

A proposed methodology for the definition of background and reference values for trace elements in fluvial sediments

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ARTICLE INFO

Edited by Dr Fernando Barbosa

Keywords:

Bootstrap
Background
Sediment
Water Framework Directive
Threshold

ABSTRACT

The Water Framework Directive (WFD, 2000/60/EC) mandates member states to consider trace element background values when establishing environmental quality standards (EQS) for sediments. This study proposes defining the “background” value as the trace element concentration that is consistently present in the unaltered natural environment, and the “reference” value as an upper limit of variation of naturally occurring concentrations, suggestive of anthropogenic enrichment if exceeded. We argue that background and reference values can be computed as the upper limits of the one-sided 95 % confidence interval for the median and for the 90th percentile, respectively. This proposition has been tested in two European river basins with different historical anthropogenic impacts: the Nalón (impacted by mining activities) and the Esva (mostly unpolluted) basins. For 110 bottom sediment samples collected from both pristine (background) and potentially impacted (non-background) locations, 19 elements were analyzed by ICP-MS/ICP-AES. The proposed background and reference values, calculated using the Bootstrap method, demonstrated consistency despite geological differences between the basins. The methodology proved particularly effective in datasets with a limited sample size and highly skewed data distributions. In the Nalón basin, with higher anthropogenic activity, the percentage of samples exceeding reference values was higher than in the Esva basin (e.g., 29 % vs 7 % for As and 11 % vs 0 % for Pb), suggesting the utility of these values in discerning potential impacts of historic mining activities. In the Esva basin, background and reference values were either near or below generic thresholds for good ecological status (LEL, TEL) unlike the Nalón basin, in which reference values for all elements, except three, exceeded these thresholds.

1. Introduction

Sediments are the particulate matter that make up the beds of rivers, floodplains, lakes, estuaries, and coastal ecosystems and provide a variety of ecosystem services (e.g., habitat for riparian, benthic and fluvial species, geomorphological balance in rivers and coasts, connection between surface and groundwater, soil fertility or water purification). The

protection of benthic communities from sediment-associated pollution is of vital importance for the conservation of aquatic ecosystems and ecosystemic services. Sediments are introduced into river systems through surface erosion processes in watersheds. They present highly variable concentrations of trace elements due to their different geological origins. Anthropogenic activities, such as mining, can modify the natural trace element content of sediments through erosion and runoff

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processes that transport and deposit these elements from upstream contaminated soils, waste dumps or mine tailings and ponds (SedNet, 2004; Garcia-Ordiales et al., 2018, 2019, 2020; Barrio-Parra et al., 2020; EU, 2022; Lerat-Hardy et al., 2022). This historical legacy of industrial and mining activity in Europe has resulted in a persistent trace element contamination in sediments even though emissions have ceased (EEA (European Environment Agency), 2011). Trace elements present in bottom sediments can be remobilized in the water column during heavy rainfall events (Rapaglia et al., 2015), bioturbation (Bosworth and Thibodeaux, 1990), or increase their availability to organisms due to changes in water chemistry (Tang et al., 2019). These processes can result in a potentially unacceptable risk to human and ecosystem health.

The Water Framework Directive (WFD, 2000/60/EC) (EU, 2000) recognizes the role of sediments as basic components of ecosystems and indicates that their physicochemical state must be characterized and evaluated (EU, 2022). Directive 2008/105/EC as amended by Directive 2013/39/EU (EU, 2008, 2013) requires member states to take into account background values for trace elements in setting Environmental Quality Standards (EQSs). EQSs are concentrations of contaminants or groups of contaminants that should not be exceeded to avoid unacceptable risks to human and ecosystem health. Risk is assessed through the calculation of the Risk Characterization Ratio (RCR) defined as the ratio of the measured concentration to the Threshold Effect Concentration (TEC) or Probable Effect Concentration (PEC) (examples of TECs and PECs for trace elements in river sediments can be found in the studies of MacDonald et al. 2000 and de Deckere et al. 2011). Background concentrations affect the response of natural biological communities to an increase in trace element concentrations due to anthropogenic emissions, and, therefore, the characterization of the natural background variability should play a key role in the establishment of sediment EQSs by member states. It is especially relevant when applying the Added Risk Approach (ARA). The ARA assumes that species are fully adapted to the natural background concentrations and that only the anthropogenic added fraction of the metal contributes to the risk (EU, 2019). According to the Scientific Committee on Health, Environmental and Emerging Risks of the European Commission (Scheer, 2017), background level estimations and the methods used to derive them can still be significantly improved. These background values are needed also to assess sediment contamination through different normalization approaches such as the enrichment factor (EF), the contamination factor (CF), pollution load index (PLI) or the geo-accumulation index (I_{geo}) (Reimann et al., 2008; Hu et al., 2013; Chen et al., 2016; Hanif et al., 2016; Jamshidi and Bastami, 2016; Schintu et al., 2016; Xu et al., 2017a, 2017b).

As stated before, the concentration of trace elements in bottom sediments is highly variable, complicating the task of differentiating natural background concentrations from enrichments produced by anthropogenic activity. To establish natural background values, as well as criteria for differentiating anthropogenic trace element enrichments in sediments, it is necessary to characterize the geogenic variability through an appropriate sampling design and statistical analysis of the data (Dulio et al., 2010). Until now, few studies have focused on the characterization of natural background levels of trace elements in continental sediments. A majority of these have targeted selected elements of particular interest (e.g., As or Hg), most often in lakes (Fang et al., 2019; Algül and Beyhan, 2020; Lintern et al., 2020) or reservoirs (Mwanamoki et al., 2015; Palma et al., 2015; Garcia-Ordiales et al., 2016; Zhao et al., 2017; Sojka et al., 2018) and less frequently in rivers (Garcia-Ordiales et al., 2017).

The objective of this study is to formulate a statistical criterion for defining (a) the geochemical background of trace elements in fluvial sediments, and (b) the reference values to discern between natural geological variability and enrichment resulting from historical mining activities. The applicability of the proposed method is assessed by comparing the results obtained in two neighbouring catchments with different degrees of anthropogenic activity.

