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Assessment of polycyclic aromatic hydrocarbon concentrations in the sediments of an estuary heavily affected by heavy industrial activities

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ABSTRACT

The Aviles estuary is one of the most anthropized in Spain due to the significant pressure exerted on it by industry. This study assesses the concentrations, origins, sources, and environmental implications of 16 polycyclic aromatic hydrocarbons (PAHs) as persistent contaminants of the estuary sediments. A total of 79 sediment samples were studied. Results indicate ∑16PAH concentrations ranging from 0.086 to 305.771 μg g^{-1}, with the highest values in the estuary's main channel. High-molecular-weight PAHs (4–6 rings) were predominant, suggesting a pyrogenic origin associated to industrial combustion processes. Lower molecular weight PAHs (2–3 rings) were mainly observed near the estuary mouth. Diagnostic ratio analysis confirmed that PAHs in the estuary predominantly originate from mixed combustion sources, including industrial processes, vehicle emissions, and maritime activities. Spatial distribution maps identified three contamination hotspots: (i) the Albares River, linked with steel industry emissions; (ii) a central estuary site near an aluminium smelter discharge point, connected to PAHs from industrial operations; and (iii) the estuary mouth, where PAHs from industrial wastewater discharges and shipping activities were detected. Cluster analysis further distinguished areas with similar contamination profiles, confirming the influence of industrial and maritime activities. Finally, the risk assessment comparisons with international pollution thresholds revealed that PAH levels in the Avilés Estuary are significantly higher than in other European and global estuarine environments. Over 90 % of samples exceeded both low and median effect range limits, indicating substantial toxicity risks. Moreover, ecological risk quotient classified 92 % of sediment samples as posing a high risk to aquatic life.

1. Introduction

Rapid industrialisation and urban growth have given rise to various anthropogenic activities that release significant amounts of pollutants that are hazardous to the environment (Mojiri et al., 2019). Among the different groups of pollutants, polycyclic aromatic hydrocarbons (PAHs) are of particular interest due to their persistence in the environment and the associated risk (Jesus et al., 2022; Rizzi et al., 2023). Due to their chemically stable structure, these pollutants have a low capacity for natural degradation (Haritash and Kaushik, 2009), and their presence poses a significant risk to organisms as they are genotoxic, carcinogenic and teratogenic (Dai et al., 2023), severely affecting ecosystems when they are introduced into them (Bianco et al., 2023). Although PAH concentrations in the environment can have a geogenic origin due, for example, to the presence of certain types of lithology or volcanic processes (Maisto et al., 2006; Chakraborty et al., 2017), anthropogenic activities are the main source of PAHs release into ecosystems, which contributes substantially to environmental pollution (Jesus et al., 2022). The high concentrations of PAHs in the environment have caused great global concern in recent decades (Bianco et al., 2023; Venkatraman et al., 2024, among others). Due to their strong adsorption in the solid particles of soil and sediment, these compartments become important sinks for these pollutants, increasing their concentrations over time (Lu et al., 2011; Kuppusamy et al., 2017). PAH pollution, whether direct or indirect, has had a profound impact on the health and quality of life of human beings, along with that of other organisms across the planet, and

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has become a considerable problem (García-Sánchez et al., 2018).

Coastal areas are ecosystems of great value due to their significant biological richness, their role in the global C-N-S cycles and because they are areas in which human beings carry out numerous and important vital and economic activities (Cooley et al., 2023). Within coastal areas, estuaries play an important ecosystem role as they are the areas where the waters rich in essential nutrients from the emerged platform are introduced into the coastal environment, enriching it and favouring its correct development (Vasconcelos et al., 2011; Jickells et al., 2014). However, the growing human pressure on these areas has influenced to the introduction of various pollutants into coastal areas, together with nutrients that are vital for ecosystems, negatively affecting the ecosystems (Gavhane et al., 2021; Lu et al., 2022; among others). In northern Spain, Asturias is one of the autonomous communities with an important mining and industrial past, which has to the presence of anthropogenic concentrations of both heavy metals and PAHs in coastal sediments being reported in its central-western coastal area (Mangas-Suarez et al., 2023; Navarro-Murillo et al., 2024). In this coastal area, together with the Nalón estuary, which has been extensively studied for its pollution (Garcia-Ordiales et al., 2018; García-Ordiales et al., 2020a, 2020b), the Avilés estuary stands out as one of the most economically important due to port traffic and the significant presence of heavy and auxiliary industries in the surrounding area. For decades, the significant industrial pressure suffered in the Avilés area made the city one of the most polluted in the world in the 1980s (Berciano et al., 1989), causing this pollution to have a significant impact on different environmental compartments (Gallego et al., 2002; Ordóñez et al., 2003, 2015). Despite important environmental actions such as the dredging in 2003 of 160,000 m3 of sediments contaminated by heavy metals, BTEX, PAHs and organic matter (Menéndez and Fernández, 2005), the reduction of most industrial discharges into the estuary from 2018 onwards and the periodic dredging carried out by the Port Authority of Avilés to maintain the nominal draught of the estuary, different studies in recent years have shown that the impact on sediments continues today (Sierra et al., 2014; Baragaño et al., 2022; Mangas-Suarez et al., 2022). However, only the study by Tomillo et al. (2024) analyses the concentrations of PAHs in recreational sandy areas within the estuary without taking into account the sediments that remain continuously under the water surface, and which are the majority in the estuary, these being able to be, in addition to a sink, a source of transfer of these pollutants to other environmental compartments. Even though urban and industrial development of the estuary has produced very significant modifications, it still harbours a very important ecological diversity, which has earned it the designation of Special Protection Area for Birds (ZEPA) and Site of Cultural Interest (LIC). Therefore, due to the lack of information about PAHs in the estuary, it is necessary to develop environmental characterisations and assessments of the area, not only to preserve its natural areas, but also to identify the extent of anthropic impacts and guide future environmental management.

Therefore, the objectives addressed in this study were: (i) to quantify the concentrations of 16 priority PAHs in the surface sediments collected in the Avilés estuary; (ii) to identify the origins and sources of these PAHs in the estuary; (iii) to carry out a preliminary environmental assessment of the concentrations identified because of anthropogenic contributions to the estuary sediments. This research aims to establish a baseline for future research in this area or in other areas dealing with similar threats.

2. Materials and methods

2.1. Study area

The Avilés estuary takes its name from the neighbouring city that grows parallel to the alignment of its main channel. The estuary is characterised by significant geomorphological modification due to the construction of numerous port areas for economic activities, with approximately 85 % of its 9 km length having been altered by these structures (Peláez, 2015). The estuary is also identified by the significant presence of heavy industry in the surrounding area, with a large zinc smelter, a steel factory, a fertiliser factory, a glass factory and an aluminium smelter (currently being dismantled). Along with these large factories, numerous small- and medium-sized ancillary companies are located in the various industrial estates near the estuary. Together with the industrial activities, in terms of port traffic, this activity moves around 6 million tonnes of raw materials annually, the majority of which are solid bulk materials such as zinc concentrates, anthracene, coals, etc., which represent more than half of the total annual traffic (Mangas-Suarez et al., 2022).

