

Natural heavy metal and metalloid concentrations in sediments of the Minho River estuary (Portugal): baseline values for environmental studies

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Abstract Forty-nine surface sediment samples from the Minho estuary sector between Tui and Caminha were analyzed for grain-size contents, Al, As, Cr, Cu, Hg, Li, Pb, Sn, and Zn concentrations. Selected heavy

metal (Cu, Cr, Hg, and Zn) and metalloid (As and Sn) distributions were normalized against Al and Li with the main goal of compensating for natural grain-size variability and to separate natural from anthropogenic contributions, by using a combination of normalization techniques (definition of regional geochemical baselines (RGB) and determination of enrichment factors (EF)). Lead did not reveal a significant relationship with Al and Li. Aluminum explained more variance than Li for As, Cu, Hg, and Zn. Assuming the general non-impacted metal character of the Minho River estuary sediments, RGBs are defined for differentiating between natural and anthropogenic contributions. Based on RGB defined for each heavy metal/metalloid, the degree of enrichment is estimated through the determination of EF. Despite the relatively low total heavy metal and metalloid concentrations, the defined RGB identifies a set of samples characterized by presenting As, Cu, Cr, Hg, and Zn enrichments relatively to expected natural levels. Mercury is the element showing the highest level of enrichment relative to the baseline values being spread through all the study area. Tin present enrichments relatively to Al and or Li always lower than 1.5 suggesting natural contributions.

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Introduction

Distinct environmental settings induce regional variability of sediments' composition. Heavy metals and metalloids (HM&M), derived from both natural and anthropogenic sources, tend to accumulate simultaneously, hence being difficult to determine what proportion belongs to each source (Loring and Rantala 1992). Changes in sediment grain-size, mineralogical composition and organic carbon content influence the total heavy metal concentrations in sediments (Loring 1991). Due to its physical and chemical characteristics, fine-grained particles (clay minerals, organic and inorganic colloids) have greater capacity to adsorb HM&M in their structures and thus form the principal way of transport these harmful substances in the aquatic environments. Therefore, fine-grained sediments are in general characterized by having higher HM&M concentrations than coarse-grained sediments. The later, where quartz, feldspars, and carbonates grains are included, are relatively HM&M poor when compared to metal-rich phases (e.g., clay minerals) and thus serve to dilute sediment HM&M concentrations (Windom et al. 1989). Other important factor that can affect HM&M concentrations in sediments is the contributions derived from weathering of natural elemental enriched formations (Karageorgis et al. 2001). Therefore, high total heavy metal concentrations do not necessarily indicate the degree of contamination (Tam and Yao 1998), except in cases of extremely high contamination, and low concentrations do not necessarily mean that the area is clean. The assessment of anthropogenic contributions to sediments must be accompanied primarily by the estimation of heavy metal contribution by natural processes (Windom et al. 1989). In order to compensate for the natural variability of sediments, to detect and quantify anthropogenic enrichments, several normalization procedures have been used (Cato 1977, 1989; Loring 1991; Loring and Rantala 1992; Mil-Homens et al. 2007; Stevenson 2001; Summers et al. 1996; Windom et al. 1989). Geochemical normalization is based on the assumption that the conservative element (ideally not affected by anthropogenic contributions) chosen as normalizing element (e.g., Al, Fe, Li, Sc) act as a proxy of the fine-grained aluminosilicated fraction and reflect the HM&M natural variability.

To our knowledge, the first published studies that included a sedimentological and geochemical characterization of the Minho River estuary are from the

beginning of the 1990s (Gouveia et al. 1993; Paiva et al. 1993). In previous studies (Bettencourt and Ramos 2003; Fatela et al. 2009; Reis et al. 2009), the Minho River estuary was considered as a heavy metal "clean" area mainly due to the relatively total low concentrations obtained. Despite the general reasonably good physicochemical quality of Minho surface waters according to the results obtained in seven sampling campaigns (between May 2009 and October 2010 covering distinct hydraulic conditions), Santos et al. (2012) identified Hg and Cr concentrations that exceeded the limits defined by the Portuguese legislation for surface waters in some of the sampling dates collected in the vicinities of Caminha, Valença and in two tributaries of the Minho River (the Coura and Louro rivers).

In order to attempt defining the natural variability of the Minho River sediments, we proposed in this study the definition of the regional geochemical baselines (RGB) for a set of selected HM&M with the main goal of estimating their contributions associated with natural processes. This methodological approach was primarily used in a set of studies developed during the end of the 1980s and the 1990s in the Canadian and USA coastal areas and estuaries (Loring 1991, Schiff and Weisberg 1999, Schropp et al. 1990, Summers et al. 1996; Windom et al. 1989). The main goal of all these studies was to provide an efficient tool for assessing elemental contamination and contribute to improve the management of estuarine and coastal areas. Briefly, RGBs are defined based on the relationship between HM&M vs. normalizing element and in the definition of its linear regression that represent the regional geochemical variability. The natural geochemical population is defined by the 95 % confidence band, indicating the level of probability that the points falling within this interval belong to a normal population and those falling outside belong to an anomalous population (Loring and Rantala 1992). After the natural variability of the studied elements in the sediments is defined and with the main objective of assessing human impacts, the level of selected HM&M enrichment is estimated through the determination of enrichment factors (EF), considering the baseline values defined by the RGBs. Despite this study being focalized in the Minho River estuary, it provides an interpretative approach that can be used in future environmental monitoring studies, thus allowing the characterization of temporal evolution trends of elemental concentrations in this specific estuary and also

comparing the obtained results with models obtained from distinct river and estuarine systems.

Materials and methods

Brief description of the study area

The Minho River is located in the western Iberian margin, in the border region between the Minho (north of Portugal) and Galicia (Spain) regions, and discharges to the Atlantic Ocean with a mean annual freshwater discharge of $300 \text{ m}^3 \text{ s}^{-1}$. It is 300 km long and has a 17,081- km^2 watershed that extends mostly over Galicia, Spain, with less than 5 % of its area in northern Portugal (Loureiro et al. 1986). The last 70 km of the Minho River forms the natural border between Portugal and Spain, which includes the main estuarine axis of approximately 40 km corresponding to the area under the influence of the spring tides (Sousa et al. 2005). The Minho River is classified as a mesotidal estuary with a tidal range varying from about 2 m at neap tides to about 4 m at spring tides (Bettencourt and Ramos 2003). The river basin occupies an area dominated by rock formations of the pre-Ordovician schist–greywacke complex and Hercynian granites (Teixeira and Assunção 1961). Associated with some of these granitic formations and quartz veins are tin (Sn) and tungsten (W) deposits, which were the main center of the mining activity located in the mining region of Covas, cut by the Coura River (one of the Minho River tributaries ends at the Caminha saltmarsh; Fig. 1). These deposits are resulting from hydrothermal systems commonly related to magmatic rocks of granitic composition that were more intensely exploited during the 1930s and 1950s coincident with the Second World War and the Korean War (Neiva 2002). The last exploitation of W and Sn ended in the middle of the eighties (e.g., Valente and Leal Gomes 2001). Quaternary terrace deposits are present along the margin of the Minho River. These deposits are constituted by thick rounded gravel deposits (quartz and quartzite), with occasional clayish-sand layers. The clasts are poorly consolidated with occasional clay cement (Teixeira and Assunção 1961).

