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Original Articles

Heavy metal concentrations and dispersion in wild mussels along the Asturias coastline (North of Spain)

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ABSTRACT

Several international organisations have recommended the use of bioindicators to improve the evaluation of ecological risk in marine ecosystems. In this context, wild mussels, a recognised bioindicator, were collected from thirty sampling points along the Asturias coastline and studied in order to identify any relationship between metal(oid) concentrations in wild mussel tissues and the geological and environmental conditions of the coastal area via biochemical analyses. Two main concentration trends were observed: Concentrations of As, Cd, Cr, Ni, Pb and Zn slightly decrease from the western to the eastern areas of the region, while the opposite occurred for Fe, Hg and Se whose concentrations increased from the westernmost part of Asturias to the east. Correlations between the elements showed how essential metals for organisms such as Fe, Ni and Cr have good correspondences among them but not with other metal(oid)s. On the other hand, Cd, Hg, Se and Zn were found to be correlated with each other, suggesting the presence of the mussels' natural bio-defence against Cd and Hg. In addition, samples were also grouped by a cluster analysis based on their element concentrations, showing two independent groups. Group 1 was associated with the sampling sites whose concentrations were related to anthropic sources, while mussel concentrations in Group 2 were attributed to natural sources. This last group was divided into two subgroups based on the lithology of the dominant geological materials of each area. Both geological and anthropic sources have caused an increase in the metal loads of mussels which at times surpassed international environmental criteria.

1. Introduction

The climate and environmental conditions of coastal areas have resulted in the settlement of a wide variety of species to their surroundings (McKinley et al., 2011; García et al., 2018; Pioch et al., 2018). In addition, accessibility to coastal areas has contributed to the creation and development of surrounding urban areas and industrial facilities. Moreover, the waste produced by industrial plants and harbour activities such as shipping or fishing introduce heavy metals to the environment (Ordoñez et al., 2014; Puig et al., 2015; Dobaradaran et al., 2018; He et al., 2019). Although metal concentrations in the environment may be generated by natural processes, anthropic sources cause the greatest increase in metal concentrations in coastal waters. These metals, generated either by natural or anthropogenic sources, are transferred from the aqueous phase to the sediments by adsorption, hydrolysis, and coprecipitation processes (Van Ael et al., 2017; Yu et al.,2017; Vetrimurugan et al., 2019). Moreover, sediments are considered contamination reservoirs which can act as sources of metals which may be released to the overlying water column (Lin et al., 2013; Delshab et al., 2017; Rao et al., 2021). Note that metal loads present in the sediments have adverse effects on biota when in a bioavailable state (Garcia-Ordiales et al., 2019b). These bioavailable metals are detected in various organisms which live and obtain nutrients from the affected ecosystems (Blanco-Rayón et al., 2019; Signa et al., 2019). Regarding these kinds of biota, filter-feeding bivalve molluscs obtain nourishment from the overlying water column and add dissolved metal(oid)s to their organism. One of the most relevant bivalve molluscs are mussels, as they have been identified as one of the best biological indicators of coastal pollution (Cevik et al., 2008; Besada et al., 2014; Cunha et al., 2017; Li et al., 2019). Mussels are excellent bioindicators because they have a wide geographic distribution range, are sedentary, can easily be sampled and analysed and in particular because mussels are able to accumulate

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both inorganic and organic contaminants in their tissues (Besada et al., 2011).

Cd, Hg, and Pb are non-essential metals for molluscs which means that these elements can cause harmful effects on bivalves even at low concentrations. These elements are considered the most hazardous metals with regard to the coastal ecosystem (OSPAR Commission, 2017). Other metals such as Cu and Zn are essential, although they can generate toxic effects at high concentrations (Türkmen et al., 2008; Besada et al., 2014; Esposito et al., 2021). Prolonged exposure to a polluted ecosystem results in the bioaccumulation of several metals in the mussels (Kumar et al., 2015; Martínez-Colón et al., 2021). This bioaccumulation can cause a significant increase in the metal concentrations in the biota with respect to the metal loads occurring in the surrounding water (Casas et al., 2008; Besada et al., 2011; Nannoni et al., 2015; Claassens et al., 2016). The accumulation ratio not only depends on the metal loads occurring in the environment, but also several other factors involved. These other factors are those with an environmental origin such as temperature, pH or salinity; or those related to the mussels' age, sex, size or stage of sexual maturity (Bartolomé et al., 2010; Besada et al., 2014; Richir and Gobert, 2014; Mandich, 2018). Elements bioaccumulated in organisms could be transferred and biomagnified throughout the trophic chain, which in turn poses a significant environmental risk (Turritto et al., 2018). Thus, an accurate environmental assessment must include not only chemical analysis in different environmental compartments, but also established biological techniques with the aim of determining the relationship between metal concentrations and their effect on marine ecosystems (Bellas et al., 2014; Riani et al., 2018; Conti et al., 2019). Because of the relevance of metal transference between environmental compartments and their effects on marine ecosystems, several recognised environmental organisations such as OSPAR, NOAA or CCME use bioindicators in order to improve the environmental assessment of ecological risks (OSPAR Commission, 2013; CCME, 2016; NOAA, 2018a;b).