Respect the estuary environment, in the nearby coastal area there are three important dune fields together with their respective sandy areas of great ecological importance for the coastal environment (Flor, 1994; Flor-Blanco et al., 2013). Considering the estuary, it can be divided (Fig. 1) into three different areas according to its dynamic behaviour. The first area, which occupies the largest surface area of the estuary, is the most protected part, which forms the main channel and is formed by the confluence of the Tamón and Alvares rivers, which are characterised by their short courses and low flow rates (Peláez, 2015). The second area is the Zeluan ZEPA, which is formed by the confluence of the Vioño stream and by the direct effect of coastal waters during periods of heavy storms due to its direct alignment with the third area, the estuary mouth, which acts as a connection with the immediate coastal area. The third area is the mouth of the estuary where the coastal environment meets the estuarine environment, and in these areas different geochemical processes occur that give rise to gradients within it (Navarro-Murillo et al., 2024). Previous studies on the coastal area such as those by Mangas-Suarez et al. (2023) or Navarro-Murillo et al. (2024) suggest that from a sedimentological and environmental point of view, the estuary acts as a sink for sediments and associated pollutants, not exporting them to the immediate coastal areas, so the potential risk due to the presence of pollutants is limited to the estuarine area.

2.2. Sampling and analytical methods

A total of 79 samples were collected in the Aviles estuary, as illustrated in Fig. 1. Sampling operations were conducted from a vessel using a Van Veen grab constructed from AISI 316 stainless steel to prevent cross-contamination. The grab had a sampling surface area of 250 cm^2 and at each site, approximately 2 kg of sediment was collected and stored in pre-clean amber glass jars, which were subsequently maintained at 4 °C in a portable refrigerator under dark conditions. The grab was carefully cleaned and rinsed with water from each station to prevent contamination between sampling stations. Representative aliquots of the collected samples were obtained in the laboratory using a rotary sample splitter and sent to certified external laboratories for further analysis.

Grain size distribution of the samples was determined through mechanical sieving in accordance with the UNE 103101 standard. The results of the particle size distribution were grouped into three general sizes: Gravel (<2 mm), sand (2 mm–63 μm) and sludge (>63 μm). Organic carbon content was quantified using the dry combustion method following the UNE-EN 15936 standard. For polycyclic aromatic hydrocarbon (PAH) analysis, the sediment samples underwent freeze-drying, sieving to remove particles larger than 2 mm, and grinding using an agate ball mill for homogenization. Following these preparatory steps, extraction of PAHs was performed using a mixture of hexane and dichloromethane (DCM) in a 1:1 ratio (100 mL). The extracts were purified and concentrated using anhydrous sodium sulfate (Na_2SO_4) under a nitrogen stream and subsequently filtered through a 0.43 μm filter.

Filtered aliquots were analysed and quantified using a Thermo Scientific TRACE™ 1310 Gas Chromatograph coupled with a TSQ 8000 Mass Spectrometer, in accordance with the laboratory's established

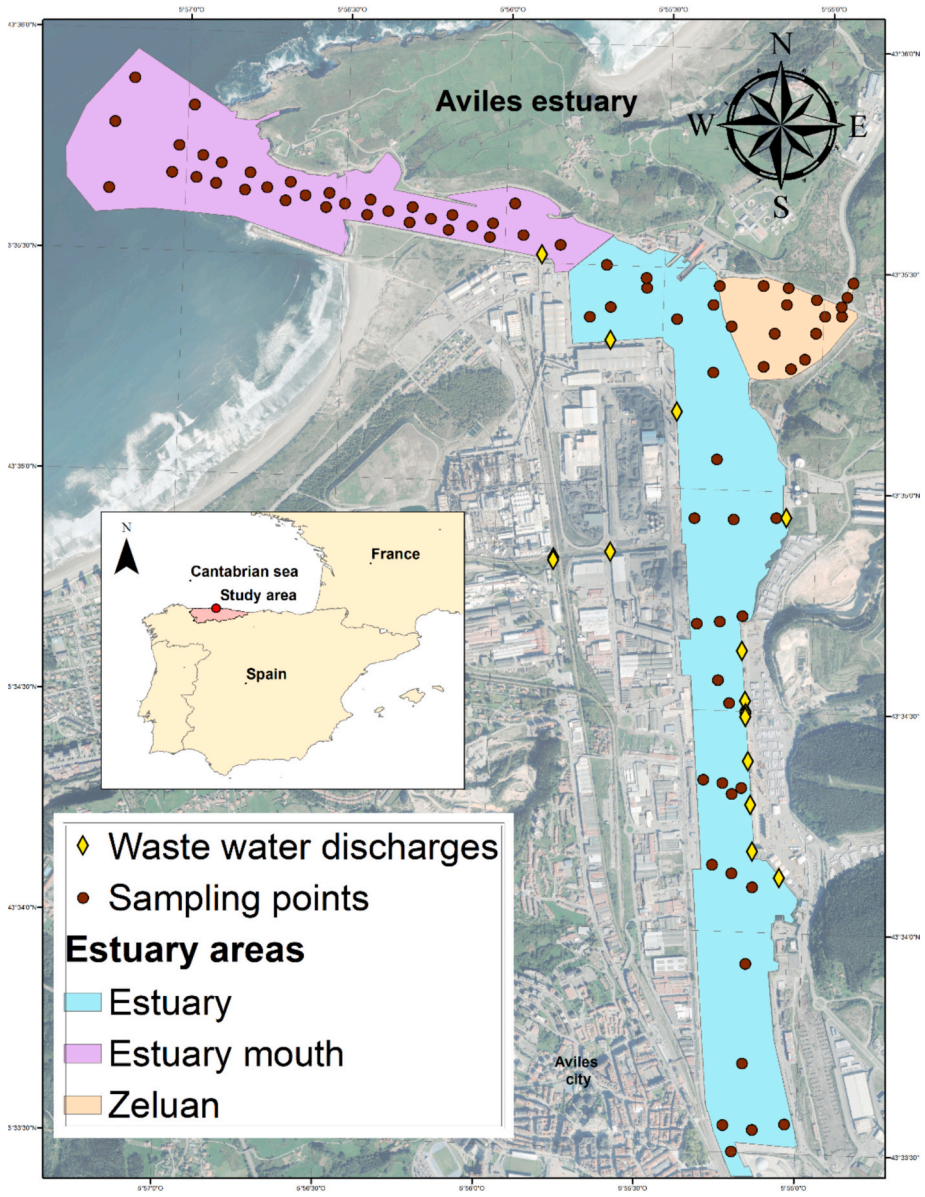

Fig. 1. Study area with the sampling stations studied, as well as the authorised points of discharge of industrial water into the estuary and the sub-areas into which the estuary is subdivided in the discussion.

protocol. The gas chromatograph injector port was initially set at 55 °C, with a programmed temperature ramp of 30.0 °C/min to 200 °C, followed by a slower ramp of 10.0 °C/min to a final temperature of 320 °C. This method was optimized by the equipment manufacturer to enhance the recovery of PAHs for quantification. Quality control measures included the use of analytical blanks, certified reference materials, and duplicate analyses. The method's detection limit (LOD) and quantification limit (LOQ) for individual PAHs were reported as 0.005 mg/kg dry weight (d.w.) and 0.010 mg/kg d.w., respectively. Two reference materials were used to ensure the quality of the analyses: IAEA-159A (sediment) and IAEA-459 (marine sediment). The recovery ranges with respect to the certified values were between 93 and 101 % for IAEA-159A and between 91 and 98 % for IAEA-459. The 16 PAHs analysed were: acenaphthene (Ace), acenaphthylene (Acy), anthracene (Ant), fluoranthene (Flua), fluorene (Flu), naphthalene (Nap), phenanthrene (Phe), pyrene (Pyr), benz[a] anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo [ghi]perylene (BghiP), benzo[*a*]pyrene (BaP), chrysene (Chr), dibenz[*a*, *h*]anthracene (DahA), and indeno[1,2,3-*cd*]pyrene (Inp).