Sediment sampling and sample preparation

Forty-nine sediment surface samples were collected along the Minho River estuary between Tui and

Caminha (Fig. 1) during the Minho09 cruise (August 2009) on board of RV Atlantic Leopard using a Van Veen Grab. Sample locations were selected based on the side scan sonar mosaic thus allowing sampling main types of sonar echoes and features. All samples were described (texture, color imagery) on board, sub-sampled for several studies (textural, geochemical, biomarkers, foraminifera, and diatoms) at the AQUAMUSEU laboratory facilities (Vila Nova de Cerveira) and stored refrigerated (ca. 4 °C). Surface samples are assumed to reflect most recent accumulation; nevertheless, surface mixing and sampling artifacts may affect its quality and representativeness. Before proceeding to laboratory analyses, all sub-samples were freeze-dried and the fraction lower than 2 mm was ground, except the sub-sample for grain-size analysis. After grounding, samples were transferred to labeled plastic vials until required for analysis.

Analytical techniques

Grain size was determined using a Coulter Laser LS230 analyzer (measuring grain sizes in the range of 0.04–2,000 μm). Samples were weighted, wet-sieved in a 2,000- μm sieve, after adding sodium hexametaphosphate (CALGON) to avoid clays flocculation and hydrogen peroxide (H_2O_2) to destroy organic matter and the fraction over 2,000 μm weighted again. The difference between the total sample weight and the weight over the 2,000- μm fraction allowed the determination of the gravel percentage in the sample.

Aluminum was determined on fusion beads by XRF using a sequential wavelength dispersive spectrometer (model AXIOS). Briefly, a mixture of about 0.1 g of sample with 9.0 g of lithium tetraborate flux ($\text{Li}_2\text{B}_4\text{O}_7$) and 20 mg of ammonium iodide (NH_4I) was fused in Pt95–Au5 crucibles at 1,150 °C for 20 min and then poured into Pt–Au dishes. A set of 16 NCS Certified Reference Materials (CRM) from the China National Analysis Center, with a range of analytes and matrices similar to those of the samples and treated in the same way, was used to establish calibration curves. To correct for matrix effects, theoretical α correction factors were applied assuming the loss on ignition as a balance compound and the flux as a compound to eliminate (SuperQ software Version 3.0 Reference Manual 2010). According to the laboratory quality control procedures, calibration was validated by daily analysis of two independent CRM.