In this context, this investigation presents an assessment of metal (oid) concentrations in mussel tissues with the aim of evaluating the contamination of different metals and metalloids along the Asturias coastline. In addition, this study attempts to determine the main sources metals analysed herein, distinguishing those originating from natural geological processes from those resulting from anthropogenic activities. This information may be useful to discern the level of impact of the possible metal sources along the coast in order to evaluate the environmental quality and ecological risks of this area with regards to the environmental guidelines.

2. Study area

Asturias is a region located in the North of Spain (SW Europe) bordered by the Cantabrian Sea which represents the transition of the Atlantic Ocean to the Biscay Gulf. The Asturias coastline represents around 30% of the Cantabrian Coast of Spain and is generally considered an environmentally well-preserved area.

According to Bastida and Aller (1995), the Asturias coastline presents a geological unconformity which divides the region into two predominant sets of rocks. The first main set is composed of the West-Asturian Leonese Zone (ZAOL) and the Cantabrian Zone (ZC). The ZAOL rocks show features of the orogen hinterlands, and as such are characterised by large recumbent folds, regional metamorphism and intense tectonic foliations, mainly of Cambrian, Ordovicic and Devonic age. Due to the presence of the ZAOL, the western Asturias coast is mainly composed of sandstone, lutite and slate. Regarding the Cantabrian Zone, this area is characterised by carbonate and siliciclastic lithologies located not only in the east Asturias coast but also around Cape Peñas, where limestones and marls are predominant. The second set of rocks has Permian-Mesozoic and Paleogene-Neogene covers. This last set, which is situated in the central area, presents a mixed lithology composed of materials such as limestone, sandstone, quartzite and lutite.

The geological wealth of the region was one of the main factors that allowed for the development of a vast and varied mining activity which is still ongoing, albeit less than in the past, the growth of industrial facilities and expansion of urban areas (Loredo et al., 2003; Álvarez et al., 2018). Moreover, several heavy industries such as steel, zinc, and aluminium factories have been built in Asturias in association with mining industries (Ordoñez et al., 2014). In addition, several studies have determined the relationship between these anthropic activities and the increment in the metal loads in coastal ecosystems (Garcia-Ordiales et al., 2018; Garcia-Ordiales et al., 2019a, Pavoni et al., 2021). Note that even though some of these industrial and mining activities have ceased operation, their waste can still impact the sediments and fluvial waters located in their surroundings and are even able to degrade areas a considerable distance from the anthropic sources (Ordóñez et al., 2013; Garcia-Ordiales et al., 2018; Ayala and Fernández, 2020). With regards to the ability of waste to affect areas distant from the source of contamination, it has been demonstrated that the principal fluvial systems of Asturias act as a means of transport for materials originating from regional industries, transporting them from industrial sources to coastal sites (Garcia-Ordiales et al., 2020). In addition, it is known that harbour activities may also have a relevant impact on the quality of coastal environments (Sierra et al., 2014; Nepote et al., 2017; Breitwieser et al., 2018). With the aim of evaluating the effect of these materials on the environment, several studies have used mussels as bioindicators of metal(oid) pollution in the Cantabrian coast (González-Quijano et al., 2006; Besada et al.,2011; Albentosa et al., 2012).

3. Materials and methods

The Asturian coastline studied extends along 334 km between Galicia and Cantabria and thirty sampling points were selected for this research (Fig. 1). Twenty specimens of wild mussels (*Mytilus galloprovincialis*) were collected manually in each sampling point in 2018 over a period of several days during low tide. The mussels were collected at the same time of day at all sampling sites in order to minimise variations caused by differences in the mussel physiology and as far as possible to avoid significant seasonal environmental variations (Besada et al., 2011). The size of the specimens was between 35 and 60 mm, as recommended by Besada et al. (2011). Samples were strored in double ziplock bags with seawater, which was taken on the same area where the mussels were collected, and then they were stored during 24 h in the fridge in order to remove the pseudofaeces as Besada et al. (2011) did. The byssus of each sample was removed to prevent possible particle contamination. The soft tissues of each pool were separated from the shells, freeze-dried and triturated with a blade mill. The water percentage of each sample was calculated by weighing the differences between the fresh and lyophilised samples.

Samples were analysed after being digested with nitric acid and microwave oven high-pressure Teflon reactors, according to the method set out by Besada et al. (2008). Analyses were performed using an ICP-MS, and certified reference material (Mussel Tissue, REF: JRC ERM-CE278K) was used to validate and monitor the measurements (Table 1). A batch of samples, duplicates, procedural blanks and control charts were made to verify the results.