2. Materials and methods

2.1. Study area

The study area comprises the basins of the Nalón and Esva rivers in the region of Asturias, NW Spain (Fig. 1). Because of their significant differences, a brief synthetic description of each one is provided below:

2.1.1. Nalón basin

The Nalón is the most important river in Asturias (NW Spain), with a catchment area of 3692 km², an average flow at the mouth of the river of 55 m s⁻¹ (maximum of 1250 m s⁻¹) and a length of 153 km (CHC, 2023). Its main tributaries from the left bank (Narcea and Caudal Rivers) originate in high areas of the Cantabrian mountain range. Given the extent of this basin, its geological variety is also wide: from East to West, this basin intercepts i) a large part of the Cantabrian Zone, ii) almost all of the Narcea Antiform and iii) the eastern edge of the West Asturian-Leonese Zone, following Lotze's (1945) division of the Iberian Massif (Fig. 1).

Regarding the Cantabrian Zone, the upper course of the Nalón River runs from its source at 1443 m.a.s.l. through the Ponga Unit, composed by about 1000 m of Cambrian-Ordovician sediments, among which quartzites predominate, overlaid with 3500 m of Carboniferous calcareous and detrital series (sandstones and limestones) (Bahamonde and Colmenero, 1993). The middle course of the Nalón River runs between the Central Coal Basin (CCB) and the Thrusts and Folds Unit. The CCB is the largest Carboniferous basin in Spain, formed by more than 4000 m of sandstones, siltstones, shales and coal beds, with scarce levels of limestones and some conglomerates (Aller and Gallastegui, 1995). The Thrusts and Folds Unit consists of a combination of detrital and carbonate rocks (sandstones, marls and limestones) ranging from Cambrian to Lower Carboniferous age. The north-eastern edge of the Nalón basin is covered by a strip of Cretaceous and Tertiary rocks (limestones, marls, sandstones and siltstones) several hundred meters thick. The Narcea Antiform extends over most of the sub-basin of the Narcea River. It is a pelitic-sandy succession of Precambrian age (meta-sandstones) and contains some levels of interstratified volcanoclastic rocks. The lower Palaeozoic series of the West Asturian-Leonese Zone, made up of thick units of sandstones, slates and quartzites with a thin level of limestones, can be found at the western limit of the Nalón basin. Igneous rocks, eminently granitic, cover small outcrop areas (Corretgé et al., 1990).

Mining activity in the Nalón basin has been intense from the end of the 18th century until the beginning of the 21st century, especially in the CCB, with more than a hundred coal mines, of which only one is currently active. Metal mining, although not as important from an economic point of view, has been relevant from an environmental perspective. In the districts of Mieres and Pola de Lena there was significant mining and metallurgical activity for Hg between 1960 and 1973. There has also been intermittent mining of Fe, Cu and, to a lesser extent, Mn, Sb or Zn. At present, there are active fluor spar mines in the upper Nora River basin and Au mines in the Narcea River basin. Due to the abundance of Fe and coal resources, there are also metal processing industries in the Nalón basin, near the towns of Mieres, La Felguera and Oviedo (Fig. 1).

There is some recent work on the impact of mining and industry on the sediments and waters of the Nalón estuary (Garcia-Ordiales et al., 2020; Mangas-Suarez et al., 2022; Sanz-Prada et al., 2022), but there are no specific studies on fluvial sediments.

2.1.2. Esva basin

The Esva River basin is adjacent to that of the Nalón River on its NW side, but its surface area is much smaller (461 km²). The average flow of the Esva River at its mouth is 10 m s⁻¹ (maximum 15 m s⁻¹) and its length is 41 km (CHC, 2023). Its contrast with the Nalón basin in terms of anthropic impact is one of the reasons for its selection as study area, since it is a sparsely populated region, with hardly any industrial or