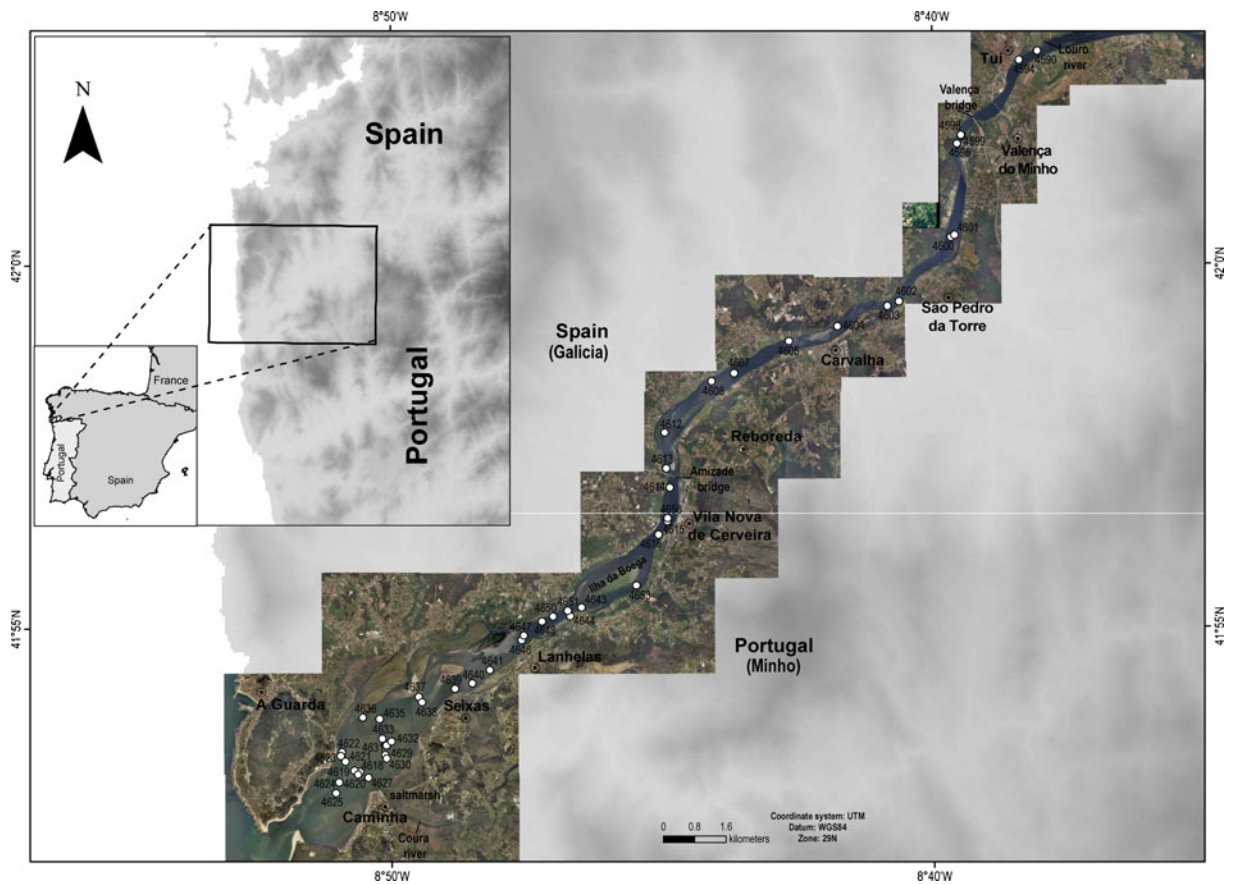


Fig. 1 Sediment sampling stations of the Minho09 cruise

Arsenic, Cr, Li, Pb, and Sn were determined by inductively coupled plasma (ICP) mass spectrometry, while Cu and Zn were measured by ICP optical emission spectrometry. Briefly, approximately 0.25 g of sediment was weighed directly into pressure vessels. Samples were mineralized by a combination of 3 mL hydrochloric acid (36 %), 9 mL nitric acid (HNO₃; 69 %), and 5 mL hydrofluoric acid (48 %) in a CEM microwave oven Mars Xpress. After microwave digestion, remaining solutions were transferred to Teflon vessels and placed on hotplate at 150 °C until near dryness. Twenty milliliters of Milli-Q water and 2.5 mL HNO₃ was added to the residue to bring the solution to a final volume, and the solution heated at 80 °C during 3 h. After cooling, the solution was transferred to 50 mL volumetric flask, and 10 % HNO₃ were added to bring the solution to a final volume and finally poured in a labeled plastic bottle.

The total Hg concentration in sediments was quantified using a Milestone Direct Mercury Analyzer DMA

80. All Hg in the sample (ca. 0.5 g) was combusted in a stream of oxygen, volatilized and trapped by amalgamation on a gold substrate, and was thermally desorbed and quantified by atomic absorption spectrophotometry.

Quality assurance/quality control for Al and trace elements determinations

For Al, CRM GBW07311 and GBW07302 (China National Analysis Centre for Iron and Steel) provided quality assurance/quality control (QA/QC) throughout the analyses. The results indicate good agreement between certified and measured values. The recovery (in percent) of Al, based on the mean values calculated for CRM, was practically complete (Table 1). Precision for Al, expressed as relative precision standard measurement uncertainty of 6 replicate samples, was lower than 1 % (Table 1).

Accuracy of analytical procedure was determined by measuring trace element concentrations in the

Table 1 Precision, trueness, and uncertainty report

CRM	Element	Certified value± expanded uncertainty	Measured value (average±SD)	Trueness (recovery) (%)	<i>u</i> (precision) (%)	U_c^{rel}
GBW 07311 (6 measurements)	Al (%)	5.49±0.02	5.37±0.08	98	0.74	0.058
GBW 07302 (6 measurements)	Al (%)	8.32±0.02	8.19±0.01	98	0.7	
NCS DC 73310 (9 measurements)	Hg (µg g ⁻¹)	0.018±0.008	0.017±0.00	94	8.8	0.15
NCS 73311 (6 measurements)	Hg (µg g ⁻¹)	0.056±0.006	0.053±0.002	95	3.8	
PACS-2 (4 measurements)	Zn (µg g ⁻¹)	364±23	354±6	97	0.81	0.13
	Cu (µg g ⁻¹)	310±12	288±6	93	1.1	0.11
	Pb (µg g ⁻¹)	183±8	157±6	86	2.0	0.17
	Cr (µg g ⁻¹)	90.7±4.6	88.1±2.6	97	1.45	0.11
	Li (µg g ⁻¹)	32.2±2	33.2±1.8	103	2.7	0.14
	As (µg g ⁻¹)	26.2±1.5	26.9±0.3	103	0.55	0.12
	Sn (µg g ⁻¹)	19.8±2.5	23.6±0.9	119	2.0	0.32

Comparison of analytical results of the certified reference materials [CRM: GBW07311, GBW070302, NCS DC 73310, and NCS 73311 (China National Analysis Centre for Iron and Steel) and PACS-2 (NRCC, Canada)] with measured values. The average of replicate CRM measurements (in percent) is reported as well as the standard deviation (in percent). Abbreviations of relative precision standard uncertainty and of relative expanded measurement uncertainty ($k=2, p<0.05$) are *u* (precision) and U_c^{rel} , respectively

PACS-2 CRM (marine sediments prepared by the National Research Council of Canada (NRCC); Table 1). Target recoveries (100±10 %) were fulfilled in PACS-2 except for Pb and Sn (Table 1). Precision for the trace elements studied, expressed as relative precision standard measurement uncertainty (*u* in percent) of four replicate samples, was lower than 4 % (Table 1). QA/QC of Hg was also evaluated through the use of two CRM (NCS DC 73310 and NCS 73311: stream sediments prepared by China National Analysis Center for Iron and Steel; Table 1). Obtained results indicate recoveries that follow inside confidence interval of both CRM with relative precision standard measurement uncertainty lower than 9 %. Relative expanded measurement uncertainty (U_c^{rel} in percent) was estimated using intra-laboratorial Nordest approach based on validation and quality control using a coverage factor of two for 95 % confidence level (Nordest 2011) (Table 1).

Definition of regional geochemical baselines for the Minho River estuary

The definition of HM&M baselines represents an important tool that helps in environmental management of estuarine and coastal areas, such as the Minho River estuary. This is achieved through the identification of samples that do not belong to the baseline population and also in defining the level of heavy metal enrichment through EF determination. In order to consider

the natural variability of HM&M concentrations in the study area, it is important to study relationships between heavy metals/metalloids and normalizing elements to define the regression lines that represent regional elemental baseline variability. A confidence band of 95 % was included to indicate a 95 % probability of samples that fall inside of this prediction interval belonging to the natural population of that heavy metal/metalloid in relation to the normalizing element and those outside belonging to an anomalous population (Loring and Rantala 1992). The points that fall outside of the 95 % prediction limit were not considered to avoid the possibility of potentially anthropogenic enriched samples to be considered in the final regression models of the natural populations. The SPSS statistical program (version 17 for Windows) was used to analyze the data.

The evaluation of the relationship between metals/metalloids and normalizing elements (Al and Li) was made through the use of regression analysis considering all dataset. Selection of surface samples representing natural population was based on the identification of statistical outliers and influential cases from the studied sites through regression analysis using Cook’s distance, leverage levels, and residual plots. A Shapiro–Wilk test was used to test the normality of distributions. Appropriated transformations (inverse, logarithm, square root) were used to meet assumptions of normality and stability of variance (Schropp et al. 1990; Summers et al.

