], and due to the high correlation detected, they play a very important role in trapping metal(oids) in the study area. Among the different correlations identified, both Ni and Cr showed the lowest correlation coefficients, below 0.65 ($p < 0.05$). This fact, contrasted with the spatial distribution maps, shows that both have different behaviors from the rest of the analyzed elements. Excluding the coastal anomalies of both elements, their highest concentrations are very localized in the innermost part of the estuary, where their concentrations decrease rapidly towards the coastal area, which indicates that the highest concentrations are derived from a source located in the tail of the estuary. The locations of anomalies inside the estuary are consistent with the locations of different authorized industrial wastewater points in surrounding industries, such as a steel complex, an industry that produces primary aluminum and an urban solid waste dump. All these facilities report significant quantities of Ni and Cr in their treated effluents, and we thus consider these effluents as the main source of both elements in the sediments.

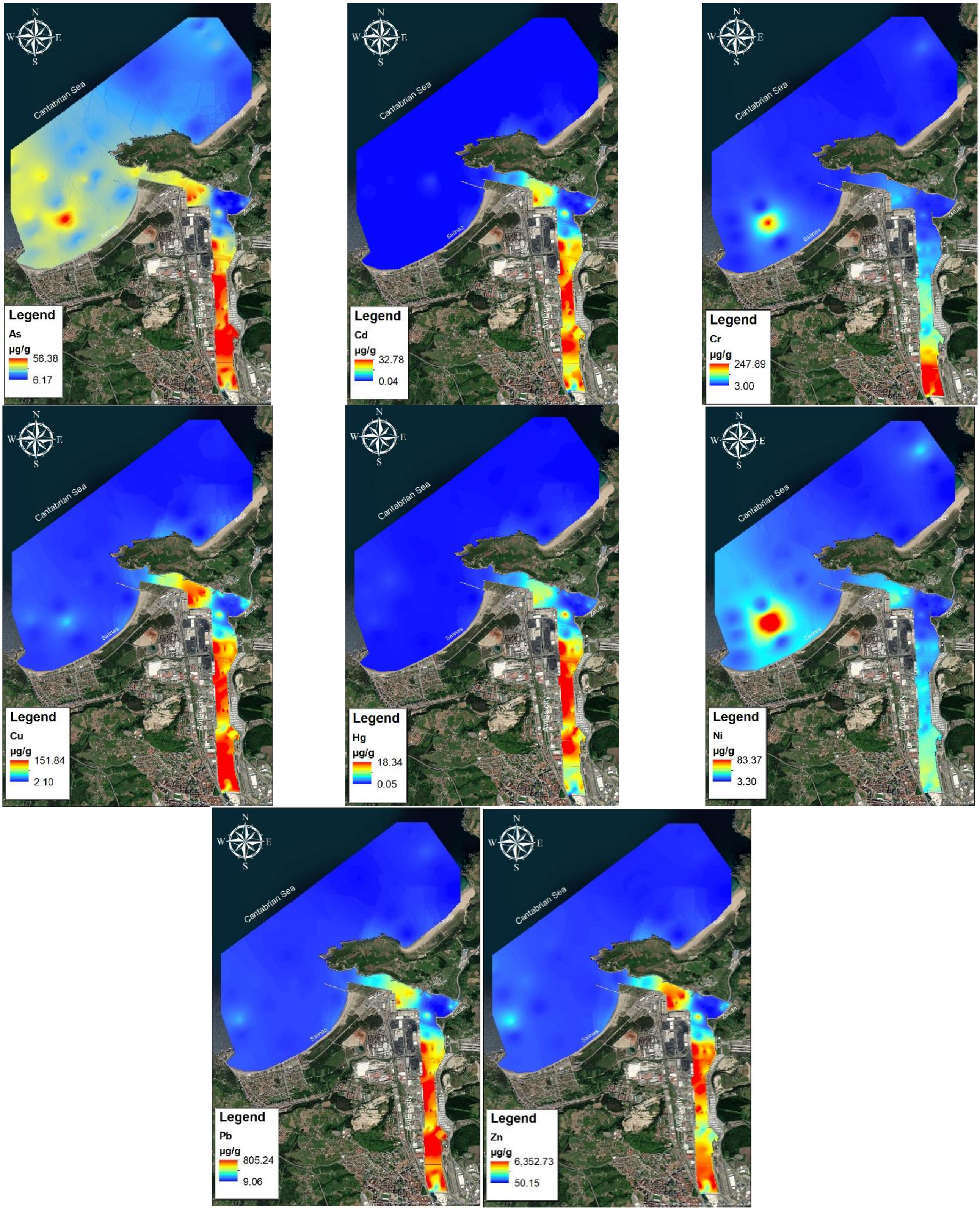

Figure 3. Spatial distributions of the concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in surface sediments of the Aviles estuary and the nearby coastal area.

On the other hand, the rest of the elements presented coefficients of correlation with the concentration of fine sediments and TOC higher than 0.73 ($p < 0.05$). While significant concentrations of Cd, Cu, Hg, Pb and Zn were not identified in the coastal zone, this is not the case for As. As previously mentioned, the general dynamics of the Avilés estuary result in the entry of material, and do not export potential contaminants out of it. Taking into account that the mean As concentration in the coastal sediments is higher than that in the port sediments (Table 1), it can be concluded that this anomaly of As in the adjacent coastal strip has a different origin. The previous works of [3,17,45,46] and [47] indicate that the Nalón River is an important source of As and Hg in the coastal environment, and that its influence might reach the study area, thus relating it to the detected coastal anomaly. Finally, inside the port area, Cd, Cu, Hg, Pb and Zn presented similar dispersion patterns, with two preferential accumulation zones. On the one hand, in the area near the mouth, an isolated anomalous zone appears near the loading and unloading dock of a local zinc smelter industry. Secondly, the most extensive anomaly seen in the concentrations for these elements appears in the middle-internal zone. Since there seems to be no clear connection between the two areas, this indicates that both anomalies may