Finally, statistical analysis was executed using the free software R, and the representation of the results were mapped out using the ArcGIS Desktop 10.8 software, under license to the University of Oviedo.

3. Results and discussion

3.1. Sediment granulometry and TOC at the study estuary

In general, the sediments of the Avilés Estuary exhibit significant granulometric variability, ranging from predominantly sandy samples (>90 % sand) to predominantly muddy samples (>90 % mud), depending on the specific area of the estuary (Table 1). Note that the gravel sizes were negligible in all the samples analysed and will not be considered in the future discussion. Based on this granulometric heterogeneity, three distinct zones can be identified within the estuary according to the predominant sediment sizes as shown in the Fig. 1. In the Zeluán area, sand sizes (range 32.0–98.1 %) are predominant, with a low overall proportion of fine silt and clay sizes (avg. 16.4 %). The grain sizes in this area are strongly influenced by coastal sand inputs during

Table 1
Statistical summary of the concentrations of the 16 PAHs analysed as well as the granulometric distributions and the concentration of TOC in the sediments studied. Note: <LOD – below detection limit (0.005 μg g^{-1}).

	General (79 samples)					Estuary (29 samples)					Estuary mouth (33 samples)					Zeluan (17 samples)				
	Min	Max	Mean	DVST	CV	Min	Max	Mean	DVST	CV	Min	Max	Mean	DVST	CV	Min	Max	Mean	DVST	CV
Ace (μg g^{-1} d.w.)	<LOD	5.900	0.601	0.849	1.412	0.130	5.900	0.996	1.211	1.216	0.037	1.230	0.534	0.409	0.766	<LOD	0.355	0.059	0.100	1.682
Acy (μg g^{-1} d.w.)	<LOD	0.845	0.159	0.204	1.289	<LOD	0.845	0.121	0.174	1.439	0.013	0.711	0.269	0.222	0.824	<LOD	0.028	0.008	0.006	0.840
Ant (μg g^{-1} d.w.)	<LOD	9.780	1.785	2.176	1.219	0.234	7.290	1.628	1.605	0.986	0.075	9.780	2.776	2.604	0.938	<LOD	0.584	0.130	0.181	1.396
BaA (μg g^{-1} d.w.)	<LOD	24.600	4.059	4.671	1.151	0.603	24.600	5.497	5.467	0.995	0.067	12.800	4.679	4.187	0.895	<LOD	1.480	0.402	0.509	1.266
BaP (μg g^{-1} d.w.)	<LOD	33.900	4.054	5.023	1.239	0.821	33.900	6.398	6.529	1.020	0.041	10.300	3.862	3.476	0.900	<LOD	1.450	0.430	0.515	1.197
BbF (μg g^{-1} d.w.)	0.011	51.300	6.323	7.877	1.246	1.580	51.300	10.844	10.256	0.946	0.067	13.700	5.286	4.693	0.888	0.011	2.130	0.622	0.754	1.212
BghiP (μg g^{-1} d.w.)	<LOD	29.800	3.379	4.353	1.288	0.813	29.800	6.007	5.743	0.956	0.031	6.780	2.645	2.341	0.885	<LOD	1.070	0.320	0.371	1.157
BkF (μg g^{-1} d.w.)	<LOD	16.600	2.179	2.627	1.206	0.518	16.600	3.630	3.345	0.922	0.020	5.060	1.911	1.726	0.903	<LOD	0.806	0.223	0.264	1.180
Chr (μg g^{-1} d.w.)	<LOD	24.900	3.670	4.407	1.201	0.609	24.900	5.357	5.480	1.023	0.050	11.700	3.881	3.544	0.913	<LOD	1.510	0.380	0.491	1.291
DahA (μg g^{-1} d.w.)	<LOD	6.840	0.833	1.029	1.235	0.240	6.840	1.480	1.328	0.897	<LOD	1.500	0.649	0.569	0.877	<LOD	0.294	0.088	0.104	1.183
Flua (μg g^{-1} d.w.)	<LOD	41.400	7.958	9.134	1.148	1.070	41.400	9.314	9.415	1.011	0.190	30.900	10.436	9.498	0.910	<LOD	3.510	0.834	1.099	1.319
Flu (μg g^{-1} d.w.)	<LOD	5.780	0.975	1.107	1.135	0.182	5.780	1.040	1.110	1.068	0.082	3.270	1.381	1.140	0.825	<LOD	0.387	0.077	0.122	1.593
Inp (μg g^{-1} d.w.)	<LOD	27.100	3.128	4.077	1.303	0.724	27.100	5.640	5.379	0.954	0.027	6.650	2.384	2.138	0.897	<LOD	0.980	0.287	0.337	1.175
Nap (μg g^{-1} d.w.)	<LOD	11.100	2.183	2.719	1.245	0.282	4.220	1.236	0.893	0.723	0.237	11.100	4.085	3.236	0.792	<LOD	0.564	0.108	0.180	1.675
Phe (μg g^{-1} d.w.)	<LOD	25.100	5.125	5.838	1.139	0.731	25.100	5.081	5.156	1.015	0.280	20.500	7.565	6.472	0.856	<LOD	2.220	0.465	0.674	1.451
Pyr (μg g^{-1} d.w.)	<LOD	30.300	5.896	6.625	1.124	0.917	30.300	7.052	6.833	0.969	0.138	22.500	7.574	6.864	0.906	<LOD	2.780	0.668	0.890	1.332
Sand (%)	<0.5	98.30	57.90	38.52	0.67	<0.5	74.40	13.84	19.13	1.38	22.30	98.30	83.36	17.22	0.21	32.00	98.10	83.63	20.99	0.25
Mud (%)	1.70	100.00	41.90	38.63	0.92	25.60	100.00	86.16	19.13	0.22	1.70	77.70	16.16	17.08	1.06	1.90	68.00	16.37	20.99	1.28
TOC (%)	0.120	11.450	3.698	2.844	0.769	2.940	11.450	6.457	2.279	0.353	0.120	6.000	2.151	1.539	0.716	0.130	5.790	1.997	1.944	0.974

periods of heavy swells due to its location, aligned in front of the estuary mouth, which favours the deposition of these granulometric materials (López Peláez, 2015). There is no data on the temporary accumulation of sand in this area, as it is a Special Protection Area for Birds (ZEPA) and is not directly controlled by the Avilés Port Authority. In the main channel, which extends from the mouth of the Albares River (south of the estuary) to the area where the estuary makes a turn towards the northwest, finer sizes are predominant (avg. 86.2 %) with a low proportion of sands overall. Only in the samples near the mouth of the Albares River did the sand proportion reach its maximum for this zone. In this case, the fine sediment size is due to being the most sheltered area of the estuary, where the low-energy environment facilitates the deposition of fine sizes, which does not occur in other areas where the environment has higher energy. According to data from the Avilés Port Authority, since 2009, when the last major dredging was carried out in this area, the variation in nominal draught has been <0.5 m on average, which supports the fact that this area is low energy. Finally, in the mouth area, a gradient of mixed sizes can be observed due to the existing dynamics. In the innermost part of this zone, finer sizes predominate, consistent with those in the main channel, but with a higher proportion of silts and clays in its composition. As one moves further out of the estuary, sandy sizes increase in prominence until the outermost part, where sand sizes dominate, making up over 90 % of the granulometric composition of the samples. This distribution is consistent with previously presented results for this zone, such as those of Mangas-Suarez et al. (2023) and Navarro-Murillo et al. (2024), supporting the idea that the estuary functions as a sink for materials and only exports materials during extreme river flood events. In addition, this area of the estuary has been the most intensively dredged in recent years, especially the strip where sand has been identified as predominant, with periodic annual or biannual dredging due to accumulations of material from the coastal environment of up to 1.5 m in one year.