4. Results and discussion

4.1. General results

Overall descriptive statistics are given in Table 2. There were different trends in the concentrations of the elements analysed along the coast. Concentrations of As, Cd, Cr, Ni, Pb and Zn (Fig. 2) decrease slightly from the western to the eastern areas, while the opposite occurred for Se. In the case of Fe and Hg, the concentrations increased significantly from the western to the eastern areas. Mussels from Avilés

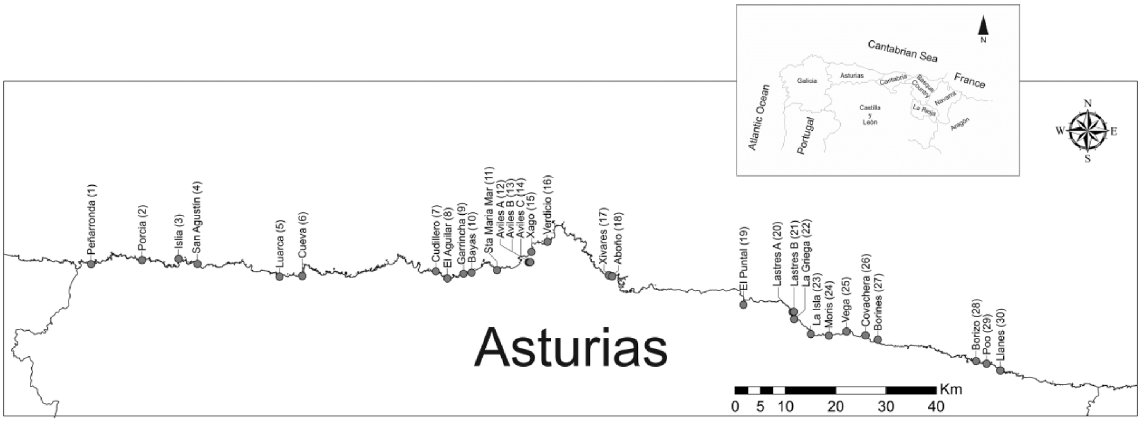

Fig. 1. Study area and sampling points.

Table 1
LODs and LOQs for ICP-MS and method precision for elements analysed.

	LOD	LOQ	Certified ERM-CE278k	Analysed ERM-CE278k
As	0.100	0.300	6.7 ± 0.4	6.69 ± 0.6
Cd	0.005	0.015	0.336 ± 0.025	0.334 ± 0.035
Cr	0.005	0.015	0.73 ± 0.22	0.72 ± 0.31
Fe	2.000	6.000	161 ± 8	160 ± 11
Hg	0.005	0.015	0.071 ± 0.007	0.071 ± 0.012
Ni	0.010	0.030	0.69 ± 0.15	0.70 ± 0.21
Se	0.010	0.031	1.62 ± 0.12	1.61 ± 0.17
Pb	0.010	0.032	2.18 ± 0.18	2.17 ± 0.25
Zn	1.000	3.000	71 ± 4	69 ± 5.6

contained the highest total metal load, followed by Moris, Vega and La Garrincha. Mussels from Avilés had the highest concentration for Cd (6.05 μg g^{-1} d.w.), Cr (87.3 μg g^{-1} d.w.), Fe (5,898 μg g^{-1} d.w.), Ni (38.2 μg g^{-1} d.w.), Pb (97.8 μg g^{-1} d.w.), and Zn (1,166 μg g^{-1} d.w.) as a consequence of anthropic pressures on the area. Avilés is one of the most anthropised estuaries in Spain with an abundance of heavy industries such as steel, zinc and aluminium. Waste generated in these factories, together with a past lack of a proper wastewater treatment system has caused notable environmental degradation in the area.