have been generated by different sources or mechanisms. Previous studies in the estuary suggest that the main origin of the contaminants is dust dispersion from the discharge and storage of ore piles by the surrounding industries [27]. However, this potential mechanism is inconsistent with the anomaly found in the middle-inner part of the estuary. In this case, due to the correlations between metal(oids) and fine sediments and TOC, and given that this area had been subjected to continuous discharges of industrial water up until 2019 when they were discontinued, industrial wastewater discharge could be the origin of the anomalies. Checking the dispersion maps for Cd and Hg, the main anomalies of both seem to be associated mainly with the mouth of the Raices River, which has received industrial discharge from different factories on the left bank of the estuary (these are annually reported in the E-PRTR (Spanish Industrial Emissions Register) with concentrations of both elements). In addition, this area has historically been a point for the storage and discharge of minerals that may also contribute these elements. As regards Cu, Pb and Zn, their anomalies are probably connected to the industrial discharge into the Raices River, and the areas of historic storage and discharge of minerals, but there also seems to be a second point of origin in the innermost part of the estuary, where the industrial discharges of several factories on the right bank (cases of Ni and Cr) of the estuary are released.

4.3. Multivariate Analysis

To study the relevance of the data to factorial analyses, the Kaiser–Meyer–Olkin (KMO) test was used, which measures the adequacy of the sampling performed for each variable in the model, as well as the whole model itself, evaluating the proportion of variance between variables, which could be caused by several factors. The results of this analysis show a general KMO of 0.892, indicative of good fitness. The multivariate analysis was performed using the main components with autoscaled values, followed by varimax rotation using Euclidean distance and Ward's clustering method, which obtaining only two factors that explained 87.9% of the variance.

The first factor explained 78.4% of the variance, and grouped all the parameters analyzed except for Ni and Cr. In this case, the only variable with a negative factorial weight is the sand size, while the rest present positive factorial weights. This allows us to link this variable with metal(oids) with a greater rate of dispersion in the studied area, the higher concentrations of which are associated with the finer size of the sediment. It should be noted that all the variables analyzed have comparable relative weights, so there is no dominant pollutant in the area.