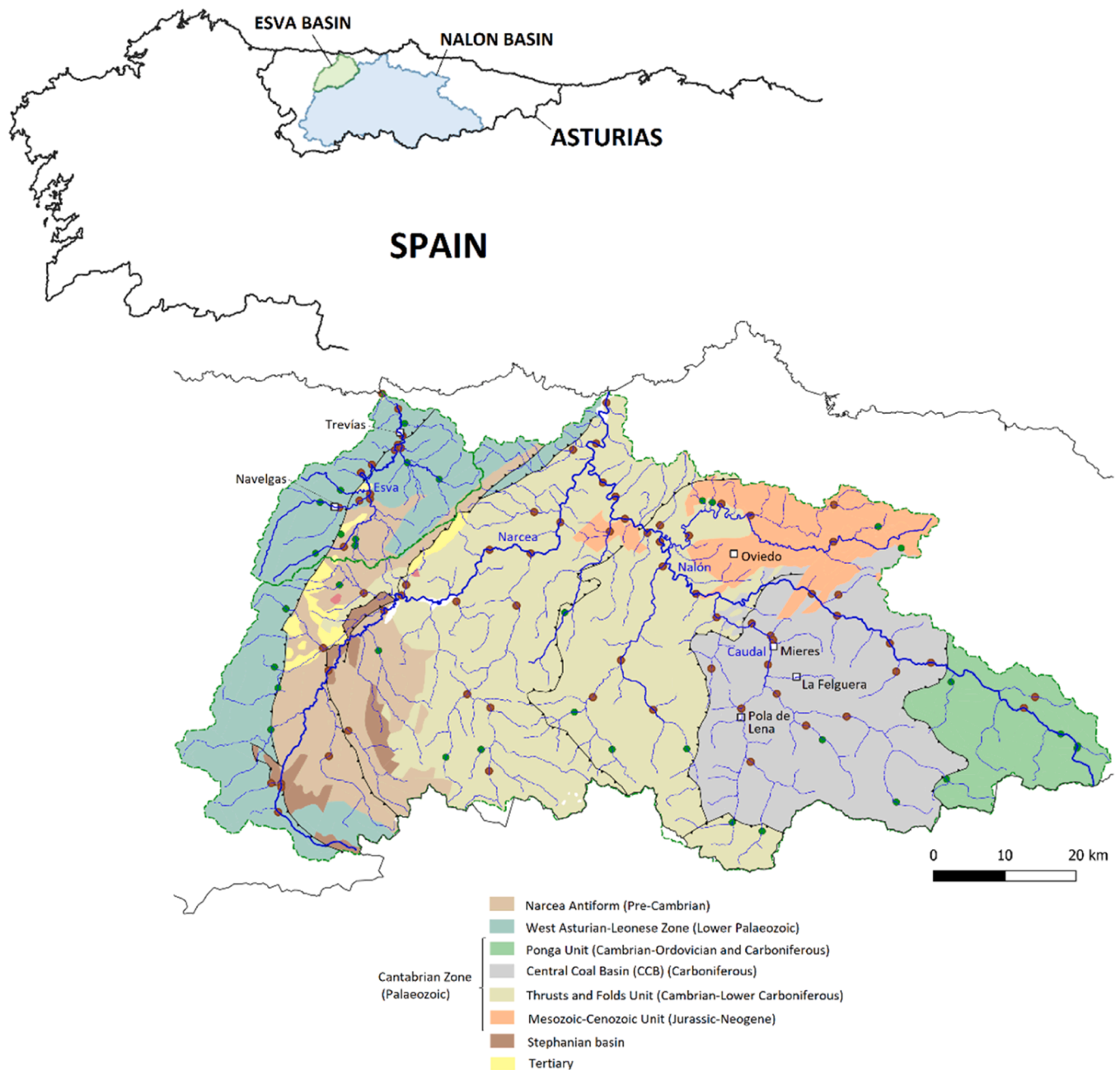


Fig. 1. Geological map of the basins of the Nalón and Esva rivers. Dots indicate the location of the sampling points; in green those selected to define the background values.

mining activity of importance. Geologically, it includes the northeastern sector of the West Asturian-Leonese Zone and a small part of the Narcea Antiform previously described. There are no significant outcrops of igneous rocks in this basin.

Although there is considerable evidence of Roman mining activity for the recovery of alluvial gold (González-Nistal et al., 2023), there was only a small gold mine at Navelgas for a few years in the mid-20th century. Other mining evidences of very limited importance are the Mn mines around Trevías and other barite and Hg mines. There are no published works dealing with the environmental state of the sediments of this river.

2.2. Sampling and analysis

In order to establish the background and reference concentrations and

assess the historical enrichment produced by anthropic activities, two sets of samples were taken at both Esva and Nalón basins. A total of 87 bottom sediment samples were collected in the Nalón basin between February and June 2022. Of these, 25 were taken at sampling points located in pristine areas, upstream of the first known industrial, mining and agricultural operations, to define background values. In the Esva basin a total of 23 samples were collected between February and May 2022, 9 of them in areas unaffected by anthropogenic activities. The sampling positions are shown in Fig. 1.

Composite samples of bottom sediment, weighing approximately 1 kg each, were collected using plastic tools near the rivers' banks. These samples, composed of four closely located sampling increments, were retrieved from the uppermost 10 cm of the sediment column. This specific depth was chosen due to its significance as the zone with the highest biological activity. Determining contaminant concentrations at this level

should yield comprehensive insights into major contaminant exposure pathways for a wide range of organisms (Simpson and Batley, 2016). Samples were transported in labelled plastic bags to the laboratory, air-dried to constant weight and sieved, and the fraction below 125 μm was sent to the ALS Global laboratory (Geochemical Division) for analysis with the Lowest Detection Limit Super Trace Analysis for Sediments, using a combination of ICP-AES and ICP-MS determinations on the same sample. The two sets of analytical data are combined to provide optimal detection and ranges for more than 50 elements, after applying the ME-MS41L™ internal method, which involves a low-temperature extraction (to preserve volatiles, such as Hg) with aqua regia (1:3 ratio HNO₃:HCl). For this study, metals historically associated with anthropogenic impacts in the region, mainly due to mining, especially Hg and Cu (Álvarez et al., 2018; Ordóñez et al., 2013), and major elements, such as Al, Ca, K or Ti, were selected, based on the knowledge of the geochemistry of the rocks that constitute the subsoil of the studied basins. QC/QA included the analysis of sample duplicates (6 % of the total number of samples), 14 method blanks, and 18 analysis of certified reference materials (OREAS 45 f, OREAS 46, OREAS 905, GBM908–10 and MRGeo08). Coefficients of variation (CV) of duplicates were less than 10 % for 87 % of the sediment samples (highlighting Ag, Hg and Se which exceeded a CV of 10 % in three samples each). The results of the analysis of laboratory blanks were always below the limits of reporting. Recovery factors relative to the reference materials were all in the range of 87–112 %, excepting S in two samples and Hg, Sb and Se in one sample.

2.3. Statistical definition of background and reference values

There is no single common definition of natural background values (Reimann and Garrett, 2005; Reimann and de Caritat, 2017). In this work, the term “background value” designates the trace element concentration that is consistently present in the natural environment and has not been influenced by localized human activities (De Miguel et al., 2002). “Reference values” are defined as threshold values that are unlikely to be exceeded within a naturally occurring population. Reference values are estimated from the upper limits of variation of naturally occurring concentrations with the assumption that if exceeded they are indicative of an anthropogenic enrichment (Tack et al., 1997, 2005; van der Gaast et al., 1998; De Miguel et al., 2002; Reimann and Garrett, 2005; Reimann et al., 2005; Sierra et al., 2007; Burgos et al., 2008; Galán et al., 2008; Pérez-Sirvent et al., 2009). As with the lack of a common definition, there is no universally agreed methodology for establishing background and reference values in sediments (Horckmans et al., 2005; Reimann et al., 2005; Zhao et al., 2007; Galán et al., 2008). Background values are commonly derived from estimates of the sample central tendency (mean, median) and some measure of dispersion (variance, minimum, maximum, interquartile range) (Tack et al., 1997; Tobías et al., 1997; Zhang et al., 2002; Horckmans et al., 2005; Reimann et al., 2005; Sterckeman et al., 2006; Tume et al., 2006; Sierra et al., 2007; Galán et al., 2008; Díez et al., 2009). Typically, reference values are defined as the 90th, 95th, or 99th percentiles of a representative sample of the natural background (van der Gaast et al., 1998; Galán et al., 2008) or as the sample mean + 2 standard deviation (Tobías et al., 1997; Tume et al., 2006). Reimann et al. (2005) rebutted this method because it is applicable only to normal (or at least symmetrical) distributions, which geochemical data rarely follow. They proposed instead calculating the reference value as median + 2 median absolute deviation. This last approach tries to avoid the influence of outliers. The decision on whether high-end values in the sample are designated as outliers and discarded or not should not be based solely on their separation from the third quartile of the sample (as indicated, for example, in ISO (2018), which establishes as a criterion the exceedance of the third quartile by 1.5 times the interquartile range). The decision needs to be supported by a geochemical study to justify that the high-end data do not belong to a natural population and are therefore invalid to characterize the

geochemical background. If anthropogenic enrichment cannot be proven, the extremes of the distribution should be included to establish the upper limits of natural variation of trace element concentrations and thus determine a reference value.