1996). Additionally, the assumption of normality based on the rule of thumb that a variable is reasonably close to normal if its skewness and kurtosis have values between -1.0 and $+1.0$ was also used when none of the transformations induced the normality distribution. The process of testing for normality and selection of outliers was iterated until a normal distribution was achieved (Schiff and Weisberg 1999).

After defining the baseline for each element, it is possible to estimate the level of elemental enrichment relatively to the baseline through the determination of EFs that was calculated by dividing its ratio to the normalizing element by the same ratio obtained from the baseline:

$$EF_{\text{metal}} = \frac{(\text{heavy metal or metalloid}/\text{normalizing element})_{\text{sample}}}{(\text{heavy metal or metalloid}/\text{normalizing element})_{\text{baseline}}}$$

where heavy metal (or metalloid) and normalizing element concentrations $((\text{metal}/\text{normalizing element})_{\text{baseline}})$ were obtained from the regression line. Enrichment factors higher than 1.5 indicate that an important fraction of metals and metalloids is derived from non-crustal materials associated with biota and/or anthropogenic contributions (Zhang and Liu 2002). The main advantage of considering these baseline values is that they reflect natural variability of sediments in the study area when compared with total elemental concentrations of crustal abundances (Loring 1991), which can differ widely from the regional baseline values, leading to a misinterpretation of the EFs.

Results and discussion

Grain-size characteristics of sediments

In brief, grain-size composition is dominated by sand, with average contents of 80 % (Table 2) in agreement with results obtained by Paiva et al (1993) and Balsinha et al (2009). Samples from the Minho River estuary were essentially defined as gravely and sandy sediment according to Schlee (1973) and Shepard (1954), respectively, suggesting high river dynamics that are responsible for maintaining in suspension fine-grained particles and exporting them to the sea. Spatial distribution does not reveal any type of east–west gradient, excepting high gravel contents that are located upstream. The coarsest sample (4590; Fig. 1), placed north

of Valença, is composed by 69 % of gravel. Other three samples containing more than 40 % of gravel were found above Vila Nova de Cerveira (4601, 4603, and 4614; Fig. 1). Sample 4630, located at the Coura River mouth (Fig. 1), presented the highest percentage of sand (98 %). Two samples showed the highest percentage of mud (fine fraction (ff)=clay+silt): samples 4633 (63 %) and 4599 (34 %) in the lower part of the estuary and Valença, respectively (Fig. 1).

Elemental concentrations and relationships

The total elemental concentrations in the surface sediments of the Minho River estuary are presented in Table 2. All results were amended considering two significant figures for expended uncertainty. The obtained results in this study are compared with previous studies developed in the Minho River estuary (Table 3). Reis et al. (2009) explained the relatively low Al concentrations obtained in their own work due to using a sample digestion with HNO_3 that not assures a total decomposition of the sample matrix. Despite this, the range of other elemental concentrations considered was generally similar between distinct studies. Additionally, the range of elemental variability does not reveal strong modifications through time, suggesting the absence of significant anthropogenic contributions with time. To the best of our knowledge, this study represents the first one to assess the As, Hg, and Sn concentrations in sediments of the Minho River estuary. Due to this, the range of these elemental (excepting for Sn that was not found in the bibliography) concentrations was compared with values obtained in some of the Galician rias marked by similar lithological and geological contexts, being however, more influenced by anthropogenic activities (paper mill industries, harbor and industrial activities). Mercury concentrations in the present study varies between 0.002 and $0.051 \mu\text{g g}^{-1}$ (with a median value of $0.04 \mu\text{g g}^{-1}$), which are much lower than those obtained in the studies of Canário et al (2007) and Carro et al (1994). Canário et al (2007) in the Vigo Ria obtained a range of Hg concentrations from 0.02 to $1.78 \mu\text{g g}^{-1}$. Carro et al. (1994) carried out a study in the Pontevedra Ria at the surroundings of the paper mill discharge effluent, finding concentrations of total Hg up to $2.5 \mu\text{g g}^{-1}$. Arsenic concentrations in the Minho River estuary are characterized by average values of $10.3 \mu\text{g g}^{-1}$, lower when

Table 2 Total Al and trace element (Li, As, Cr, Cu, Hg, Pb, Sn, Zn) concentrations, gravel, sand, silt, and clay contents and (all on a dry weight basis) in surface sediments from the Minho River estuary