The second factor explained 9.5% of the total variance, and in this case, the factorial weights of the Ni and Cr variables were both negative. Between both, Ni, which is the element with the lowest variability, is the one with the greatest discrimination. This allows us to link this factor with natural geochemical factors, except in the innermost zone of the estuary, where it seems to be linked to the anthropic contribution of these metal(oids), especially Cr.

With the matrix of factorial weights of the previous PCA (Table 2), a cluster hierarchy analysis was carried out, which resulted in two main geochemical groups of samples (Figure S2, Supplementary Material) that can be divided into three subgroups each, the geographical distributions of which are shown in Figure 4.

Table 2. Factor matrix obtained by principal components analysis (PCA).

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Sand	Mud	TOC
PC1	0.311	0.326	0.249	0.329	0.309	0.187	0.331	0.317	−0.318	0.318	0.284
PC2	−0.139	0.176	−0.494	0.081	0.259	−0.749	0.122	0.131	−0.126	0.126	−0.070

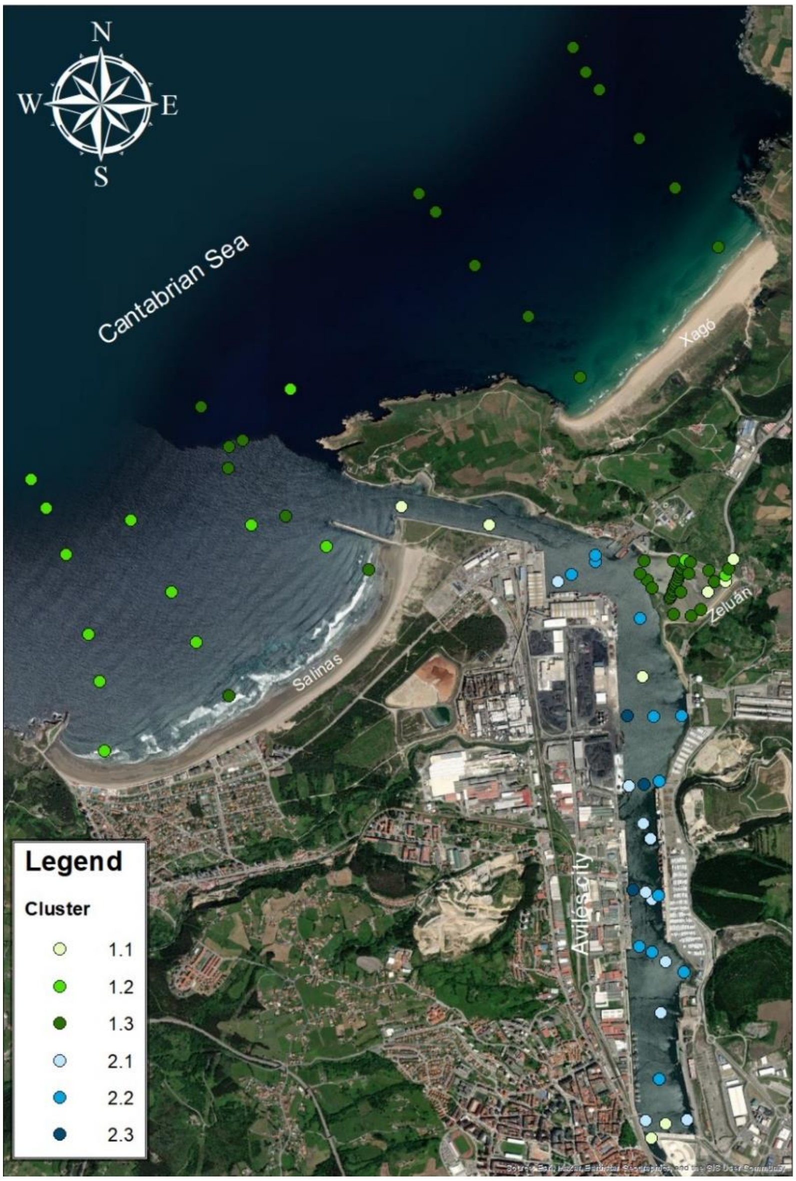

Figure 4. Geographical representation of the cluster hierarchy analysis results.