Regarding TOC (Total Organic Carbon), the overall concentrations ranged from 0.12 to 11.45 %, with the highest concentrations in the main channel (avg. 6.46 %) due to the strong correlation between TOC and fine sizes ($r = 0.821$, $p < 0.05$), which are predominant in this zone and act as traps for organic matter. Notably, significant TOC concentrations were found in the Zeluán area with a maximum of 5.79 %, despite the predominance of sandy sizes. In this case, the high TOC content is attributed to the discharge of wastewater with simple treatment during peak river flow periods from the Maqua wastewater treatment plant, which discharges in this area. Finally, in the estuary mouth, the average TOC concentrations were found to be below 3 % because of the grain size variability in this area.

3.2. PAHS concentrations and origins in the estuary

The total concentrations of PAHs are reported as the sum of the 16 EPA priority congeners, ranging from 0.086 to 305.771 μg g^{-1} d.w., with an average ± standard deviation value of 52.308 ± 57.951 μg g^{-1} d.w. Considering the three areas previously defined within the estuary, the main channel where mud sizes dominates the sediments, exhibits the highest total PAH concentrations (71.322 ± 66.177 μg g^{-1} d.w.), followed by the mouth (59.918 ± 52.551 μg g^{-1} d.w.), and finally, the protected area of Zeluan (5.101 ± 6.512 μg g^{-1} d.w.).

The heavy PAHs with four or more rings (BaA, BbF, BghiP, BkF, Chr, DahA, Flua, Inp and Pyr) were the majority compounds in the estuary sediments, being predominant in 91 % (72 samples) of the analysed stations. In contrast, the light PAHs with two or three rings (Ace, Acy, Ant, Flu, Nap, Phe) were predominant in only 9 % (7 samples), all of which were in the outermost part of the estuary's mouth. Considering these distributions, the abundance of heavy PAHs (4–6 rings) is attributed to their strong tendency to accumulate in sediments due to their low solubility resulting from high hydrophobicity, the significant stability of their molecular structures, and their low susceptibility to degradation (Corminboeuf et al., 2022; Duker et al., 2024). Among these

compounds, the 4-ring PAHs contributed the most, predominating in 62 of the 79 stations analysed, representing 78 % of the study sites. Following this group, the 5-ring PAHs were the next most abundant, predominating in 13 % (10) of the sampled stations, while the light PAHs with 3 rings were predominant in only 7 of the 79 stations analysed. The predominance of compounds with 4 or more rings suggests that their origin is primarily linked to high-temperature combustion processes. These medium- to high-molecular-weight compounds are widely associated with anthropogenic activities, such as the incomplete combustion of petroleum products and/or coal (Ambade et al., 2022; Grmasha et al., 2023). Conversely, low-molecular-weight PAHs are typically attributed to petrogenic sources, such as hydrocarbon spills or the presence of coal in sediments (Han et al., 2020; Tomillo et al., 2024).

In order to make an initial assessment of the possible impact suffered by the estuary because of the identified PAH concentrations, a comparison has been made with different areas of the world, as presented in Table 2. According to this, the range of ∑16PAH concentrations in the Avilés estuary is an order of magnitude higher than in the areas compared. Only the high concentrations identified can be compared with those of areas such as the Urdaibai estuary in Spain, the Delaware River Estuary in the USA or the estuary of the same name in South Africa, but all of them with maximum concentrations much lower than those identified in Aviles, which confirms that the estuary is strongly affected by human activity.

Table 2
Polycyclic aromatic hydrocarbon (PAHs) levels in sediments from around the world. Data in ng g^{-1} d.w.

Region	Continent	∑16 PAHs	Reference
Aviles estuary, Spain	Europe	86–305,771	This study
Ria Arousa, Spain	Europe	45–7901	Pérez-Fernández et al., 2015
Urdaibai estuary, Spain	Europe	338–16,778	Puy-Azurmendi et al., 2010
Sele River, Italy	Europe	632–845	Di Duca et al., 2023
Sarno River, Italy	Europe	5–679	Di Duca et al., 2023
Volturno River, Italy	Europe	435–872	Di Duca et al., 2023
Priolo Bay, Italy	Europe	56–847	Di Leonardo et al., 2014
River Conwy Estuary, Wales	Europe	18–1578	Vane et al., 2020
Mersey Estuary, U.K.	Europe	626–3766	Vane et al., 2007
Estuary and coast CanGio, Vietnam	Asia	1–518	Thuy et al., 2021
Musa estuary, Iran	Asia	67–90	Zoveidadianpour et al., 2023
Mahanadi River, India	Asia	13–685	Ambade et al., 2022
Subarnarekha estuary India	Asia	37–670	Ambade et al., 2022b
Yangtze estuary, China	Asia	107–663	Liu et al., 2008
Pearl river estuary, China	Asia	24–3075	Cheng et al., 2024
St. Lawrence estuary, Canada	North America	247–5672	Corminboeuf et al., 2022
Delaware River Estuary, USA	North America	5–22,324	Kim et al., 2018
Esterode Urias Estuary, Mexico	North America	27–418	Jaward et al., 2012
Bahia Blanca Estuary, Argentina	South America	20–30	Oliva et al., 2015
São Paulo's estuary, Brasil	South America	12–1825	Nascimento et al., 2017
Itajaí-Açuestuary, Brazil	South America	64–1459	Frena et al., 2017
Lenga Estuary, central Chile	South America	290–6118	Pozo et al., 2011
Awoye Estuary, Nigeria	Africa	27–40	Nubi et al., 2022
Abereke Estuary, Nigeria	Africa	23–39	Nubi et al., 2022
Durban Bay, South Africa	Africa	350–4700	Nel et al., 2015
Buffalo River Estuary, South Africa	Africa	1107–22,310	Adeniji et al., 2019
Rufijiestuary, Tanzania	Africa	19–223	Shilla and Routh, 2018

To better discern the origin of PAHs in estuarine sediments, diagnostic ratio analysis was employed. This methodology is widely recognised in the scientific literature as a valuable tool for identifying PAH sources in a straightforward manner (Famiyeh et al., 2021; Wu et al., 2021; Suresh et al., 2024). In this study, the diagnostic ratios Ant/(Ant+Phe), Flua/(Flua+Pyr), BaA/(BaA+Chr), and InP/(InP + BghiP) were used, as they are the most applied ratios in the literature consulted for this research. As shown in the Fig. 2, the ratio Ant/(Ant+Phe) ranged from 0.13 to 0.50, with values consistently above 0.1, indicating a combustion origin from coal, petroleum, or wood. In the case of the ratio Flua/(Flua+Pyr), it varied between 0.50 and 0.70, suggesting a mixed origin from petroleum combustion and coal or wood combustion. The ratio BaA/(BaA + Chr) ranged from 0.35 to 0.58, also indicating mixed combustion sources and finally, the ratio InP/(InP + BghiP) ranged from 0.31 to 0.50, reinforcing the findings of the previous ratios, pointing to a pyrogenic origin from mixed combustion sources.