Sample ID	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Al (%)	Li (μgg^{-1})	As (μgg^{-1})	Cr (μgg^{-1})	Cu (μgg^{-1})	Hg (μgg^{-1})	Pb (μgg^{-1})	Sn (μgg^{-1})	Zn (μgg^{-1})
4590	69	31	1	0.1	4.18	35.0	5.32	13.8	3.93	0.0083	15.2	4.1	32.3
4594	16	79	4	0.9	4.76	48.3	6.52	24.3	6.18	0.0110	15.2	5.1	54.2
4595	15	76	8	1.6	4.27	43.8	5.77	34.3	3.79	0.0053	15.0	4.3	37.7
4598	32	60	6	2.2	4.13	43.6	11.2	21.3	5.81	0.0112	15.6	4.3	46.5
4599	0	66	25	8.9	4.95	50.8	12.3	25.1	10.2	0.0209	17.2	5.6	67.2
4600	4	91	3	0.8	5.09	50.4	7.98	29.4	5.53	0.0072	15.8	4.9	51.4
4601	58	31	9	2.3	4.55	46.7	9.3	23.2	8.65	0.0164	16.5	5.0	63.0
4602	18	78	3	0.6	3.78	34.2	3.91	14.5	2.89	0.0035	13.4	4.2	26.9
4603	47	52	1	0.1	3.70	31.4	3.76	10.9	1.69	0.0023	13.3	3.5	20.3
4604	30	64	5	0.9	3.88	38.4	5.35	13.7	2.71	0.0037	14.6	4.1	28.9
4605	6	86	7	0.9	3.82	36.2	4.61	15.6	2.72	0.0028	14.0	3.7	28.6
4607	6	90	3	0.6	4.37	40.7	6.24	19.8	3.63	0.0042	14.6	4.1	37.1
4608	8	90	2	0.4	4.12	41.0	5.63	18.9	3.43	0.0036	16.0	4.4	35.3
4612	6	92	2	0.3	4.23	39.5	6.60	17.2	3.18	0.0043	18.1	3.9	35.2
4613	33	54	12	1.4	3.74	35.1	7.14	14.6	3.12	0.0076	15.3	3.4	29.4
4614	40	55	4	0.5	4.18	38.1	6.54	17.0	3.21	0.0050	15.1	4.0	30.9
4615	4	79	16	1.7	3.82	37.8	7.05	12.8	2.09	0.0019	13.6	4.3	26.3
4616	0	96	4	0.4	3.88	41.2	7.03	13.9	2.58	0.0020	13.2	4.2	27.9
4618	0	79	16	4.6	6.42	77	16.5	43.5	13.8	0.0250	15.8	6.3	73.9
4619	0	94	5	1.0	5.77	59.6	14.5	36.3	8.91	0.0082	13.3	4.4	56.5
4620	1	85	11	3.3	6.22	70	17.6	41.5	12.6	0.0151	12.8	5.6	66.1
4621	3	76	16	5.2	6.48	78	17.1	41.7	13.9	0.0220	14.1	6.8	80
4622	1	96	3	0.6	4.66	49.8	11.9	24.2	5.13	0.0027	14.5	4.4	39.4
4623	1	96	3	0.4	4.70	50.6	11.9	25.9	5.60	0.0032	14.4	4.3	41.5
4624	2	95	3	0.5	4.95	54.9	9.1	27.6	5.54	0.0035	15.2	4.4	41.9
4625	1	95	3	0.5	4.74	52.4	8.15	25.9	5.70	0.0039	14.2	4.4	39.5
4627	15	80	4	0.7	4.77	50.5	11.3	24.1	7.04	0.0037	14.8	6.1	39.8
4629	4	94	2	0.4	4.02	42.7	7.96	18.1	3.46	0.0018	15.2	4.1	29.8
4630	0	98	2	0.4	3.76	37.3	6.52	17.5	3.25	0.0018	14.4	3.2	131
4631	3	91	5	0.7	4.73	51.4	9.7	23.7	5.32	0.0028	16.7	4.7	39.7
4632	7	89	3	0.5	4.77	50.9	10.1	27.4	6.02	0.0044	14.4	4.1	41.5
4633	1	36	49	14.3	7.87	85	69.4	64.6	26.8	0.0510	17.5	5.2	90
4635	17	72	9	1.7	4.99	53.0	18.1	28.6	12.4	0.0358	17.4	4.6	46.6
4636	0	97	2	0.4	4.48	43.6	10.0	21.9	4.91	0.0037	16.1	4.1	39.7
4637	2	92	5	0.9	4.87	50.6	12.4	27.0	6.24	0.0038	15.3	4.5	45.0
4638	0	94	5	1.0	5.49	55.0	15.5	33.6	8.29	0.0048	15.3	4.4	55.7
4639	3	89	7	0.8	4.23	43.7	8.7	20.6	4.11	0.0024	14.4	3.9	34.9
4640	4	85	9	1.4	4.24	42.0	8.6	18.8	4.14	0.0033	15.2	4.7	33.5
4641	17	70	11	2.0	3.79	34.4	6.91	11.6	1.87	0.0020	14.9	4.0	20.3
4643	6	79	13	2.3	3.73	30.9	7.39	8.7	2.10	0.0016	13.4	4.2	19.6
4644	2	92	5	1.0	4.19	37.9	9.9	16.4	4.03	0.0049	12.7	4.6	31.4
4646	2	92	5	0.8	4.79	45.6	9.7	18.6	4.36	0.0052	11.7	5.8	32.2
4647	8	89	3	0.4	4.90	43.6	9.6	22.4	5.06	0.0036	15.9	4.7	37.4

Table 2 (continued)

Sample ID	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Al (%)	Li ($\mu\text{g g}^{-1}$)	As ($\mu\text{g g}^{-1}$)	Cr ($\mu\text{g g}^{-1}$)	Cu ($\mu\text{g g}^{-1}$)	Hg ($\mu\text{g g}^{-1}$)	Pb ($\mu\text{g g}^{-1}$)	Sn ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)
4648	3	90	6	0.6	4.13	36.4	8.23	14.9	3.27	0.0026	11.7	4.5	25.1
4649	12	85	2	0.4	4.56	42.3	9.3	20.0	4.49	0.0038	nd	4.8	nd
4650	7	85	7	0.6	4.19	36.6	7.84	14.7	3.53	0.0034	11.4	4.7	24.0
4651	7	85	7	0.6	4.07	35.1	6.97	11.4	2.42	0.0016	11.9	4.7	19.4
4653	7	77	15	1.1	3.91	34.4	5.90	9.8	1.95	0.0020	14.7	4.8	22.2
4656	12	71	16	1.4	3.85	33.3	5.70	10.5	2.40	0.0025	11.1	4.2	21.3

nd not determined

compared with the average values ($19.1 \mu\text{g g}^{-1}$) obtained by Rubio et al (2000) for sandy sediments in Vigo Ria.

Table 4 shows the correlation matrix of the studied elements together with sand, clay, and ff contents. The positive and significant correlation between Al, Li, clay, and ff indicates their association with fine-grained fraction. The relatively low total As, Cr, Cu, Pb, Sn, Zn, and Hg concentrations observed can be associated with high sand contents that act as an inert diluent of their concentrations (e.g., Aloupi and Angelidis 2002). This can be resulting from hydrodynamic conditions that permit an efficient transfer of the most fine-grained (including fine sands such as observed by Balsinha et al. 2009) particles to the sea during spring tides. Despite these low concentrations, they may reflect contributions of the drainage of both Sn–W mineralizations (and associated minerals such as arsenopyrite, pyrite, galena, pyrrhotite) and tailings [resulting from mining activity that happened in the past (e.g., mining region of Covas)]. This drainage (acid rock drainage) may cause the elemental remobilization to the Coura River, thus contributing to increase the elemental background concentrations, at least to a local scale. According to Fatela et al (2009), the Caminha saltmarsh is characterized by sediments with high percentage (ca. 75 %) of ff

contents. The accumulation of fine particles suggests the role of the saltmarsh as a sediment trap of these particles transported by the Coura River.

Strong and significant ($p < 0.01$) correlation coefficients of all elements (excluding Pb) with fine-grained sediment components suggests their association with fine-grained particles (especially clay minerals). Lead reveals a distinct distribution pattern of those elements indicating that other sediment components (e.g., organic matter, Mn–Fe oxi-hydroxides) besides those associated with fine-grained sediments, are controlling its distribution and/or the existence of a wide Pb contamination in the Minho River estuary, despite the relatively low Pb concentrations.