As it has been discussed, sample statistics are commonly used to obtain background and reference values (Reimann et al., 2008; Reimann and de Caritat, 2017). When the sample is of limited size, however, the statistics of a single sample may not accurately estimate the true values of the parameters of the original population. To account for the uncertainty arising from the intrinsic heterogeneity of the original population and the limited sample size, in this work background and reference values are defined as the upper limit of predefined confidence intervals for the population parameters. Specifically, background and the reference values are defined as the upper limit of the one-sided 95 % confidence interval for the median and for the 90th percentile, respectively. In this study, these confidence intervals have been estimated non-parametrically with the Bootstrap method (Davison and Hinkley, 1997; Brodin, 2006; Ander et al., 2013; Millard, 2013). For each of the 10,000 datasets generated by iteratively sampling with replacement the original sample, the median and 90th percentile are obtained, and these 10,000 values are used to generate a median and a 90th percentile vector, respectively. The 95th percentile in each of these vectors constitutes the respective upper limits of the one-sided 95 % confidence interval and will be used as background and reference values respectively in this work. The computational routines were programmed in R Studio (R Core Team, 2022). With this approach, the upper limits of the confidence intervals cannot exceed the maximum value obtained in the sample, which may result in the defined reference values corresponding to an actual confidence level lower than the design confidence level (i.e., 95 % in this work).

3. Results and discussion

A statistical summary of the analytical results obtained for both basins, and for the “background” and “non-background” subsets, is presented in Table 1 (Nalón basin) and Table 2 (Esva basin). Both “background” data subsets were investigated to identify potential anomalies, i.e., data misclassified as belonging to the background population that could actually be impacted by anthropogenic activity. To this end, the concentration values for each element were ordered from lowest to highest and those values above significant interruptions (i.e., those for which the difference between the two values defining the interruption was higher than 25 % of the value of the higher one) in the higher end of the series (above the 90th percentile) were classified as potential anomalies and were further investigated (De Miguel et al., 2002; Chacón et al., 2020). Of the 25 field samples initially selected for the characterization of the geochemical background in the Nalón basin, 10 had at least one anomalous concentration value according to this criterion. In the Esva basin, 5 out of the 9 background samples presented anomalies. The possibility of human influence on these samples was investigated and in most cases was ruled out due to the absence of urban or industrial centers, agricultural lands, recreational areas, or mining activities in the area. Only one sediment sample in the Nalón basin with a mercury concentration of 6.52 mg·kg⁻¹ had to be reclassified. An investigation into the proximity of historical mercury extraction operations in the area revealed that there was a small mercury mine located 5 km upstream from the sampling point. This specific field sample was therefore reclassified as “not background”, leaving 24 values to characterize the natural geochemical background in the Nalón basin and 63 values to describe the trace element composition of the entire basin.

Tables 1 and 2 also include the background and reference concentration values obtained following the methodology described in Section 2.3. The skewness and kurtosis of the data were calculated using the EnvStats library (Millard, 2016). Most of the datasets exhibited positive skewness, indicative of a tail of high values in their distributions, and positive kurtosis, suggesting a peak of data around the mean that

Table 1
Descriptive statistics of the trace element concentrations obtained for the subsets of background and non-background samples in the Nalón basin, Background and Reference Values (in bold) calculated from the subset of background samples, and values of skewness and kurtosis. Min: Minimum; Max: Maximum; 1st Qu and 3rd Qu: First and third Quartile, respectively. The value of Mean + 2 Standard Deviation (s) is included for comparison purposes. Number of background samples: 24. Number of non-background samples: 63.

Samples	Trace element	Ag	Al	As	Ba	Ca	Cd	Co	Cu	Fe	Hg	K	Mn	Ni	Pb	S	Sb	Se	Ti	Zn	
	Units	mg·kg ⁻¹	%	mg·kg ⁻¹	mg·kg ⁻¹	%	mg·kg ⁻¹	mg·kg ⁻¹	mg·kg ⁻¹	%	mg·kg ⁻¹	%	mg·kg ⁻¹	mg·kg ⁻¹	mg·kg ⁻¹	%	mg·kg ⁻¹	mg·kg ⁻¹	%	mg·kg ⁻¹	
Nalón Basin	Min.	0.008	0.29	6.5	19.40	0.11	0.039	2.32	2.83	0.80	0.013	0.03	80.0	3.88	6.67	0.01	0.152	0.066	0.001	24.60	
	1st Qu.	0.023	0.53	10.0	37.67	0.26	0.097	7.34	9.23	1.73	0.041	0.06	326.8	15.40	10.53	0.03	0.398	0.174	0.003	42.95	
	Median	0.029	0.70	12.0	55.80	0.86	0.142	10.50	14.32	2.44	0.057	0.07	483.0	21.60	13.38	0.04	0.491	0.269	0.004	53.75	
	Mean	0.034	0.74	13.1	68.67	0.94	0.141	10.09	14.41	2.56	0.129	0.07	473.9	22.19	13.84	0.05	0.630	0.315	0.008	55.14	
	3rd Qu.	0.035	0.90	14.4	76.45	1.22	0.170	11.95	17.06	3.23	0.093	0.08	592.0	26.30	16.14	0.05	0.769	0.381	0.010	67.30	
	Max.	0.113	1.39	25.5	212.00	3.38	0.297	17.80	29.30	5.32	1.305	0.11	853.0	47.40	32.80	0.11	1.985	0.865	0.034	95.10	
	Skewness (-)	2.1	0.6	1.1	1.8	1.3	0.5	0.0	0.5	0.5	0.6	4.4	0.1	0.0	0.4	1.7	1.1	1.8	1.4	1.9	0.3
	Kurtosis (-)	5.3	-0.3	0.8	3.1	2.1	0.4	-0.3	0.0	0.0	0.3	20.7	0.0	0.0	-0.3	4.6	1.9	3.3	2.5	3.2	-0.4
	Mean+2*s	0.081	1.33	22.6	165.68	2.58	0.260	17.72	27.66	4.85	0.650	0.11	829.8	45.24	25.10	0.09	1.51	0.680	0.030	92.17	
	Background Reference	0.043	0.84	14.7	85.64	1.22	0.162	11.35	16.65	2.95	0.230	0.11	825.4	26.05	15.76	0.05	0.786	0.378	0.011	61.28	
Min.	0.012	0.16	5.8	20.30	0.08	0.042	2.48	3.94	0.67	0.019	0.03	104.5	5.48	6.13	0.01	0.255	0.062	0.001	27.20		
1st Qu.	0.025	0.51	11.8	41.65	0.48	0.094	7.75	13.30	2.14	0.054	0.05	350.0	16.00	14.00	0.04	0.583	0.177	0.003	55.10		
Median	0.035	0.60	17.4	59.90	1.09	0.119	9.92	16.20	2.55	0.107	0.05	405.0	20.30	17.80	0.06	0.721	0.233	0.004	65.60		
Mean	0.064	0.69	50.3	79.04	1.60	0.147	9.68	22.54	2.58	5.908	0.07	428.5	20.63	20.39	0.09	1.331	0.300	0.007	69.09		
3rd Qu.	0.052	0.84	25.9	79.70	2.07	0.172	10.88	21.20	2.92	0.595	0.07	480.0	24.15	21.80	0.11	1.133	0.369	0.007	71.85		
Max.	0.520	2.27	1045.0	756.00	6.77	0.474	34.50	208.00	6.11	194.500	0.70	1460.0	61.40	84.10	0.44	20.600	1.075	0.087	332.00		
Skewness (-)	3.5	2.2	5.9	5.8	1.7	2.9	5.2	5.2	1.3	6.4	6.5	2.7	1.7	3.1	2.6	6.6	2.0	5.6	5.3		
Kurtosis (-)	13.2	7.7	37.5	38.4	2.9	3.1	13.1	28.2	4.6	44.1	46.0	14.0	8.5	12.4	8.2	47.7	4.8	36.7	35.7		