In the Avilés Estuary, pyrogenic sources were attributed to the incomplete combustion of coal and petroleum derivatives in large industrial facilities located in the surrounding area. These industries utilize these fuels as thermal energy sources for their industrial processes. Additionally, for PAHs derived from the incomplete combustion of petroleum, their origin may also be linked to emissions from vehicles traveling daily along the estuary's margins and the intense maritime transport activities occurring within the estuary.

3.3. Dispersion and sources of PAHs

To identify the main sources of the PAH concentrations identified in the sediments, dispersion maps have been produced for each of the compounds analysed, as shown in Fig. 3.

As shown in the dispersion maps (Fig. 3), three hot spots can be identified where significant concentrations of the different PAHs analysed were found. Firstly, at the end of the estuary at the mouth of the river Albares, high concentrations of 14 of the 16 PAHs studied were identified (Ace, Acy, Ant, BaA, BbF, BghiP, BkF, Chr, DahA, Phe, Flua, Flu, Inp, Pyr). In this case, the source of the input could not be fully identified at first because this river receives different inputs of industrial before flowing into the estuary. It should be noted that the high concentrations of PAHs related to the Albares River are nothing new in the history of this estuary. In 2003, approximately 160,000m^3 of sediment were dredged, decontaminated and encapsulated in a secure landfill due to the high concentrations of heavy metals, BTEX, PAHs, PCBs, cyanides and organic matter from the nearby industry (Menéndez and Fernández, 2005). Because the identified origin of the PAHs has to do with mixed sources, but predominantly by combustion of petroleum or petroleum products, the sources of these PAHs are related to the industry existing in the basin of this river (steel factory, and on a smaller scale metal processing industries, metal component manufacturing industries, gas industries, and others not directly related to the potential release of PAHs into the environment) and mainly, they have been historically related to the steel industry because it is the largest industry and uses different fossil fuels as an energy source (Menéndez and Fernández, 2005). In this case, the steelmaking processes carried out in the facilities mainly generate heavy PAHs with four or more rings (Yang et al., 1998; Wang et al., 2024), which are the predominant PAHs in the samples taken close to the river mouth. Likewise, in the research of Yang et al. (2002) it is shown that the concentrations of BaA, BbF and BghiP tend to be very high in waste derived from this type of industry. In the case of Avilés, comparing the average concentration of these three PAHs in samples taken near the Albares river (BaA: 11.47 μg g^{-1} d.w.; BbF: 22.06 μg g^{-1} d.w.; BghiP: 11.68 μg g^{-1} d.w.) with the average in the rest of the estuary (BaA: 3.56 μg g^{-1} d.w.; BbF: 5.26 μg g^{-1} d.w.; BghiP: 2.82 μg g^{-1} d.w), it can be seen that in the area around the river Albares the concentrations of the 3 PAHs were significantly higher than in the rest of the estuary and that they can therefore be attributed to the steel industry.

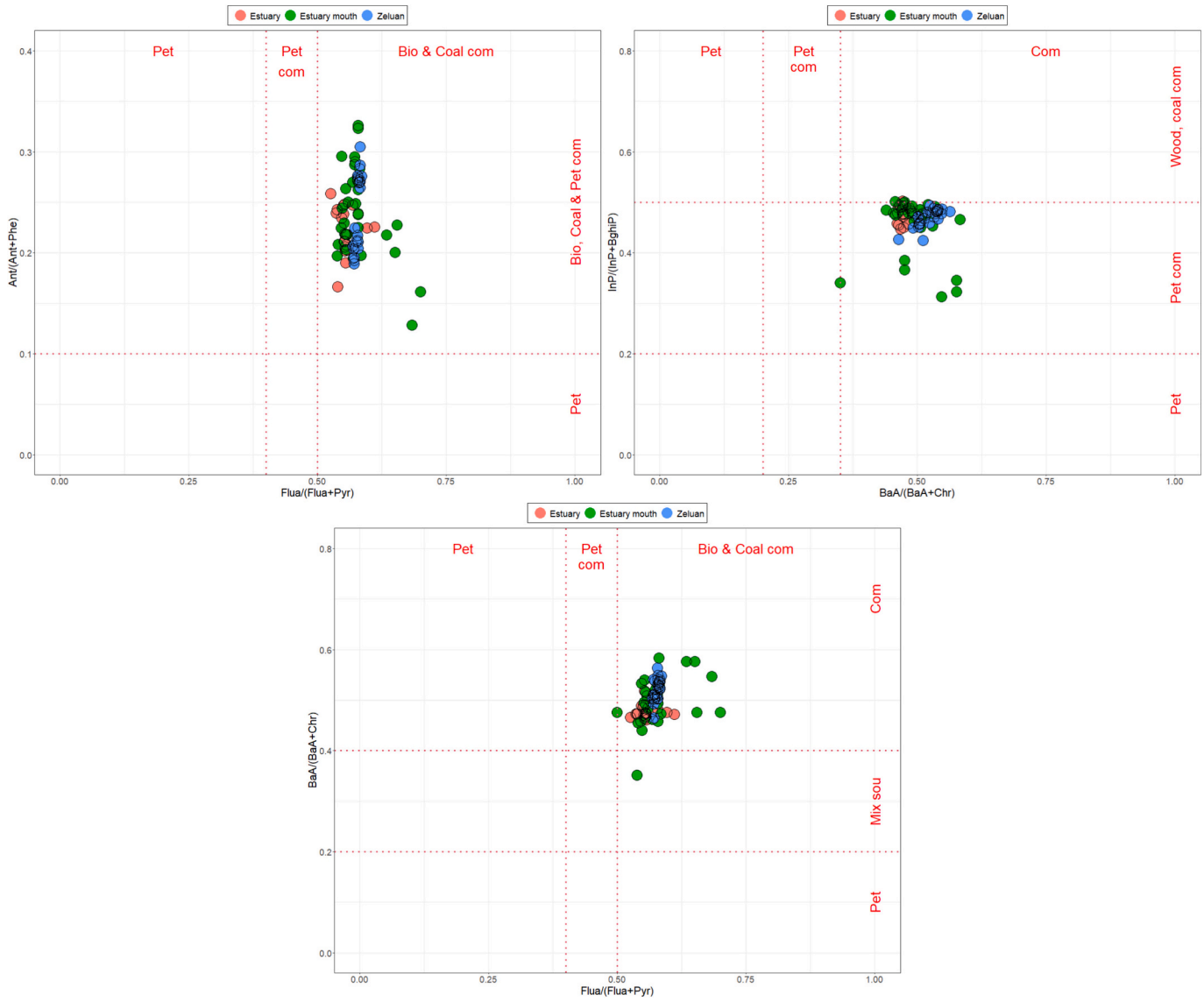

Fig. 2. Diagnostic PAH ratios of Ant/(Ant/Ant + Phe) versus Fla./(Fla + Pyr); BaA(BaA + Chr) versus Fla./(Fla + Pyr) and Inp/(Inp + BghiP) versus BaA/(BaA + Chr). Labels: Pet-Petroleum, Pet com-Petroleum combustion, Bio & Coal com-Biomass and Coal combustion, Bio, Coal & Pet com- Biomass, Coal and Petroleum combustion, Mix sou-Mixed sources, Wood, coal com- Wood and coal combustion.

Additionally, considering the information on existing discharge authorisations, the concentrations of Flua and BghiP are monitored monthly in the steel factory's discharges, while for the rest of the industry, the PAHs monitored are low molecular weight compounds associated with fuels or other products. In this case, considering only Flua, as BghiP was explained above, samples near the Albares River showed much higher average concentrations (19,78 μg g^{-1} d.w) than those in the rest of the estuary (7,33 μg g^{-1} d.w), providing information that reinforces what was explained above about the main source of pollution.