Normalization of heavy metal and metalloid concentrations and regional geochemical baseline models

In order to balance the effect of sediment composition, total heavy metal/metalloid concentrations are normalized against a grain-size proxy (conservative elements such as Al or Li). Both Al and Li are positively correlated with clay size particles ($r = 0.68$ and $r = 0.63$, $p < 0.01$, respectively (Table 4)) and with fine fraction [$r = 0.58$ and $r = 0.52$, $p < 0.01$, respectively (Table 4)]. Most of the metals and metalloids studied

Table 3 Comparison of elemental range concentrations in surface sediments of the Minho estuary obtained in this study with other published studies

	Study location	Al (%)	Cu ($\mu\text{g g}^{-1}$)	Cr ($\mu\text{g g}^{-1}$)	Pb ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)
Paiva et al. (1993)	Estuary mouth—Tui	2.2–6.5	5–29	5–56	18–50	22–94
Fatela et al. (2009)	Estuary mouth—Tui and Caminha saltmarsh	4.2–7.7	9–36	20–62	12–42	32–157
Reis et al. (2009)	Caminha saltmarsh	0.8–2.3	2.8–22	7–20	4.8–15	38–92
This study	Caminha—Tui	3.7–7.9	1.7–26.8	9–65	11–18	19–131

Table 4 Pearson’s correlation coefficients (*r*) for the studied variables of Minho River estuarine surface samples (considering 48 samples for Pb and Zn and 49 samples for the rest of the studied variables)

	Sand	ff	Clay	As	Pb	Cu	Cr	Sn	Li	Zn	Hg	Al
Sand	1.00											
ff	-0.45 ^a	1.00										
Clay	-0.44 ^a	0.96 ^a	1.00									
As	-0.28 ^b	0.80 ^a	0.83 ^a	1.00								
Pb	-0.24	0.22	0.33 ^b	0.31 ^b	1.00							
Cu	-0.28 ^b	0.73 ^a	0.82 ^a	0.90 ^a	0.39 ^a	1.00						
Cr	-0.06	0.55 ^a	0.66 ^a	0.79 ^a	0.38 ^a	0.91 ^a	1.00					
Sn	-0.03	0.40 ^a	0.47 ^a	0.36 ^b	0.04	0.59 ^a	0.53 ^a	1.00				
Li	-0.00	0.52 ^a	0.63 ^a	0.72 ^a	0.32 ^b	0.90 ^a	0.95 ^a	0.67 ^a	1.00			
Zn	-0.04	0.36 ^b	0.49 ^a	0.49 ^a	0.35 ^b	0.65 ^a	0.66 ^a	0.31 ^b	0.64 ^a	1.00		
Hg	-0.47 ^a	0.76 ^a	0.83 ^a	0.82 ^a	0.45 ^a	0.92 ^a	0.74 ^a	0.48 ^a	0.72 ^a	0.54 ^a	1.00	
Al	-0.07	0.58 ^a	0.68 ^a	0.80 ^a	0.29 ^b	0.93 ^a	0.95 ^a	0.67 ^a	0.96 ^a	0.60 ^a	0.75 ^a	1.00

^aCorrelation is significant at the 0.01 level (two-tailed)

^bCorrelation is significant at the 0.05 level (two-tailed)

in the Minho River estuary sediments exhibited significant linear correlations with Al and Li (correlation coefficients ranged between 0.60–0.95 and 0.63–0.95, respectively). Nevertheless, Pb is not correlated with both conservative elements (Table 4).

The regression analysis results between each metal/metalloid and normalizing element (Al and Li) are shown in Tables 5 and 6. In all cases, Al and Li concentrations were inverse-transformed. For most metals (Cu, Hg, Zn) and As, a log transformation was sufficient to meet the assumption of normality. For Sn, no transformation was required. Both Al and Li are considered a good proxy for the natural variability of As, Zn, Cu, and Cr concentrations due to their regression coefficient (*r*²) values that accounted for 72–94 and 67–93 % of their natural variability’s,

respectively. However, Al explained slightly more variance in As, Cu, and Zn concentrations than Li (Tables 5 and 6) and also explained substantially more variance in Hg than Li (Tables 5 and 6).

The high *r*² can be related to textural and mineralogical changes of sediments, supporting the association of these elements with fine-grained aluminosilicates (Tables 5 and 6). On the other hand, the existence of intercept values different from zero indicates that there are other sources (e.g., organic matter, Mn–Fe oxi-hydroxides) of As, Cr, Cu, Hg, and Zn in addition to the aluminosilicated fraction. The relatively low *r*² values for Sn with both Al and Li (Tables 5 and 6) can be due to the high degree of scatter in the Sn data (Figs. 2 and 3), suggesting that natural variability is controlled by other

Table 5 Transformations and regression results of HM&M to Al relationships for the Minho surface samples

Element	Transformation	<i>N</i>	<i>r</i> ²	Slope	Intercept	±95 % prediction interval
Cu	log (Cu), 1/Al	43	0.94	-7.26	2.26	0.13
Cr	log (Cr), 1/Al	47	0.89	-5.22	2.47	0.12
Zn	log (Zn), 1/Al	44	0.87	-4.38	2.54	0.12
As	log (As), 1/Al	46	0.72	-4.38	1.91	0.38
Hg	log (Hg), 1/Al	33	0.68	-5.50	-1.24	0.32
Sn	Sn, 1/Al	41	0.38	-8.19	6.22	0.78

N is the number of samples selected to define the regional geochemical baseline and *r*² represents percentage of total response variation explained by Al

Table 6 Transformations and regression results of HM&M to Li relationships for the Minho surface samples

Element	Transformation	<i>N</i>	r^2	Slope	Intercept	±95 % prediction interval
Cu	log (Cu), 1/Li	44	0.89	-44.23	1.66	0.12
Cr	log (Cr), 1/Li	47	0.93	-34.47	2.10	0.07
Zn	log (Zn), 1/Li	45	0.88	-29.75	2.24	0.08
As	log (As), 1/Li	47	0.67	-27.75	1.57	0.33
Hg	log (Hg), 1/Li	30	0.42	-22.02	-2.01	0.25
Sn	Sn, 1/Li	43	0.30	-51.50	5.60	0.60

N is the number of samples selected to define the regional geochemical baseline and r^2 represents percentage of total response variation explained by Li

sediment components. In the case of Pb, it was not possible to establish a significant relationship with both Al and Li, thus preventing the definition of the baseline model.