Table 2
Descriptive statistics of the trace element concentrations obtained for the subsets of background and non-background samples in the Esva basin, Background and Reference Values (in bold) calculated from the subset of background samples, and values of skewness and kurtosis. Min: Minimum; Max: Maximum; 1st Qu and 3rd Qu: First and third Quartile, respectively. The value of Mean + 2 Standard Deviation (s) is included for comparison purposes. Number of background samples: 9. Number of non-background samples: 14.

Samples	Trace element	Ag	Al	As	Ba	Ca	Cd	Co	Cu	Fe	Hg	K	Mn	Ni	Pb	S	Sb	Se	Ti	Zn	
	Units	mg·kg ⁻¹	%	mg·kg ⁻¹	mg·kg ⁻¹	%	mg·kg ⁻¹	mg·kg ⁻¹	mg·kg ⁻¹	%	mg·kg ⁻¹	%	mg·kg ⁻¹	mg·kg ⁻¹	mg·kg ⁻¹	%	mg·kg ⁻¹	mg·kg ⁻¹	%	mg·kg ⁻¹	
Esva basin	Min.	0.010	0.37	2.88	21.4	0.05	0.066	4.38	4.77	0.76	0.030	0.03	114.5	5.97	6.95	0.01	0.168	0.140	0.005	17.9	
	1st Qu.	0.017	0.51	5.60	29.4	0.09	0.092	5.49	8.03	1.17	0.034	0.04	193.0	8.22	9.19	0.02	0.379	0.229	0.006	36.5	
	Median	0.028	0.74	5.89	30.7	0.10	0.123	7.43	8.89	1.34	0.036	0.05	243.0	13.85	13.30	0.02	0.533	0.306	0.006	43.9	
	Mean	0.028	0.76	6.35	41.1	0.10	0.168	7.01	10.40	1.44	0.046	0.05	268.9	12.36	14.10	0.02	0.771	0.335	0.009	43.6	
	3rd Qu.	0.033	1.01	7.17	42.4	0.12	0.229	7.59	10.85	1.72	0.046	0.06	320.0	14.70	14.95	0.02	0.755	0.467	0.011	56.6	
	Max.	0.052	1.17	10.25	104.5	0.14	0.395	11.15	22.90	2.31	0.093	0.11	594.0	19.50	32.30	0.03	2.80	0.492	0.025	61.5	
	Skewness (-)	0.6	0.2	0.5	2.2	-0.6	1.3	0.8	1.8	1.8	1.9	1.9	1.5	0.0	0.0	0.0	2.6	-0.1	2.3	-0.5	
	Kurtosis (-)	-0.7	-1.5	0.1	5.2	1.2	1.5	1.4	4.2	4.2	0.4	2.4	4.3	3.1	-0.7	4.7	-0.3	7.1	-1.5	5.8	-1.1
	Mean+2*s	0.059	1.34	10.88	93.0	0.15	0.380	11.04	21.01	23.6	0.090	0.10	555.3	21.01	29.27	0.03	2.35	0.590	0.020	76.0	
	Background Reference	0.033	1.01	7.17	42.4	0.12	0.229	7.59	10.85	1.72	0.046	0.11	594	19.5	32.3	0.02	0.755	0.467	0.011	56.6	
Min.	0.011	0.54	4.53	25.4	0.06	0.048	5.56	7.34	1.16	0.021	0.03	81.6	10.75	6.18	0.01	0.586	0.129	0.007	24.0		
1st Qu.	0.013	0.58	6.06	34.7	0.08	0.098	6.66	8.75	1.43	0.034	0.04	214.5	11.65	7.85	0.01	0.668	0.151	0.009	31.0		
Median	0.018	0.77	6.45	44.9	0.10	0.107	7.49	10.75	1.61	0.046	0.05	253.5	13.43	10.21	0.02	0.831	0.203	0.009	38.6		
Mean	0.022	0.74	7.29	66.8	0.11	0.122	7.54	10.65	1.68	0.052	0.05	256.2	14.14	11.24	0.02	0.830	0.245	0.010	39.1		
3rd Qu.	0.022	0.88	8.69	62.8	0.14	0.145	8.40	12.08	1.95	0.051	0.06	271.5	15.57	13.00	0.02	0.996	0.319	0.010	42.5		
Max.	0.085	1.02	13.55	185.5	0.22	0.243	9.48	14.45	2.31	0.167	0.07	495.0	19.00	23.80	0.03	1.070	0.489	0.016	66.9		
Skewness (-)	3.3	0.4	1.6	1.5	1.2	1.3	0.1	0.2	0.5	2.6	0.6	0.6	0.5	0.5	0.7	0.0	0.9	1.7	1.7		
Kurtosis (-)	11.4	-1.4	3.1	0.8	1.9	3.2	-0.9	-1.1	-0.6	8.1	-0.6	1.4	-0.9	-0.9	2.4	-0.3	-1.6	-0.1	3.4	2.7	