The second hot spot was located on the right bank of the estuary towards its central area. In this case, 12 of the 16 PAHs studied (Ace, BaA, BaP, BbF, BghiP, BkF, Chr, DahA, Phe, Flua, Inp, Pyr) showed significant concentrations in the sediments compared to their surroundings. In this case, the hot spot coincides with a discharge point of an aluminium smelting industry that has now been dismantled. Given that aluminium smelters are recognised as a source of PAHs in the environment (Booth and Gribben, 2005; McIntosh et al., 2012; Johnson et al., 2015 among others), and especially those that use Soderburg processing (Næs and Oug, 1998) as in the case of this factory, it is considered that this industry is the main source of contribution to the sediments in this area. In addition, the average concentrations of the points close to the discharge with respect to the rest of the estuary for Chr (9.33 μg g^{-1} d.w. vs 3.36 μg g^{-1} d.w) and Pyr (9.57 μg g^{-1} d.w vs 5.70 μg g^{-1} d.w) are significantly higher and coincide with other studies in aluminium smelting environments, in which significant values of these two PAHs associated with this industrial activity have been reported (Borgulat and Staszewski, 2018; Li et al., 2023).

Finally, the third hot spot identified was located along the mouth of the estuary and in it, 9 of the 16 PAHs (Acy, Ant, BaA, Chr, Phe, Flua, Flu, Nap, Pyr) studied showed higher concentrations than in adjacent areas. In the estuary, unlike the other hot spots identified, the anomalous concentrations correspond to low to medium molecular weight PAHs (2–4 rings). The widespread presence of these PAHs suggests a possible petrogenic origin in addition to the general origin by high temperature combustion that dominates in all the sediments of the estuary. In this case, the anomaly coincides with the existence of an authorised discharge point that may be a source of these compounds. This discharge point receives industrial wastewater from a company that cleans machinery used for work in different industries at its facilities.

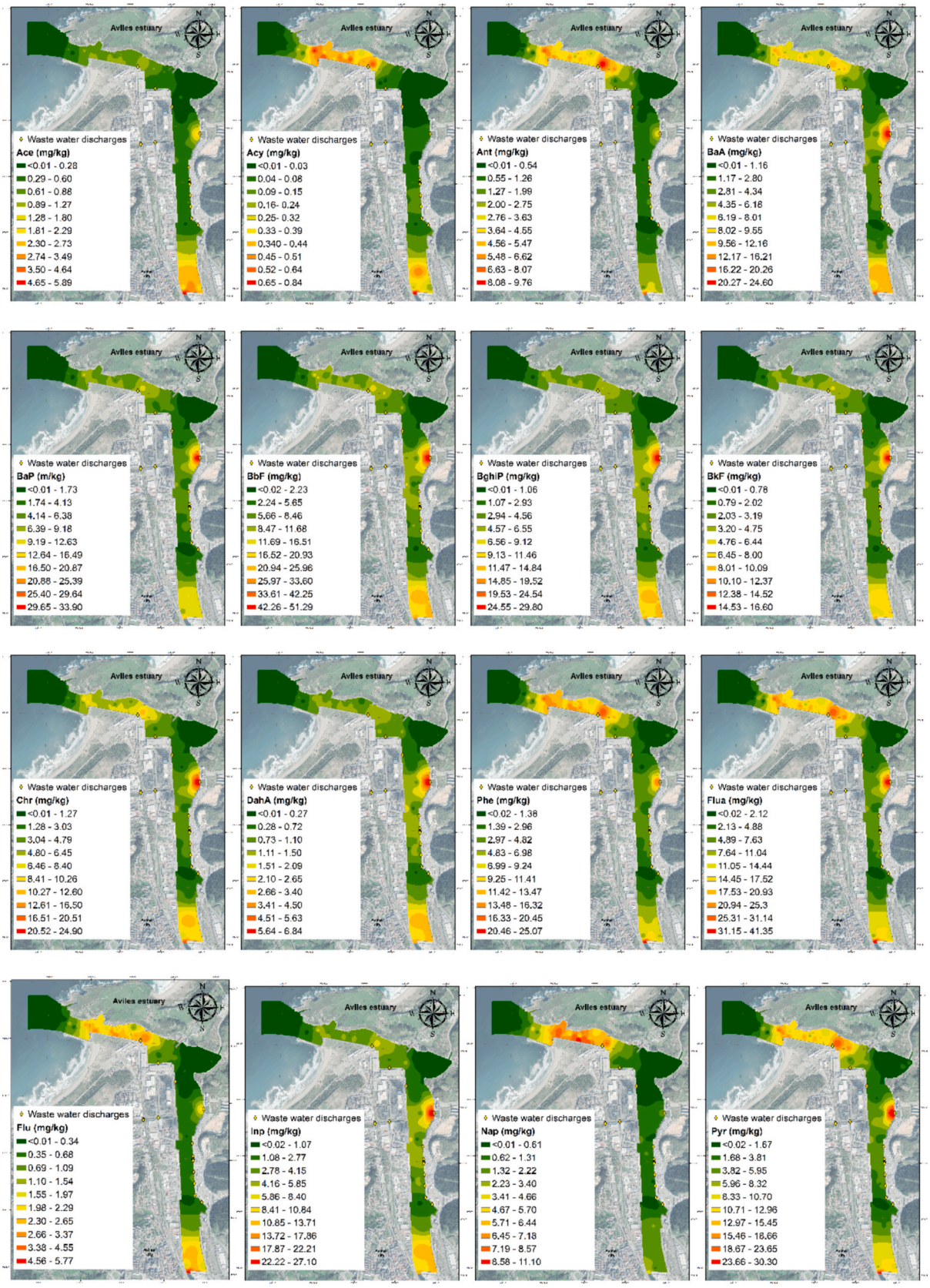

Fig. 3. Spatial distributions of the concentrations of each analysed PAH in the sediments of the Aviles estuary.

Furthermore, together with the potential source, this area suffers from intense maritime traffic due to the arrival and departure of boats to and from the port facilities, which may be another possible source of input (Bajt, 2014). Because the burning of fossil fuels by vehicles is a recognised source of PAHs into the environment (Fu et al., 2024; Seibert et al., 2024) and because these sources routinely result in high concentrations of Pyr in their waste (Lin et al., 2019; Yao et al., 2024) as happens when studying this area in detail (mean estuary mouth vs rest of the estuary: 12.11 μg g^{-1} d.w vs 4.31 μg g^{-1} d.w respectively), it is considered that the burning of fuels by vehicles is the source of the anomaly. However, because none of the identified sources could be ruled out, both are considered to be the origin of the identified anomaly.

3.4. Cluster analysis

In order to identify associations between samples and to be able to identify similar or different areas in the estuary, a cluster analysis was carried out on the samples studied. The best results for the cluster analysis were obtained using Euclidean distance and Ward's clustering method, which is based on the sum of squares criterion to measure the proximity between groups, allowing the creation of compact and uniform-sized clusters. The results of this analysis are shown in Fig. 4 and are presented spatially in Fig. 5.