Estimation of As, Cu, Cr, Hg, Sn, and Zn enrichment factors

After the natural variability (and consequently their baseline values) of HM&M concentrations in the

sediments being defined through RGB models, it is possible to assess human impacts by determining the heavy metal EF relative to baseline values. The difference between EFs (for As, Cu, Hg, and Hg) obtained using Al and Li as normalizing elements was tested using the Mann–Whitney test. This test shows that these approaches were not significantly different. Surface samples with EF greater than 1.5 indicate that additionally to elemental concentrations associated with the detrital (natural) component,

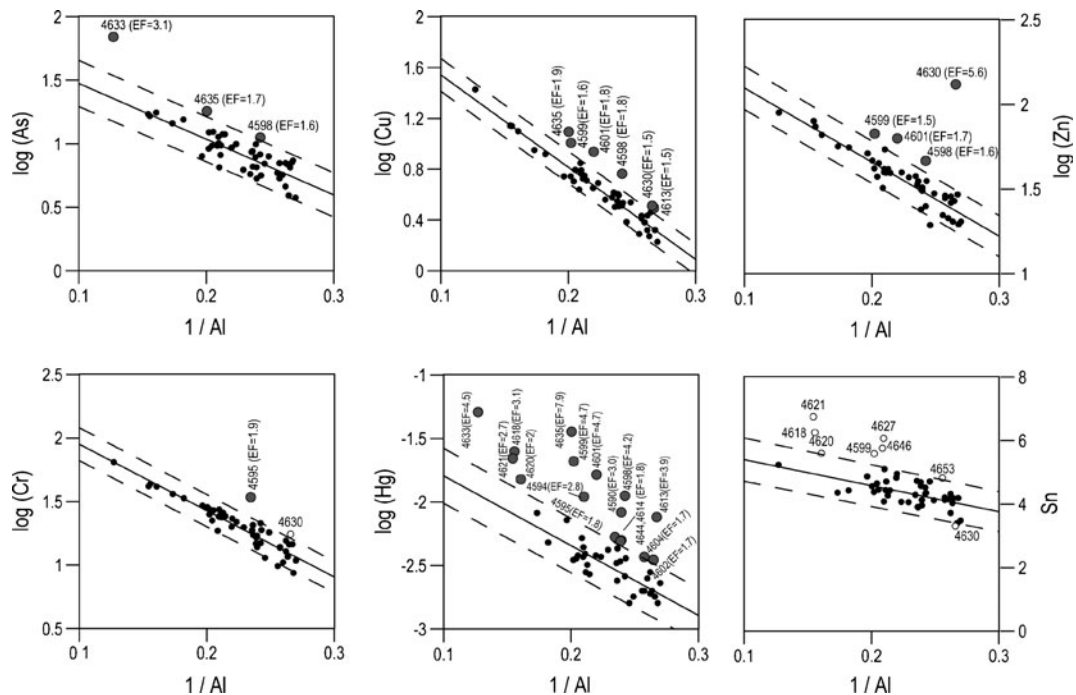


Fig. 2 Scatter plots showing relationships between As, Cr, Cu, Hg, Sn, and Zn (in micrograms per gram) vs. Al (in percent) for Minho surface sediments. Dashed lines define the 95 % confidence limit. Sample sites which fall within the prediction interval are considered uncontaminated (black dots); sample sites

that fall above the upper 95 % confidence limit are considered anomalously enriched. Samples presenting enrichment factors (EF) greater than 1.5 are represented by gray open circles. Samples with EF varying between 1 and 1.5 are represented by open circles

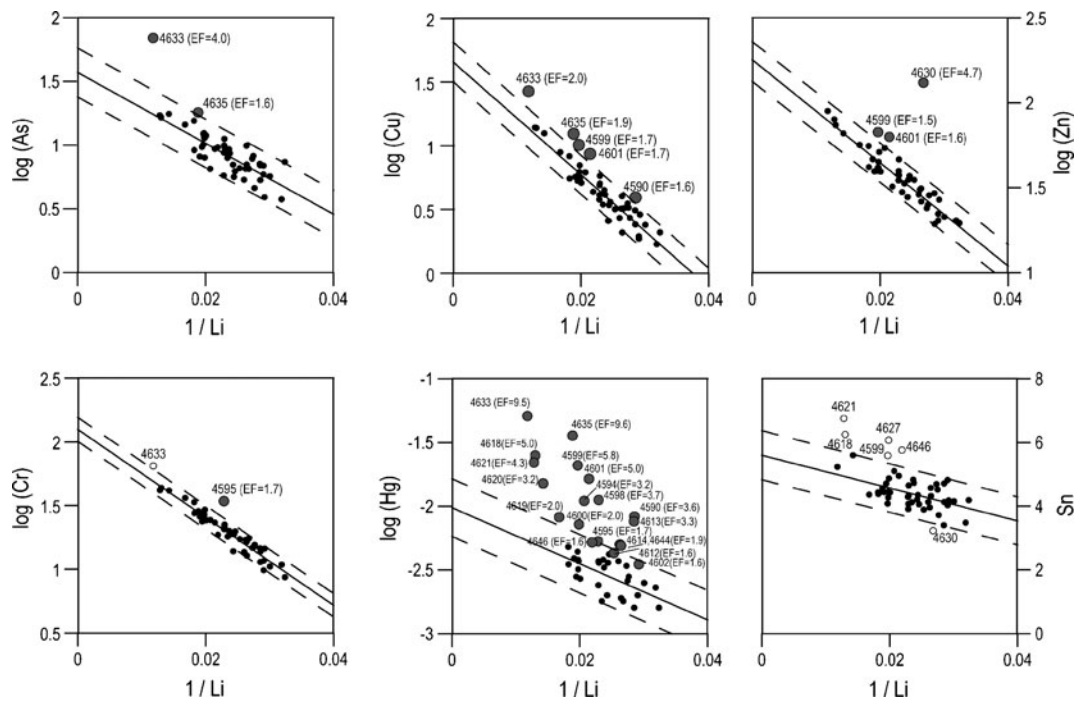


Fig. 3 Scatter plots showing relationships between As, Cr, Cu, Hg, Sn, and Zn (in micrograms per gram) vs. Li (in micrograms per gram) for Minho surface sediments. Dashed lines define the 95 % confidence limit. Sample sites which fall within the prediction interval are considered uncontaminated (black dots);

sample sites that fall above the upper 95 % confidence limit are considered anomalously enriched. Samples presenting enrichment factors (EF) greater than 1.5 are represented by gray open circles. Samples with EF varying between 1 and 1.5 are represented by open circles