Two different groups of samples were identified based on As concentrations. Samples from Peñarronda to Cudillero showed As concentrations higher than 20 μg g^{-1} d.w. and the same held true for samples from Moris to Poo. In both cases, given that there is no relevant anthropic source of contribution, As concentrations seem to be more linked to natural geological anomalies. Cambric and Ordovician metamorphic rocks (mainly slate and quartzite), with the presence of igneous rocks such as granite dominate the area from Peñarronda to Cudillero. According to INDUROT (2008), this component of Asturian geology presents high As concentrations as a result of the metamorphisms undergone by the materials what is supported by the results of IGME (2012) which reports As concentrations in river sediment from this area between 19 and 1,900 μg g^{-1} which are well above the As normal range for the region sediments, between 8 and 16 μg g^{-1}. Also in the area, the main rives (Navia and Esva, and other small streams) present an annual average As concentrations in waters above the average of the regional rivers according to the annual (4.7 μg l^{-1} and 3.1 μg l^{-1} respectively). Since this anomaly in As is in agreement with the sampling points, it is thought that arsenic levels detected in mussels are possibly related to the geological materials inherent in the area. On the other hand, the group of samples from Moris to Poo located in east Asturias are connected to another anomalous geological area rich in arsenic. This area is formed by materials dating back to between the Carboniferous and Jurassic periods, in which hydrothermal processes generated ores (mainly fluorite) with metal sulphides and carbonates rich in this element (Iglesias and Loredo, 1994). In this case, there are not important streams around this area however, important groundwater flows occurred in this part. According to the river basin organization the groundwaters from this part of the region have an As natural maximum level of 4.5 μg l^{-1} which is above the regional value of 3 μg l^{-1}, supporting the link to the geological materials inherent in the area. However, this last group of samples from La Isla to Poo also showed high Hg concentrations whose origins must be more closely examined. In this area, Forján et al. (2019) suggested that Hg levels in the Vega beach are linked to past and current fluorite mining which could be a potential source of Hg. However, in the same area, Gallego et al. (2019) ruled out the presence of bioavailable Hg species from mining discharge and Flor and Flor Blanco (2009) suggested a dynamo-sedimentary balance of the beach with a low to null export of sediments due to beach rotation processes (Bird, 1993; Short et al., 1995). Thus, the potential impact of mining on the marine environment is limited and may be discarded due to the extent of the anomaly of this element in mussels. The most plausible explanation of this anomaly is that it is related to the same geological anomaly as As because, according to Iglesias and Loredo (1994), Hg is widely present in the hydrothermal ores present in this area. Nevertheless, Llanes port requires special attention since it was found to have the highest Hg concentration. During the last 15 years, sediment monitoring conducted by the regional port authority has revealed the presence of high Hg concentrations which did not previously exist. The most plausible explanation for these concentrations are anthropic sources currently under investigation. The concentrations found in this sample were therefore attributed to anthropic sources.

Table 2
Descriptive statistics of the elements analysed in the mussel samples.

	As	Cd	Cr	Fe	Hg	Ni	Se	Pb	Zn
Mean	18.13	1.46	6.42	699.25	0.68	3.26	3.41	9.63	291.02
Median	17.30	0.85	2.97	601.92	0.30	1.83	3.20	2.58	250.55
Max	29.44	6.05	87.28	2910.95	2.66	38.23	7.96	97.81	1165.97
Min	9.30	0.50	1.39	224.30	0.10	0.62	2.38	0.83	91.07
DVST	4.74	1.50	15.42	555.75	0.78	6.69	1.09	22.21	191.50