The cluster analysis showed two main groupings as shown in Fig. 4. According to the representation in Fig. 5, Group 1 is mainly composed of samples from the interior of the estuary, with the exception of some samples located in the Zeluan area and the estuary mouth. This group is characterised by having the highest concentrations of PAHs and it was possible to identify their sources. Group 2 is made up exclusively of samples from the estuary mouth and the Zeluan area, which differ from the other group in that they have lower concentrations of PAHs and no potential source has been clearly identified. Analysing each of the previous groups, Group 1 can be divided into two subgroups (Fig. 3): SG 1.1 contains samples from the innermost part of the estuary while SG 1.2 mainly groups together samples from the intermediate zone, as well as samples close to the Albares river and the Vioño stream. Accordingly, SG 1.1 would classify the samples that have high concentrations of PAHs but in which the direct influence of the sources is diluted by their mixture with clean materials, while SG 1.2 would group together the areas directly influenced by the sources and which have the highest concentrations. In addition, in the analysis presented in Fig. 4, it can be seen that the SG 1.2 samples from the central part of the estuary are the most similar to those of Group 2, making it possible to identify that the source of these has an influence on the samples in this group. Analysing Group 2, this can be divided into two subgroups: SG 2.1 which contains

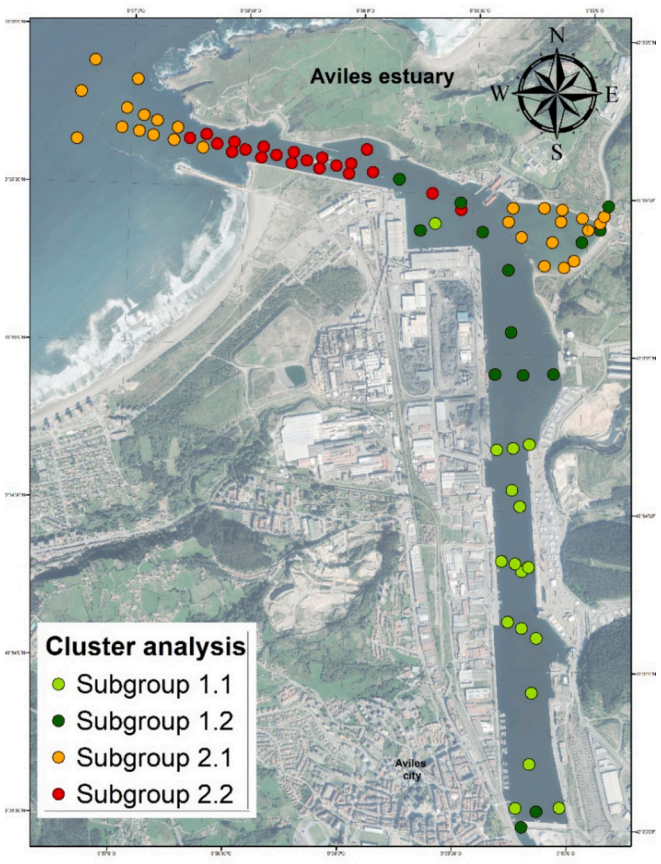

Fig. 5. Sample points and the different groups determined by cluster analysis on an Aviles estuary map.

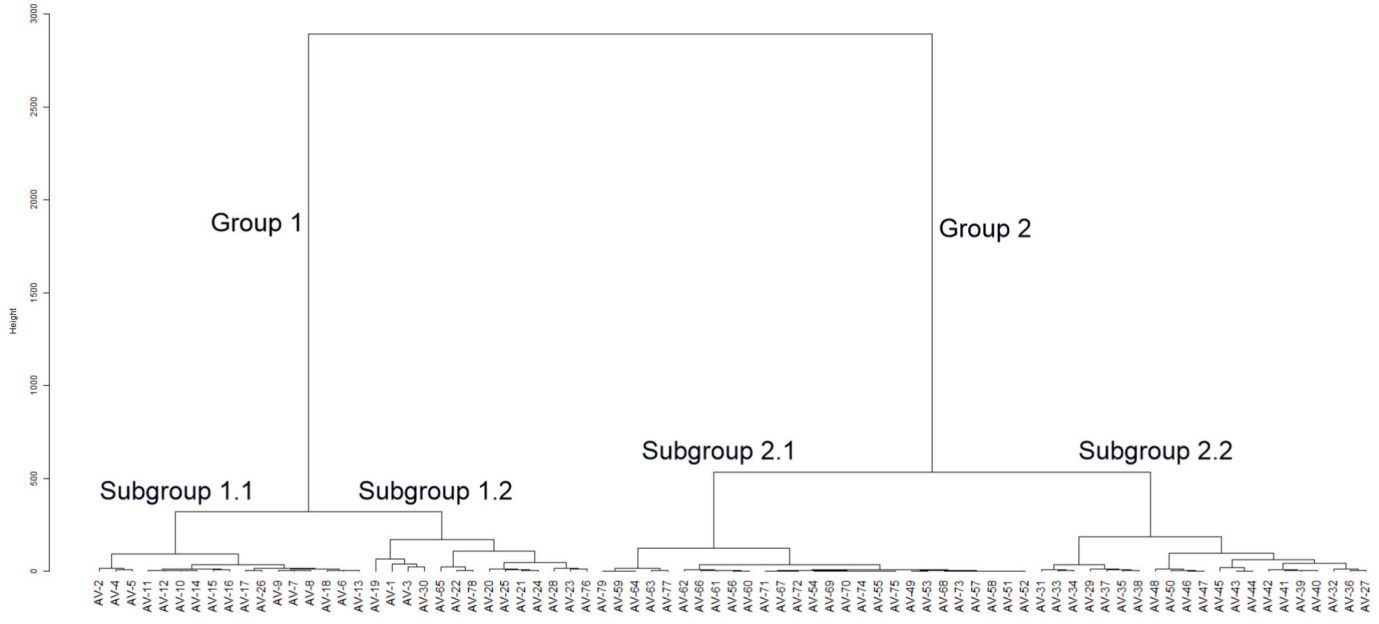

Fig. 4. Dendrogram obtained using Euclidean distance and the Ward clustering method.

the samples from the Zeluan area and the outermost ones from the estuary mouth, and SG 2.2 which contains the samples from the estuary mouth. In the case of SG 2.1, this would classify the samples that present the lowest concentrations of PAHs in the entire estuary, as they do not have nearby sources or these are very low, and SG 2.2 would group together the samples that present a moderate concentration of PAHs but which differ from those classified in Group 1, in the potential presence of an unidentified source that would favour this classification. According to Fig. 4, the SG 2.1 samples would be affected both by the identified source of the SG 1.2 samples and by the unidentified source of the SG 2.2 samples, but with a greater predominance of the effect of the unidentified source. In the case of SG 2.2, it can be considered that the unidentified source is the one that has the greatest influence on the samples in this area.

4. Risk assessment

For the evaluation of the existence of anthropogenic impact in the studied estuary, the concentrations of the analysed PAHs have been compared with the Background Assessment Concentration (BAC) for pristine locations from OSPAR and with the concentration range from the central Asturian coast reported by Navarro-Murillo et al., 2024. Compared with the BAC values shown in Table 3, the average concentration values in the sediments of the Avilés estuary for the 9 priority PAHs in marine sediments for OSPAR significantly exceed the concentrations found in a pristine environment.

Considering these concentrations in relation to those reported for the Asturian coast (Table 3), the average concentrations in the sediments of the estuary for 11 of the 16 PAHs studied (Ace, BaA, BaP, BbF, BghiP, BkF, Chr, DahA, Flua, Inp, Pyr) exceed those reported for the coastal area. Since Navarro-Murillo et al., 2024 reported that the coastal strip is anthropogenically impacted, this comparison reinforces that the impact is much greater in the sediments of the Avilés estuary as a result of the anthropogenic pressures to which it is subjected.