decreases rapidly towards a heavy tail. Both skewness and kurtosis values varied across elements and subsets of data, as do the theoretical probability distribution functions that can be fitted to those data. The process of fitting the data to a theoretical probability distribution function is affected by a high degree of subjectivity because of the limited size of the statistical samples of background populations (i.e., 24 and 9 values for the Nalón and Esva basins, respectively). To illustrate this problem, the Anderson-Darling test (Gross and Ligges, 2015) was run on the background data series of four selected elements (As, Cu, Hg and Zn) in the Nalón basin (Table 3). The results show that the distributions of Cu and Pb could be assumed to be both normal and log-normal, the distribution of As is distinctly log-normal while the distribution of Hg data would not fit either of the proposed distributions. Table 3 also shows the parametric estimates obtained with the EnvStats library (Millard, 2016, 2013) of the upper limit of the 95 % one-sided confidence intervals of the median and of the 90th percentile assuming log-normality of the data. In the selected examples, parametric and nonparametric estimates are notably similar, producing comparable results for background and reference values, in distributions that can be reliably assumed to be log-normal according to the Anderson-Darling test. However, in the case of Hg, with a distribution characterized by a more pronounced asymmetry and discontinuities in its tail, the differences between parametric and nonparametric estimates are significant (two and three times lower for the background and reference values, respectively, when assuming a log-normal distribution than with the non-parametric estimation). The Bootstrap method employed in this study allows to circumvent unreliable assumptions about the underlying statistical distribution when the sample size is small. For most trace elements, background concentrations were similar in both basins, with only slight variations within the same order of magnitude. The consistency of these results underlines the suitability of the use of the confidence interval of the median, instead of the mean, as a robust estimator of the central tendency (less affected by the presence of tails of high values). It also validates the selection of a priori pristine sampling points to characterize the variability of the natural background. As, Ba, Ca, Mn and Hg were the exceptions to this general trend, with higher background and reference concentrations in the Nalón basin than in the Esva basin. The reason for this is to be found in the geological substrate of both basins. The higher Ca content is due to the higher proportion of carbonate rocks in the Nalón basin, and it is precisely in this type of rock where hydrothermal mineralization are usually hosted. These are the most frequent mineralization in the Cantabrian Zone and some of the metal(loid)s typical of this type of mineralization are Hg, As, Mn or Ba. These elements are expected, therefore, to be enriched in the sediments of the Nalón basin regardless of the anthropic activity that has taken place there.

Reference values were similar in both basins except for Ca, Hg and S which were significantly higher in the Nalón basin. These differences could be attributed to the small sample size of the Esva basin, which may not have captured the entire natural variability of these elements. For small samples, as in this case, the Bootstrap method produces conservative estimates of reference values, in terms of risk, because they are limited to values included in the sample of background concentrations while estimations derived from fitting the data to a probability

distribution function may yield reference values exceeding the sample maximum. On the other hand, the parametric estimation of the confidence interval for the 90th percentile includes the true value of the percentile at the designated confidence level (i.e., 95 % in this study) whereas with the Bootstrap method the estimated upper limit of the confidence interval will normally correspond to confidence levels lower than the designated 95 %. If the reference values were defined as the mean plus two times the standard deviation of the data, as in most previous studies, eight of the nineteen elements (i.e., Ag, Al, As, Ca, Fe, Ni, Se, and Zn), all of them in the Esva basin, would have been assigned reference values higher than the sample maximum (Table 2).

Fig. 2 presents superimposed the frequency distributions of the log-transformed background (blue histograms) and non-background data (red histograms) for the same four trace elements (As, Cu, Hg, and Pb) selected earlier in the Nalón basin. Non-background distributions are strongly asymmetrical with heavy and discontinuous tails of elevated concentrations. Except for these tails, there is substantial overlap between the distributions of background and non-background data, and the estimated background value (blue dashed line) appears to accurately represent the central tendency of both distributions equally. There are two reasons for this apparent paradox and the challenges it presents in distinguishing between natural and impacted samples. Firstly, non-background samples correspond to sampling points that may not necessarily be contaminated but for which, due to their proximity to areas of human activity, it cannot be categorically ruled out that natural concentrations have not been modified. Secondly, different human activities contribute different suites of trace elements to sediments. A sampling point potentially impacted by a specific source of contaminants will be classified as non-background and may present enriched concentrations of the elements associated with that specific source but will exhibit “natural” (i.e. background) concentrations of the others.

The percentage of non-background samples surpassing reference values for each trace element was computed in both basins (Fig. 3). In the Nalón basin the median concentration of four elements (As, Pb, S and Zn) exceeded the respective background values, and the mean concentrations of As and Hg were two and five times higher, respectively, than their reference values. The heightened concentrations of Hg are attributed to Hg mining in the basin, which is also responsible for the significant concentrations of As, inherent in the paragenesis of these Hg deposits. Copper mining likely contributes to elevated Cu, As and Sb contents, while concentrations of Pb-Zn can be linked to a small-scale metal sulphide mining. The substantial levels of S most likely result from the beneficiation of primary sulphide mineralization (notable amounts of barite can be found in the dense fraction of the Nalón River mouth sediments). In the Esva basin, the mean concentration of As, Ba, Hg and Sb slightly exceeded their respective background values. Elevated Ba and Hg contents are associated with barite mining, and the relatively high As contents appear to be related to the presence of Au mineralization (González-Nistal et al., 2023). It is interesting to note that when approximately more than 7.5 % of the samples surpass the reference value of a given element, the impact of mining on the sediment becomes evident. In the Nalón basin, this happens for Ag, As, Cd, Cu, Hg, Pb, S, Sb, and Zn, i.e. the complete collection of the epithermal domain. In the Esva basin, it only happens for Ba, which corresponds to the sole

Table 3

Results of the Anderson-Darling test for four series of background concentrations in the Nalón basin and estimates of Background and Reference values assuming a log-normal distribution and with the Bootstrap method.