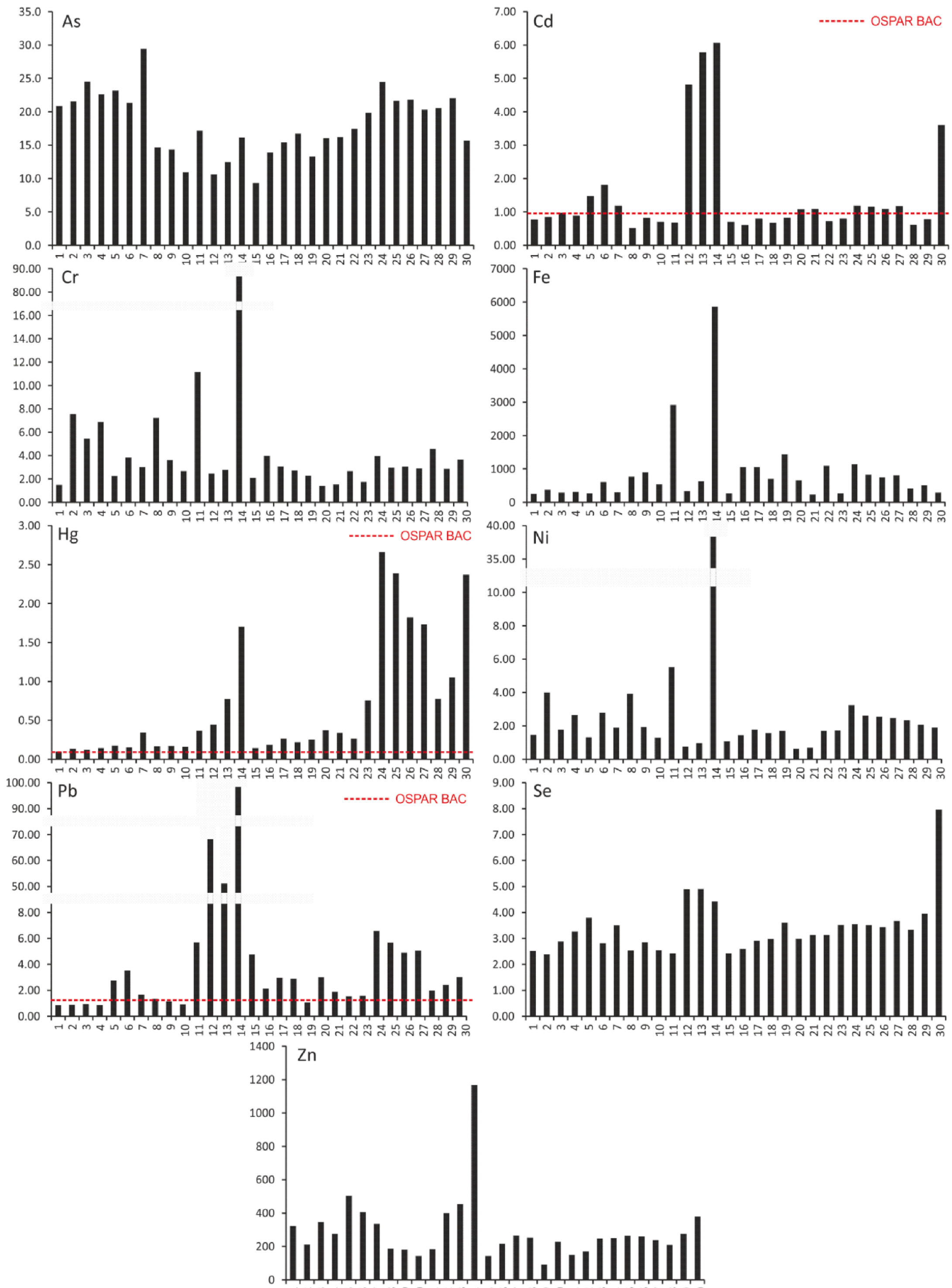

Fig. 2. Concentrations in mussel tissues from the Asturian coastline and BAC OSPAR's levels for Cd, Hg and Pb. Concentration expressed in μg g^{-1} d.w. Red dotted lines indicate BAC values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To put in our study into perspective, the data were compared to heavy metal concentrations obtained in similar studies (Table 3). It is observed that the Hg loads present on mussels is higher on North Spanish areas, such as the analysed in this study or the ones located on Galician, Cantabrian or Basque coast. Regarding Cd and Pb it seems that the higher values are observed in Black Sea areas. Ni is not one of the most monitored elements on this kind of studies according to the studies collected on Table 3, however it is interesting to notice that their lowest values were register on Mediterranean zones. According to Table 3 Zn values show a high contrast between North Spanish areas and the other ones.

4.2. Correlation between metal(oids)

To identify associations between metal(oids), correlation coefficient of Pearson and Spearman were calculated depending on the normal

Table 3
Trace metals concentrations in mussels in similar studies. Concentration expressed in μg g^{-1} d.w.

Location	As	Cd	Cr	Hg	Ni	Pb	Zn
Galicia and Cantabrian (NW Spain)Besada et al., 2014	6.39–13.3	0.357–2.01	–	0.055–0.623	–	0.658–28.1	141–361
Basque coast (N Spain)Franco et al., 2002	1.33–2.45	0.7–1.33	–	0.28–0.70	–	1.12–5.83	353–580
NW MediterraneanSquadrone et al., 2016	0.942	0.05	0.513	0.011	0.425	0.513	28.868
Cala Iris Al Hoceima (Northern Morocco)Azizi et al., 2018a		0.850	3.33	–	3.218	–	162.9
NE Adriatic SeaKanduč et al., 2018	22.1	0.6	1.8	–	1.7	6.2	193.8
Bahía Blanca Estuary (Argentina)Buzzi & Marcovecchio 2018	–	1.98	0.64	–	2.06	–	56.93
South Africa (Saldanha Bay)Firth et al.,2019	1.8	1	0.2	0.004	–	0.5	25.9
Turkish Black SeaÇulha et al.,2017	–	5.949	–	–	–	7.881	41.876
Present study	18.13	1.46	6.42	0.68	3.26	9.63	291.02

statistical distribution of the data. The correlation matrix obtained is shown in Table 4.

As and Pb did not interact with other analysed elements, thereby suggesting a different bioaccumulation mechanism. Considering the other analysed elements, two different groups based on the correlation can be distinguished. One group is formed by Fe, Ni and Cr, which correlate with each other but not with other elements. These elements are considered essential for mussels (Azizi et al., 2018b; Riani et al., 2018), so their grouping is attributed to the normal life cycle of mussels. In addition, no problems have been documented in specimens of molluscs with high levels of these elements (Eisler, 2009). Therefore, they are potentially non-toxic for these organisms.