In contrast, regulatory agencies in the United States use the low effect range (ERL) and median effect range (ERM) as evaluation mechanisms to preliminarily assess toxicity in sediments (Table 3). According to both thresholds, on average of 89 % of the stations exceeded the ERL for some of the PAHs analysed, while on average of 70 % of the stations also exceeded the ERM for some of the PAHs. In detail, Acy was the PAH with the fewest exceedances of both thresholds, with 61 % of the samples exceeding the ERL and only 23 % exceeding the ERM, whereas, on the contrary, in the cases of Ace, Phe, and Flua, >90 % of the stations exceeded the ERL threshold and >82 % of them exceeded the ERM. By areas, the estuary channel is the zone where the highest number of samples exceed the thresholds, with an average of 99 % and 93 % of them exceeding the ERL and ERM, respectively, followed by the mouth with 96 % and 76 %, respectively, and finally the Zeluan area with 94 % and 79 %.

Finally, to assess the potential risks to aquatic ecosystems due to the presence of PAHs, and after comparing the levels detected in the sediments of the analysed stations with the SQG thresholds, the average risk quotients (RQ) were calculated, defined as the ratio between the individual concentration of a specific PAH in the environment and the corresponding quality values in the same, following the methodology described by Kalf et al. (1997), Liu et al. (2010), and Cao et al. (2010). The values used for the negligible concentrations (NCs) and the maximum permissible concentrations (MPCs) for the calculation were those reported by the same authors in their research and summary in the Table 3.

Furthermore, since these equations are used to assess the risk to the ecosystem based on the risk of each individual PAH, in order to perform an integrated assessment of Σ16PAH, the method proposed by Cao et al. (2010) was applied, and the evaluation method proposed by Kalf et al. (1997); Ashayeri et al. (2018) was used, based on the following intervals: RQΣPAHs(NCS) <1 shows that the sum of the PAHs exhibits negligible risk; 1 ≤ RQΣPAHs(NCS) <800 and RQΣPAHs(MPCS) <1 show low to moderate risk; RQΣPAHs(NCS) ≥800 and RQΣPAHs(MPCS) ≥1 show high risk. According to the results obtained and represented in the Fig. 6, 84 % of the analysed stations, that is, 67 of them, showed a high risk due to the concentrations of PAHs in the sediments.

On the other hand, only 6 of the 79 analysed stations showed a moderate risk and 6 a negligible risk. In this scenario it is notable that major part of then are located in the Zeluan area, which is predominantly sandy and exposed to the air during the tidal cycle. These characteristics cause the risk in this area to be reduced due to possible degradation mechanisms, as well as the sedimentological characteristics of the materials, which aligns with the findings of Tomillo et al. (2024),

Table 3
Reference values used for risk assessment.

	BAC OSPAR	Asturias coastline	ERL	ERM	NC_S	MPC_S
Ace		<0.010–1.03	0.044	0.64	0.0012	0.12
Acy		<0.010–0.594	0.016	0.5	0.0012	0.12
Ant	0.003	<0.010–6.550	0.085	1.1	0.0012	0.12
BaA	0.009	<0.010–11.100	0.261	1.6	0.0036	0.36
BaP	0.015	<0.010–8.860	0.43	1.6	0.027	2.70
BbF		<0.010–12.400	0.32	1.88	0.0036	0.36
BghiP	0.045	<0.010–5.860	0.43	1.6	0.075	7.50
BkF		<0.010–4.280	0.28	1.62	0.024	2.40
Chr	0.011	<0.010–9.120	0.384	2.8	0.107	10.70
DahA		<0.010–1.753	0.063	0.26	0.027	2.70
Flua	0.020	0.012–24.000	0.6	5.1	0.026	2.60
Flu		<0.010–2.820	0.019	0.54	0.0012	0.12
Inp		<0.010–4.970	0.24	1.4	0.059	5.90
Nap	0.045	<0.010–8.230	0.16	2.1	0.0014	0.14
Phe	0.017	0.017–16.300	0.24	1.5	0.0051	0.51
Pyr	0.013	<0.010–17.200	0.665	2.6	0.0012	0.12

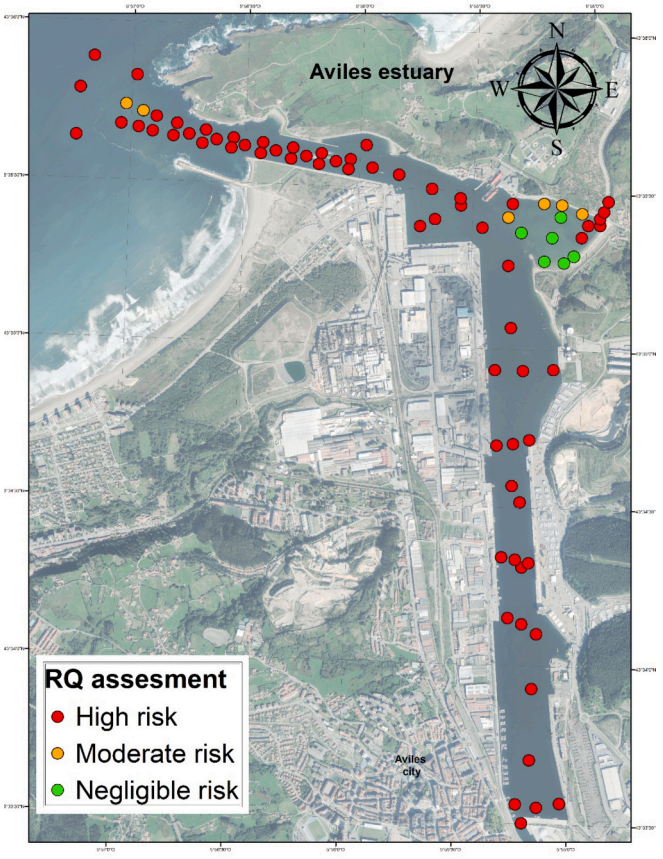

Fig. 6. Risk quotients (RQ) assessment at the different sampling points in the Aviles estuary.

who determined that in the recreational areas of the estuary, which are sedimentologically and dynamically similar to the Zeluan area, the risk was moderate to high due to the concentrations of Σ16PAH.

5. Conclusions

The Avilés estuary is subject to significant anthropic pressure which has led to significant concentrations of PAHs in its sediments due to industrial activity, despite efforts to mitigate its impact. The sediments in the inner part of the estuary, where the finer sizes are predominant, have high concentrations of PAHs that can generate high risks for the estuarine environment, and can transfer the existing contamination to other environmental compartments. The results obtained in this research, together with those previously reported by Mangas-Suarez et al. (2022) on heavy metals, show an estuary whose sediments are significantly contaminated by different groups of pollutants, which increases their environmental risk. Together with this factor, the fact that the estuary acts as a sink and does not export the pollution to the coastal system, makes this area of special concern due to the potential risk of hyperaccumulation of pollutants increasing their concentrations over time. For this reason, the prevention of direct discharges into the estuary together with continuous monitoring and mitigation strategies should be future measures to be adopted for the proper management of this space. Future research should focus on the development of remediation techniques and on the long-term ecological impacts to safeguard this ecologically important estuarine system.

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CRediT authorship contribution statement

Mario Mangas-Suarez: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jose Ignacio Barquero:** Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Noemi Barral:** Writing – original draft, Validation, Formal analysis, Data curation. **Nieves Roqueñí:** Writing – original draft, Data curation, Conceptualization. **Efren Garcia-Ordiales:** Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

Efrén Garcia-Ordiales as the corresponding author of the manuscript and on behalf of the rest of the co-authors declares:

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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