Element	Normal distribution			Log-normal distribution					Bootstrap	
	Fit to normal?	p-value	AD Statistic	Fit to log-normal?	p-value	AD Statistic	Background (mg·kg ⁻¹)	Reference (mg·kg ⁻¹)	Background (mg·kg ⁻¹)	Reference (mg·kg ⁻¹)
As	No	3.70E-02	7.79E-01	Yes	7.33E-01	2.45E-01	13.94	23.35	14.7	23.88
Cu	Yes	4.63E-01	3.42E-01	Yes	3.27E-01	4.05E-01	15.43	34.16	16.65	28.55
Hg	No	8.82E-14	5.40E+00	No	4.01E-02	7.65E-01	0.10	0.39	0.23	0.99
Pb	Yes	6.20E-02	6.91E-01	Yes	8.99E-01	1.84E-01	14.72	25.74	15.76	29.32

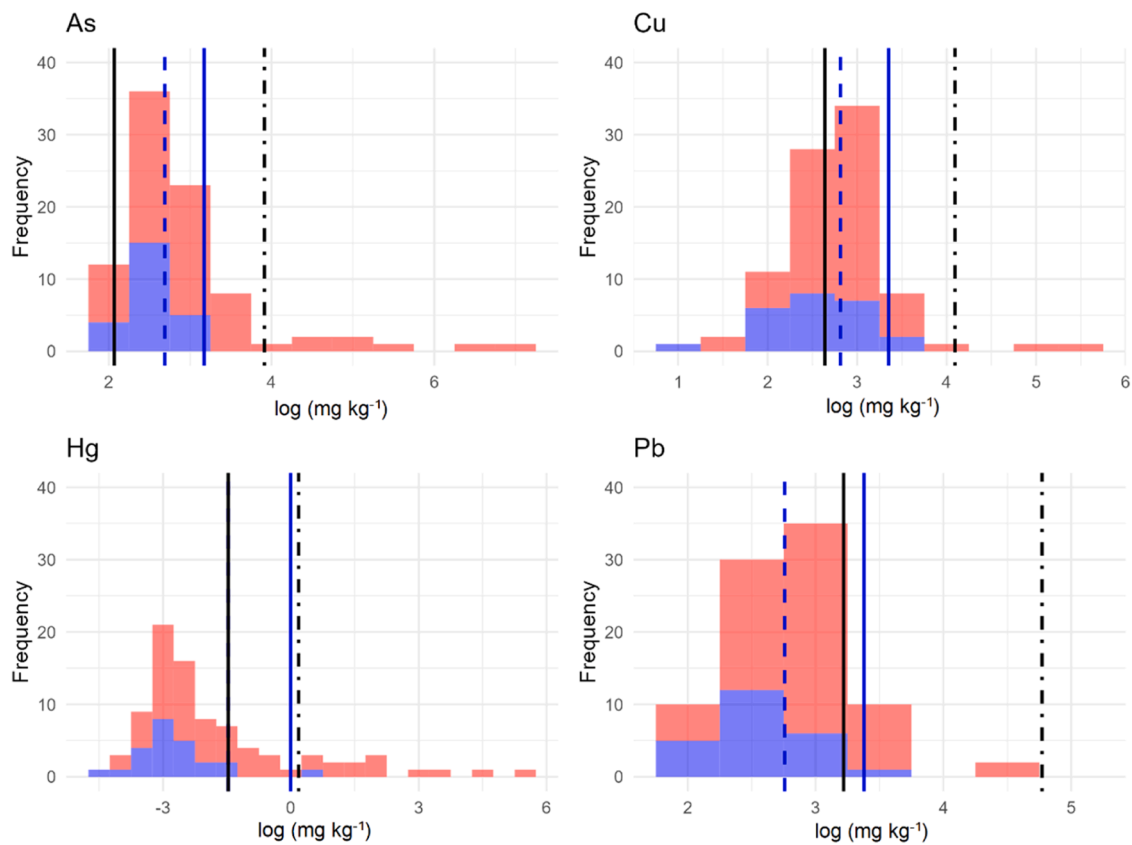


Fig. 2. Histograms of log-transformed data for the Nalón basin for As, Cu, Hg and Pb. Red areas correspond to non-background samples and blue areas to background samples. Blue vertical lines indicate the Background (dashed) and Reference (solid) values. Black vertical lines mark the Consensus values #1 (solid) and #2 (dashed) respectively. In the case of mercury, the lines for the Background value and Consensus #1 overlap.

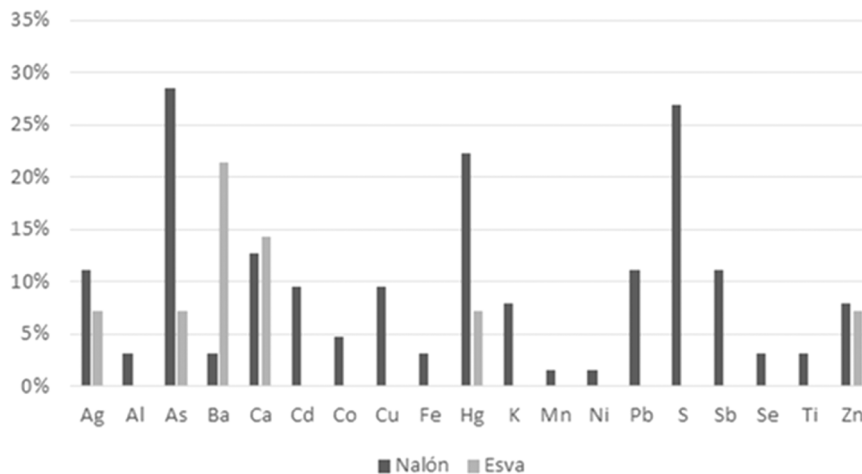


Fig. 3. Percentage of samples above the reference values in the possibly impacted areas of the Nalón and Esva basins from a total of 63 and 14 samples, respectively.

significant mine in this basin (barite).