On the other hand, the second identified group comprises the elements Cd, Hg, Se and Zn. This group comprises two essential metals (Zn, Se) and two non-essential metals (Cd, Hg) that have been recognised as two of the most dangerous heavy metals for the marine ecosystem (Marković et al., 2012; Hwang et al., 2017; Cao et al., 2017). Interactions between these elements have already been studied in the scientific literature given that Se and Zn are known as protectors against the metal-induced toxicity of Hg and Cd (Hemelraad et al., 1987; Ibrahim et al., 2019; Rahman et al., 2019). Thus, this group could be considered the by-product of the response of these organisms to potentially toxic elements. Note in these interactions the Se-Hg pair, which has been widely studied in marine organisms (Tran et al., 2007; Bjerregaard et al., 2018; Gajdosechova et al., 2018; Martínez-López et al., 2019). It has been proposed that Se moderates the bioaccumulation and toxicity of inorganic and organic mercury (Hg) in marine organisms and in a wide variety of animal species (Yang et al., 2008; Ralston, 2008; Peterson et al., 2009; Khadra et al., 2019; Melgar et al., 2019). The protective effect of Se can be estimated using the molar ratio Se/Hg when a more detailed Se and Hg speciation analyses is unavailable (Ralston, 2008). In this case, this ratio exceeded a value of 1 in all the samples (Table 5), which is indicative of the adaptation of this species to the levels of Hg in the marine environment (Cuvin-Aralar and Furness, 1991).

4.3. Cluster analysis

A cluster analysis was performed to identify associations between samples. The best results for cluster analysis were found by employing autoscaled data, the Euclidean distance and Ward's grouping method. The results of this analysis are shown in Fig. 3.

Two main groups of samples can be visualised (Fig. 3). Group 1 corresponds to the sampling sites whose concentrations were related to anthropic sources, whereas Group 2 links samples whose concentration were attributed to natural sources. Group 1 showed the highest concentrations for all the heavy metals analysed, except for the As concentrations. Samples form Group 1 correspond to the Avilés and Llanes sites, which are highly anthropised areas, so it appears that their metal concentrations in mussels may be caused by human activities. Note the marked difference in the Cd, Hg, Fe, Ni, Pb and Zn concentrations of Group 1 and Group 2, since all these metals are strongly linked to some of the industrial activities which take place on Avilés, such as steel, iron and zinc production. On the other hand, two subgroups can be observed in Group 2 (Fig. 3): G2.1 containing samples from the west and east of the region while G2.2 is made up of samples from the central area of the region. Comparing the mean concentration of both subgroups (Table 6), samples from G2.1 showed higher values than G2.2 for almost all metal (oid)s, especially for As, Hg and Zn concentrations, while only Fe values in G2.2 samples surpassed Fe amounts in G2.1. Note that G2.2 also showed the lowest values for all the assessed metal(oid)s.

Group 2 discrimination fits perfectly with the geological domains of the region, as shown in Fig. 4. Moreover, Sanz-Prada et al., (2020) also observed similar geological grouping in Asturian beach samples. Sediments are a common source of metal(oid)s in mussels, as has been widely reported in the scientific literature (Eisler, 2009 and references therein). In uncontaminated sites, metal(oid) concentrations in sediments come from geological materials and local geochemical anomalies can be distinguished in G2.1 areas which have been previously mentioned in the "4.1 General results". In the case of Subgroup 2.2, the geology of the area is a mix of detritic and carbonated materials characterised by notable iron deposits exploited since the Roman period (Peraza and Suárez, 2006; IGME, 2012). As the geology of this area is comprised of similar materials to those of Group 2.1, the discrimination of this group is a result of the higher concentration of Fe found in the samples. Even though heavy industry in the region is located in this area and Fe is a basic element used in industrial processes, its dispersion concentration in the samples did not fit with the general sea currents from east to west (Lavín et al., 2004). Thus, the most likely sources of this element are geological in nature. As a consequence, the geology inherent to this area is the most plausible source that governs the metal (oid) concentrations in mussels in the absence of obvious anthropic

Table 4
Correlation matrix between analysed metal(oids). Values with (*) are statistically significant $p < 0.01$.

	Cd	Hg	Pb	Cr	Fe	Ni	Zn	As
Hg	0,219							
Pb	0,463	0,051						
Cr	−0,170	−0,104	−0,126					
Fe	−0,190	0,056	−0,069	0,519*				
Ni	−0,299	0,180	−0,271	0,865*	0,580*			
Zn	0,643*	0,127	0,452	−0,129	−0,366	−0,180		
As	−0,277	0,256	−0,377	0,153	−0,158	0,329	0,329	
Se	0,706*	0,554*	0,391	−0,217	−0,228	−0,230	0,491*	−0,058

Table 5
Ratio Se/Hg calculated for each sample.