In detail, cluster 1 shows areas where the predominance of sand sizes produces a lower metal(oids) load, therefore indicating a low impact of anthropogenic contributions, as is shown in Figure 4. In general, this group includes the entire coastal area and the inland area of Zeluán. Within this group, subgroup 1.1 (Figure S2, Supplementary Material) constitutes the sandy samples of the general group that present the highest metal(oid) loads, and that are related to the confluence zones of the main rivers containing flushed fresh materials, giving rise to the metallic load in the sediments (Figure 4). Subgroup 1.2 (Figure S2, Supplementary Material) samples were taken in front of Salinas beach (Figure 4) and present significant amounts of metal(oids) despite being sandy, possibly because of aerial depositions of contaminated particles from the city of Aviles [22], as E–W is the prevailing direction of winds in this area. Finally, subgroup 1.3 (Figure S2, Supplementary Material) is formed of sandy samples with the lowest metal(oids) load, and most of the samples are grouped in front of the Xagó beach and in the Zeluán area (Figure 4).

The second main cluster (Figure S2, Supplementary Material) fits perfectly with the samples from the port area, located in the navigation channel, characterized by a predominance of fine sizes and a significant metal(oids) load. The statistical analysis clearly differentiates the zones where anthropogenic contributions have altered the natural geochemical partitioning of the sediments. Within this group, subgroup 2.1 (Figure S2, Supplementary Material) differs because its samples have the highest concentrations of Cr and Ni, and are found in the innermost part of the estuary, where the steel complex, primary aluminum industry and urban solid waste dump discharges are located (Figure 4). Subgroup 2.2 (Figure S2, Supplementary Material) samples are scattered throughout the estuary, and present significant loads of all the elements analyzed (Figure 4). Finally, subgroup 2.3 (Figure S2, Supplementary Material) is formed from samples presenting the highest loads of all metals analyzed, mainly Cd, Hg, Pb and Zn, and that are found in the area of the Raices River and historic points for the storage and discharge of minerals, making this area one of the main sources of contaminants in the estuary (Figure 4).

4.4. Environmental Considerations

As shown in Figure S3 of the Supplementary Material, more than 50% of the total samples show significantly increased Cd, Pb and Zn concentrations. In detail, more than 50% of the samples showed considerable to very high enrichments in Pb and Zn, while for Cd, more than 50% of the samples could be considered very highly enriched. The samples showed only moderate enrichment in the remaining analyzed elements. However, when the estuary and coastal areas are compared within this index, notable differences can be found, as is shown in Figure S3 (Supplementary Material). Except for As, the enrichment of which was higher in the coastal area than in the estuary, the rest of the elements presented greater enrichment in the estuary area than in the coastal area. Specifically, Cd and Cu showed moderate increases in their concentrations inside the estuary, compared with the coastal area, supporting the hypothesis of the existence of sources inside the estuary. In the cases of Pb and Zn, both elements showed moderate to extreme enrichment in the estuary and coastal areas, but this was much more significant inside the estuary, where Pb and Zn showed Cf values of 58 and 135, respectively. For this reason, both elements are widely dispersed throughout the whole area, but the main sources seem to be located inside the estuary.

Regarding the pollution load index (PLI) values (Figure 5), most of the sediment samples from the internal estuary showed a high degree of pollution, with a clear decreasing trend moving towards the coastal environment, where most of the samples presented an unpolluted to moderately polluted status. This corroborates the thesis that the estuary acts as a pollution sink, and does not spread the pollution beyond it. Notable in this aspect are the samples located at the front of the Xagó beach, which do not present contamination, despite the fact that the general dynamics of coastal sediment transport operate in the W–E direction [48], supporting the previous statement.