sediment contains other HM&M contributions delivered from non-crustal contributions interpreted as being associated with anthropogenic contributions, derived from agricultural, urban and industrial [mining (e.g., exploitation of granitic quarries, tailings of abandoned mines) activities, food and drink processing, metallurgies, textiles, and wood transformation] activities that exist in the study area. Samples considered as belonging to an enriched population are in general enriched in more than one element (Fig. 4) suggesting that these locations (nearby Tui, Valença and Amizade bridges, and the lower part of the estuary) are affected by diverse anthropogenic influences or reflecting favorable environmental conditions for occurring the accumulation of contaminated particles. In the lower part of the estuary, these elemental enrichments may also reflect the closeness of the Caminha saltmarsh, where fine-grained “enriched” particles transported by the Coura River from (both from natural rock formations and tailings of abandoned mining areas) tend to accumulate. Additionally, the proximity of the Tui and Valença bridge locations

with the Louro River [a tributary of the Minho River (see Fig. 1) that drains important industrial and urban areas (Filgueiras et al. 2004)] may explain their elemental enrichments. Mercury is characterized by showing the highest level of enrichment with nearly 33 % of the studied locations being spread through all study area (Fig. 4). In the case of Sn, despite a set of samples that are considered as belonging to an anomalous population, the enrichments were always lower than 1.5 (Figs. 2 and 3) suggesting natural contributions or relatively low anthropogenic influences not enough strong to reach these threshold.

Conclusions

The comparison of total heavy metal and metalloid concentrations with reference values by itself was not considered adequate for a correct identification of possible anthropogenic enrichments because it does not account for the regional variability. The research

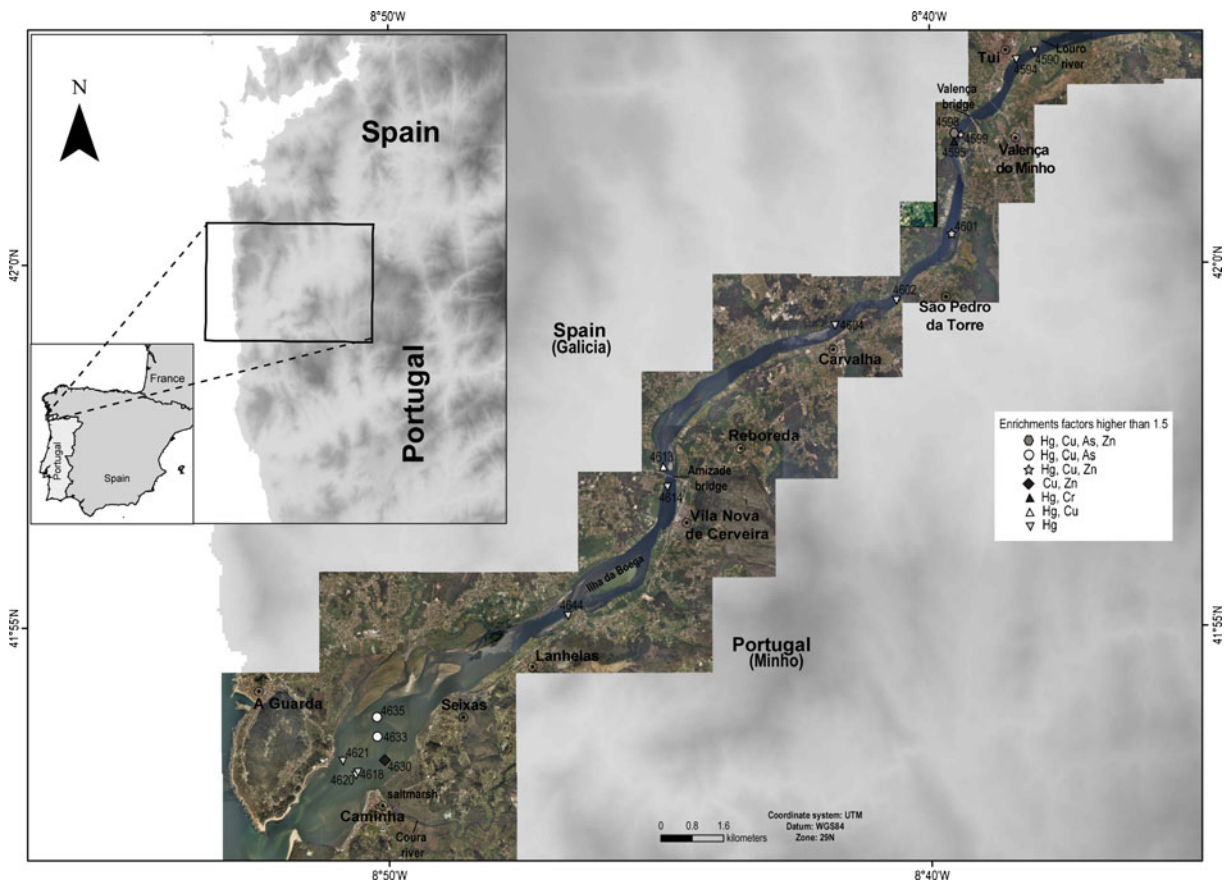


Fig. 4 Spatial distribution of samples with EF higher than 1.5

approach applied in this study involves the definition of RGB models. These models allow estimating natural components of studied HM&M in sediments, identifying enriched samples and estimating their enrichment levels through the estimation of EF.

Aluminum and Li can be used as normalizing elements for most heavy metals (except Pb) and metalloid (except Sn) concentrations in sediments of the Minho River estuary. Nevertheless, Al explained slightly more variance in As, Cu, Hg, and Zn concentrations than Li. Normalization of As, Cu, Cr, Hg, and Zn concentrations to both normalizing elements (Al and Li) allows estimating their detrital components in Minho River estuary sediments. The relatively low regression coefficient (r^2) for Hg and for Sn relatively to Al and Li suggests the influence of other sediment components (in a minor scale for Hg), such as organic matter, controlling its spatial distribution. The identification of enriched locations in areas characterized by

coarse-grained sediments (and consequently total low elemental concentrations) demonstrates the importance of considering normalized elemental concentrations together with the definition of RGB models. The supply of slopes, intercepts, and the 95 % prediction limits for each RGB can be used by other researchers in future monitoring programs for evaluating the quality of the obtained results. It also represents an interpretative approach that helps in the environmental characterization and therefore can be used as a monitoring tool considering both spatial (comparing elemental data within the estuary, tracking the spread of a known contamination source) and temporal (monitoring the temporal evolution trend of heavy metal and metalloid concentrations) dimensions. Additionally, the identification of critical contaminated areas allows promoting a most efficient management of financial resources to be used in other tests (e.g., ecotoxicity) involving the heavy metal effects on biological communities.

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