Lastly, a comparison with Environmental Quality Standards (EQSs) was performed (Fig. 2 and Table 4) to put the results of this study into an environmental perspective. Ideally, EQSs should be derived from ecotoxicological studies (Swartz, 1999; MacDonald et al., 2000, 2003) that consider the response to an increase in trace element concentrations in the sediment of organisms already exposed to background levels in the watershed. In the absence of such data for the Nalón and Esva basins, the background and reference values obtained in this study were compared to the EQSs developed by de Deckere et al. (2011) (cited by

EU, 2022). These authors calculated two consensus EQSs. Consensus 1 is estimated from the Lowest Effect Level (LEL) and the Threshold Effect Level (TEL) values and should be considered as the target concentrations to achieve a good ecological state of the sediments. Consensus 2 SQGs are estimated from Severe Effect Level (SEL) and Probable Effect Level (PEL) values and can be regarded as values above which the probability of observing toxic effects in situ increases. In the Esva basin, both background and reference values are similar to or lower than Consensus 1 values. In the Nalón basin, background concentrations are in the range of Consensus 1 values except for As and Ni, which approximately

Table 4

Environmental Quality Standards (EQSs) calculated by de Deckere et al., (2011). Consensus 1 values are described as a long-term objective or good ecological sediment status concentrations. Consensus 2 values are those above which toxic and in situ effects are most likely to be observed. For comparison purposes, Interim Sediment Quality Guidelines (ISQGs) and probable effect levels (PELs) from the Canadian Council of Ministers of the Environment (CCME, 2002) have been included. Concentrations are expressed in $\text{mg}\cdot\text{kg}^{-1}$. NA: Not Available.

Trace Element	Consensus 1	Consensus 2	ISQGs	PEL
As	7.9	50	5.9	17.0
Cd	0.93	7.8	0.6	3.5
Cu	14	60	35.7	197
Hg	0.23	1.2	0.17	0.486
Ni	11	32	NA	NA
Pb	25	118	35.0	91.3
Se	1.5	6.4	NA	NA
Sn	1.4	12	NA	NA
Zn	146	800	123	315

duplicate their respective values. In this basin the reference values of all the elements available for comparison, except Cd, Se and Zn, exceed their Consensus 1 values, and Hg and Ni even surpass their Consensus 2 levels. As it was discussed previously, this fact reflects the abundant presence of mineralizations in the Nalón basin that results in abnormally high background values for certain elements, including Hg and Ni, which occur naturally. However, mining activity has significantly increased the concentrations of these elements, which were already naturally high. For these elements with background and reference concentrations above the generic EQS (Tier 1) in the Nalón basin, an ecotoxicological analysis should be performed to quantify the effects of exposure to sediment concentrations above the reference levels, to study their bioavailability, and to carry out a risk assessment following the Added Risk Approach (EU, 2019). The importance of conducting ecotoxicological assessments at a basin scale becomes evident when comparing generic toxicological thresholds from various sources. For instance, Table 4 presents a comparison of the Consensus 1 and 2 values used in this study with the Interim Freshwater Sediment Quality Guidelines (ISQGs) and Probable Effect Levels (PELs) established by the Canadian Council of Ministers of the Environment (CCME, 2002). The discrepancies among these thresholds highlight the potential combined effect of species sensitivity and their adaptation to varying regional background exposure levels.

4. Conclusions

The consistency of the results obtained from a comparative analysis of background and reference concentrations of trace elements in sediments from two river basins, each exhibiting distinct levels of anthropogenic activity, has affirmed the viability of employing the upper limit of the one-sided 95 % confidence interval for the median and the 90th percentile as robust estimators for the central tendency and upper bounds of the natural population, respectively. When dealing with small datasets featuring heavily tailed distributions, the bootstrap method provides more conservative estimates of reference values than parametric methods by constraining these values to the sample maximum. Reference values were similar for both basins and they were exceeded more frequently in samples that could potentially be influenced by historical anthropogenic activities, particularly mining. Consequently, the suggested methodology for sediment sampling and statistical analysis of sediment trace element concentrations to establish background and reference values appears to be valuable in the context of the European Water Framework Directive for the formulation of environmental quality standards.

The aforementioned methodology has been used to establish background and reference values for 19 elements in the sediments of two adjacent watersheds: the first and larger one, the Nalón basin,

characterized by extensive anthropogenic influence, and the second, the Esva basin, with minimal human impact. While, in most instances, reference values are similar in both basins, higher reference concentrations of As, Ba, Hg, Cu, Mn, Ni, S, and Zn have been determined for the sediments of the Nalón basin, indicating the presence of important mineral deposits. All these elements are representative of epigenetic hydrothermal mineralizations, the predominant type of metal occurrences in the Nalón basin. This effect on background and reference levels of the geological substrate and of the presence of different mineral deposits underlines the need to establish such values at the individual basin scale.

In the Esva basin, both background and reference values for all elements fall within the order of magnitude proposed by the Belgian legislation for concentrations indicating good ecological status (LEL, TEL). This alignment is similarly observed in the background levels of all elements in the Nalón basin, with the exception of As and Ni, which surpass their respective thresholds. Of particular concern in this basin are Ni and Hg, for which reference values surpass the thresholds beyond which the probability of observing toxic effects increases (SEL and PEL). Future research efforts should incorporate site-specific ecotoxicological studies to establish thresholds for minimum, admissible, probable, and severe toxic effects specific to each river basin and to improve the precision of risk assessments based on the Added Risk Approach (ARA). Lastly, further efforts should also focus on developing methodologies to correlate increases in sediment trace element concentrations with the impact of specific types of anthropogenic activities in different river basins.

Ethics approval

This study did not involve human or animal subjects so it did not require ethics approval.

Funding

This study was funded through the FLUCOS [PID2020-115313RB-I00/AEI/10.13039/501100011033] research grant of the Spanish Ministry of Science and Innovation.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Almudena Ordonez reports financial support was provided by Spanish Ministry of Science and Innovation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was funded through the FLUCOS [PID2020-115313RB-I00/AEI/10.13039/501100011033] research grant of the Spanish Ministry of Science and Innovation.

Author Contributions

All authors contributed to the study conception and design. The design and execution of the sampling was carried out by R. Álvarez and C. García. The statistical methods and software were developed by F. Barrio-Parra. The formal analysis, investigation and visualization were performed by M. Izquierdo-Díaz and H. Serrano-García. The first draft was prepared by F. Barrio-Parra and A. Ordóñez. E. De Miguel, R. Álvarez and C. García reviewed and edited the final version of the manuscript. A. Ordóñez and R. Álvarez acquired funding and perform the project administration. All authors read and approved the final

manuscript.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ecoenv.2024.117517](https://doi.org/10.1016/j.ecoenv.2024.117517).

Data availability

We added as supplementary material the complete data base and the R functions developed

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