Sample point	*Peñarronda*	*Porcia*	*Isla*	*San Agustín*	*Luarca*	*Cueva*	*Cudillero*	*El Aguilar*	*Garrincha*	*Bayas*
Ratio Se/Hg	65.86	45.47	60.81	59.20	55.04	48.04	26.09	38.76	42.43	40.72
Sample point	*Sta Maria Mar*	*Aviles A*	*Aviles B*	*Aviles C*	*Xago*	*Verdicio*	*Xivares*	*Aboño*	*El Puntal*	*Lastres A*
Ratio Se/Hg	16.91	28.02	16.17	6.59	43.80	35.88	27.91	34.92	36.38	20.30
Sample point	*Lastres B*	*La Griega*	*La Isla*	*Moris*	*Vega*	*Covanchera*	*Borines*	*Borizo*	*Poo*	*Llanes*
Ratio Se/Hg	23.66	30.19	11.83	3.39	3.73	4.79	5.39	10.94	9.58	8.54

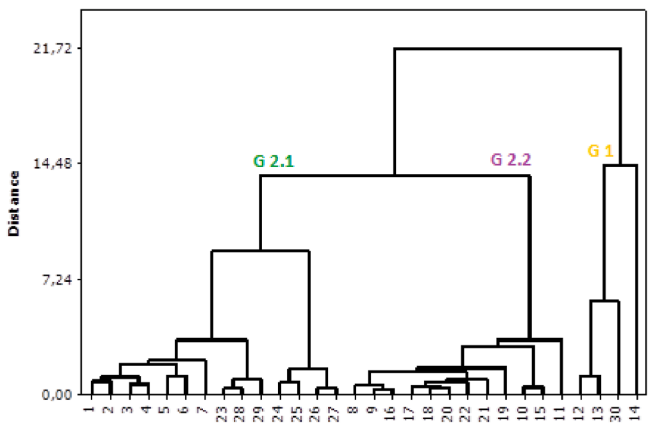

Fig. 3. Dendrogram obtained using autoscaled data, the squared Euclidean distance and the Ward clustering method.

sources.

4.4. Comparison with international quality criteria

OSPAR Commission Background Assessment Concentrations (BACs) for OSPAR maritime areas (OSPAR Commission, 2013) and the Norwegian Pollution Control Authority environmental classification system of contaminants in blue mussels (Molvær et al., 1997; Green et al., 2008) were used to assess the environmental quality of the Asturian coastline. Both criteria only take into consideration the concentration of 3 (Cd, Hg, Pb) of the 9 analysed elements as these three are the most harmful heavy metals to the marine ecosystem (Türkmen et al., 2009; Micheline et al., 2019). The rest of the elements are either considered not to be dangerous or there is not enough information regarding their toxicity to the marine environment.

Table 7 shows the levels established by those environmental organisations. Twelve of thirty sample sites (Table 8) were found to have Cd concentrations higher than the Cd OSPAR BAC (Fig. 2). These samples are located in five different sites: the area between Luarca to Cudillero, the area from Moris to Borizo, and three villages Avilés, Lastres, and Llanes. According to the Norwegian Environmental Classification, in the previous samples only Avilés and Llanes presented degrees of pollution from II to III, (4.79 μg g-1 Avilés Des., 5.76 μg g-1 Avilés Zel., 6.05 μg g-1 Avilés Macua, and 3.59 μg g-1 Llanes). Both sites were included in Group 1 and were attributed to anthropic pollution as a result of the cluster analysis. Thus, considering both criteria the potential risk of Cd to the marine environment is low and only limited to heavily anthropised areas.

Table 7
Environmental levels established for Cd, Hg and Pb concentrations in mussels by OSPAR and Norwegian Environmental Classification Pollution (values in μg g^{-1} d.w).

		Cd	Hg	Pb
OSPAR	BAC	0,96	0.09	1.3
Norwegian Environmental Classification	Degree of pollution	Cd	Hg	Pb
	I (Slight)	2	0.2	3
	II (Moderate)	5	0.5	15
	III (Market)	20	1.5	40
	IV (Severe)	40	4	100
	V (Extreme)	>40	>4	>100

Table 6
Mean element concentrations of the different groups determined via cluster analysis. Data in μg g^{-1} d.w.

	Cd	Hg	Pb	Cr	Fe	Ni	Zn	As	Se
G1	5.05	1.32	55.01	24.03	1773.78	10.46	599.17	13.71	5.54
G2	0.90	0.59	2.64	3.71	715.20	2.15	243.61	18.81	3.08
G2.1	1.04	0.88	2.82	3.74	503.12	2.34	295.16	22.42	3.29
G2.2	0.75	0.24	2.43	3.69	962.62	1.93	183.48	14.61	2.84