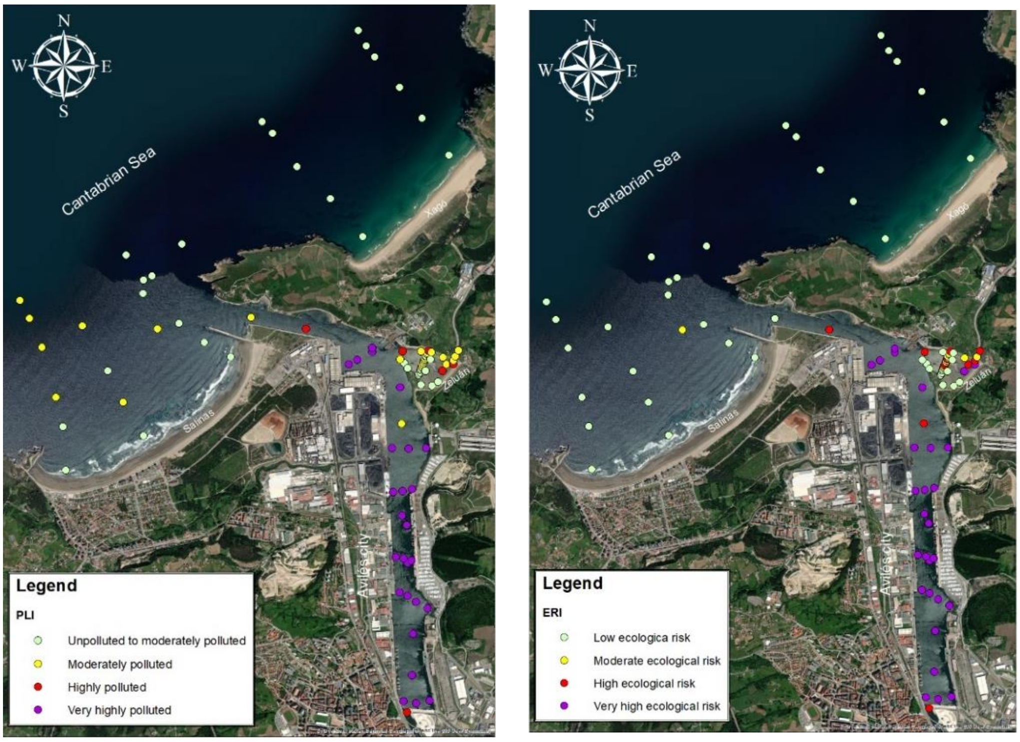

Figure 5. Geographical representation of the pollution load index (PLI) and environmental risk index Values (ERI) classified according to [18] criteria.

Finally, for a complete evaluation of the study area, it is necessary to develop an environmental risk assessment of the sediments. In this case, the ERI index was selected, as it takes into consideration the toxicity of the elements [34,49] and is thus the best option to provide a reasonably reliable evaluation. Based on this index, as was the case with the PLI, the most risky sediments were in the middle-internal area of the estuary, as a consequence of the significant contaminant load. In the rest of the areas, most of the sediments pose a low-to-moderate environmental risk, with some isolated samples showing a higher environmental risk, but without any apparent spatial continuity. It should be noted that the Zeluán area, despite being within the estuary, generally presents a low risk of transference due to the predominance of sandy sediments with a low metallic load.

5. Conclusions

The Avilés estuary is one of the transitional ecosystems in Spain that is placed under the greatest human pressure. Due to the significant presence of industry in its surroundings, high concentrations of pollutants have been stored in its sediments, generating a high degree of non-natural enrichment in metal(oids), despite the efforts and investments into reducing wastewater discharge. The sediments in the main channel of the estuary, where the finest materials accumulate, show significant concentrations of Cd, Hg, Pb and Zn, which may generate risks to the estuarine environment. Even with a significant amount of contaminated sediment stored inside the estuary, this material is not exported to the coastal system, and the environmental problem remains very localized inside it. For this reason, the prevention of direct discharges into the estuary, together with future management measures for these contaminated sediments, may be effective strategies to improve the environmental quality of this ecosystem, reversing the pollution that is currently affecting it.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app122110998/s1, Figure S1: Pearson's correlation matrix of the concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, TOC and grain size in surface sediments of the Aviles estuary and the nearby coastal area, Figure S2: Cluster hierarchy analysis based on the coefficients of the PCA multivariate analysis with varimax rotation, Figure S3: Comparison of the C_f values between the estuary samples, coastal samples and the general area comprising both environments.

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