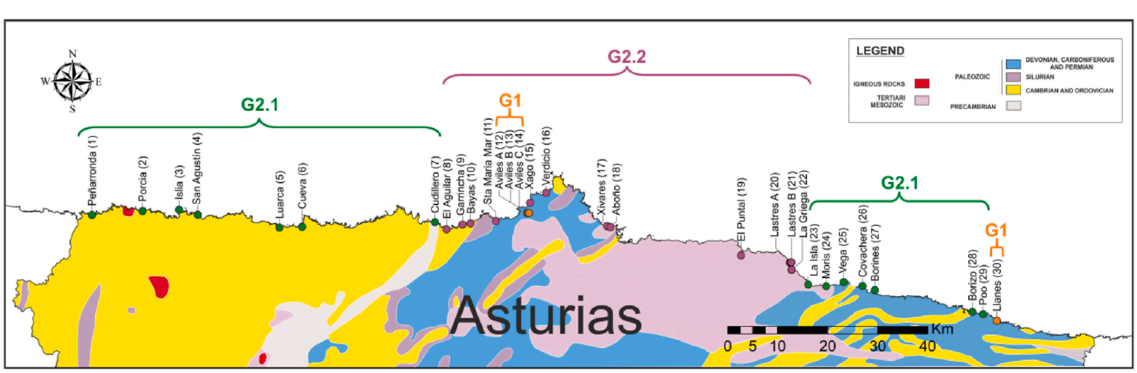

Fig. 4. Relationship of the groups of samples identified by cluster analysis with geological regions of Asturias.

Table 8
Number of samples which surpass the Environmental levels established by OSPAR and Norwegian Environmental Classification Pollution.

		Cd	Hg	Pb
OSPAR	BAC	12	30	23
Norwegian Environmental Classification	Degree of pollution	Cd	Hg	Pb
	I (Slight)	26	11	19
	II (Moderate)	2	9	8
	III (Market)	2	4	3
	IV (Severe)	40	6	100
	V (Extreme)	>40	>4	>100

Regarding Hg, all the sites showed concentration values higher than the Hg OSPAR BAC. Thus, the use of this quality criterion is not appropriate, as it is surpassed by the regional background Hg level. Compared to the Norwegian criteria, nineteen samples showed degrees of pollution from II to IV. However, Hg median concentration was 0.3 μg g^{-1} which exceeds level I of this criterion and as a consequence, the established levels should be modified. As the Hg background concentrations surpass the Hg OSPAR BAC and the median Hg concentration (0.3 μg g^{-1}) exceeds level I of the Norwegian criteria, it is possible that a modification of this criterion could be made. Specifically, we propose that level II as set out by the Norwegian criteria, which is above the median Hg sample value, be considered level I here, thus only ten samples showed significant degrees of pollution. This group of samples was located in two different areas. On one hand, samples from Avilés whose concentrations are attributed to anthropic sources; and on the other hand, the samples between la Isla and Llanes whose concentrations may be attributed to both natural and anthropic sources. In the case of Llanes, the Hg levels were attributed to an anthropic source, while the Hg origin of the rest of the samples was considered natural. Given that, the majority of the Hg in the samples can be considered natural, excluding samples from ports known to be polluted (Aviles and Llanes), and the Se-Hg ratio suggested protection mechanisms for Hg concentrations, so the potential risk of Hg to the marine environment can be considered low despite the concentrations detected.

About 77% of the sampling sites showed Pb concentrations higher than the OSPAR BAC and eleven samples presented significant degrees of pollution (higher than level II). However, the regional Pb background level may be considered below the BAC as some samples were found to be lower in concentration. Thus, other Pb sources may be the cause of the concentrations detected in the marine environment. The dispersion of the samples considered polluted does not show a clear relationship with a single source, so the most plausible causes may be multiple sources such as urban wastewaters, industrial wastewaters, or fishing activities. According to the dispersion of samples, their connections, and not being able to identify a specific source of Pb, the potential environmental risk of Pb can be considered moderate.

5. Conclusions

Metal(oid) concentrations registered in mussel tissues along the Asturias coastline are derived from both anthropic and natural sources. A deeper assessment of those sources has demonstrated the strong link between the Asturias geological dominants and the metal(oid) loads of mussels. Thus, mussels settled in areas without industrial inputs can be clearly grouped thanks to the vast influence of the lithology on their concentrations. These geological anomalies have resulted in mussel concentrations having surpassed recognised environmental quality levels, such as OSPAR BAC and the Norwegian criterion. Consequently, these environmental criteria do not deliver realistic results for the Asturias coastline due to the geological conditions which characterise this region, emphasising the need to revise environmental levels in order to adjust them to the regional features of the studied areas. Cd, Hg and Pb have surpassed the OSPAR and Norwegian levels on some sample points, however, the risk to regional biota is low due to the protection mechanisms that mussels can develop. Regarding Hg, which showed a notable natural anomaly in Asturias, its potential risk is considered low due to the protective effect of Se concentrations accumulated in the mussels. The amounts of this essential metal have increased the Se-Hg ratio reaching values higher than 1, which indicates the adaptation of these organisms to the Hg loads found in the Asturian marine environment.

CRediT authorship contribution statement

Lorena Sanz-Prada: Writing – original draft, Investigation, Formal analysis, Resources, Visualization, Writing – review & editing. **Efrén Garcia-Ordiales:** Writing – original draft, Formal analysis, Resources, Visualization, Conceptualization, Investigation. **Nieves Roqueñí:** Resources, Project administration, Writing – review & editing, Supervision, Conceptualization, Investigation. **Jose Manuel Rico:** Resources, Writing – review & editing, Investigation. **Jorge Loredo:** Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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