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Uranium as reference element to estimate the background of "Anthropocene" sensitive trace elements in sediments of the land-ocean continuum (Ulla-Arousa, NW Iberian Atlantic Margin)

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A B S T R A C T

Determining the background is a crucial step in differentiating between natural and anthropogenic components in environmental samples. Geochemical normalization is a standard procedure for determining the background contents of trace elements in sediment samples, which involves the careful selection of a reference element. Aluminum (Al), iron (Fe), and other major, minor, and even trace constituents of sediments are commonly used as reference elements. A suitable reference element should behave conservatively, with contents that are not significantly affected by anthropogenic factors or post-depositional processes.

In this study, the performance of uranium as a reference element in sediment samples taken from the Ulla River was tested. The Ulla River drains a mainly granitic basin in the Iberian Atlantic Margin, and samples were collected from headwaters to the coastal area. Iterative least squares simple regression was used to estimate the background contents (as background functions) of six trace elements of environmental concern, including arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn).

Uranium demonstrated satisfactory performance with correlation coefficients ranging from approximately 0.7 for Cu to 0.9 for As. The background-estimated contents of the six target elements were in good agreement with several references at different geographical scales, with differences possibly attributed to peculiarities in the local lithology. Thus, uranium can be considered a suitable normalizing element. However, it was tested in a relatively homogenous granitic basin and, like any other reference element, should not be used automatically without empirical corroboration.

1. Introduction

Elements such as Cd, Cr, Cu, Hg, Ni, Pb and Zn (industrial metals, Waters et al., 2016) have been closely linked to human activities since ancient times, and even before (Montero, 2014). Their significance as human tracers is highlighted by the fact that anthropogenic Pb and other metals were suggested as potential auxiliary stratotypes for the geological definition of the "Anthropocene" (Zalasiewicz et al., 2017; Lewis and Maslin, 2015), particularly after the Industrial Revolution and the so-called mid-20th century Great Acceleration (Steffen et al., 2007). Their anthropogenic release into the environment preserves memory in the Earth's stratigraphic records (e.g., in sediments). Many studies have used sediment contents of anthropogenic elements to reconstruct the nature-society relationships.

For instance, in the context of the Iberian Atlantic Margin, Mil-Homens et al. (2016) reconstructed the mining history of the Iberian Pyrite Belt since the Roman period by analysing Cu, Pb and other metals in a sediment core from the SW-Iberian Atlantic shelf. In the N-Iberian Margin (Nalón River Estuary), García-Ordiales et al. (2020) described the human impact related to mining activities in four long cores by determining Pb isotopic ratios and enrichment factors of As, Hg, Pb and Zn. Irabien et al. (2018) studied the contents of Cu, Pb, Zn and other metals (also magnetic susceptibility and benthic foraminifera) in sediments from the Bilbao Estuary (N-Iberian Peninsula) addressing the transformation from a former heavily industrialized area. The impact of environmental protection policies was assessed by Álvarez-Vázquez et al. (2018), who found a significant reduction in the anthropogenic input of Cr, Cu, Ni and Pb to the sediments of the Umia-O Grove Ramsar

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Wetland (NW Iberian Peninsula) occurring in the first decades of the 21st century.

Anthropogenic elements, sometimes referred to as risk elements (Menšík et al., 2021) or potentially toxic elements (Aruta et al., 2022), are intrinsic components of the Earth and, therefore, they are natural constituents of geostratigraphic records. In sediments they are typically present in trace amounts, and thus, the term trace elements (TEs) is commonly used in the scientific literature, in accordance with the IUPAC definition of the concept (i.e. any element having an average concentration of less than about 100 parts per a million atoms or less than 100 $\mu g\ g^{-1}$; International Union of Pure and Applied Chemistry, 2014). Since they are natural components of environmental samples, the determination of a possible human input depends on the estimation of a reference baseline. Consequently, background estimation is a crucial step in any environmental assessment work on sediment contents by trace elements.

The concept of background has been extensively discussed (see e.g. Reimann and Garrett, 2005). The point where many authors coincide is that the background represent the content of any given element in the absence of anthropogenic influence (Birch, 2017; Matys Grygar and Popelka, 2016). The estimation of the background is not a trivial task, particularly in fluvial sediments, since less than 17% of the continental surface can be considered pristine today, and those systems are restricted to particular remote areas of our planet (Meybeck, 2003). Many techniques have been and are being developed with the aim to estimate background (Birch, 2017), from the use of global averages (e.g. Rudnick and Gao, 2014) to more sophisticated statistical instruments. Among the numerous possibilities, some authors opt for interpretable tools with empirical meaning (Matys Grygar et al., 2023), highlighting the good performance of empirical background functions (Matys Grygar and Popelka, 2016) referred to an appropriate reference element.

This work aims to consider the suitability of uranium as a reference element in fluvial sediments of the land-ocean continuum, from bedrock headwaters, through the alluvial channel and the estuary, until the marine domain. To achieve this, a regression procedure will be performed between U and some selected trace elements (i.e. As, Cr, Cu, Ni, Pb and Zn) to estimate background in a mainly granitic basin of the NW-Iberian Peninsula, the Ulla River and its influence area in the Ria of Arousa (Iberian Atlantic margin).

2. Material and methods

2.1. Study area

The Ulla River occupies a basin of 2,806 km^2, draining from NE to SW in the NW of the Iberian Peninsula, specifically in the Spanish region of Galicia. The study area consist of the river basin from the Portodemouros dam to the river mouth, as well as the surrounding area within the Ria of Arousa (Fig. 1A). The Portodemouros dam was chosen as the base point because studies in neighboring areas have shown that river impoundments retain up to 72–96% of geochemical fluvial fluxes of trace elements, taking into account both dissolved and particulate transport (Álvarez-Vázquez et al., 2017). The Ulla River drains an area of 1,638 km^2 from the reservoir, with the bedrock comprising metamorphic rocks (62%), granitic rocks (24%), basic/ultrabasic rocks (8%) and quaternary sedimentary deposits (6%) (Fig. 1B). The references from which the presented spatial data were extracted are included in the caption of Fig. 1.

2.2. Sampling and sample analysis

A total of 78 surface sediment samples were collected from the basin of the Ulla River (NW Iberian Peninsula) and its estuarine and coastal area in the Ria of Arousa (Fig. 1). Samples were collected by hand directly from the river channel, and telescopic arm with a plastic container was used when access was difficult. In the estuary and adjacent marine area, samples were collected from a small boat using a Van Veen grab. In all cases, the uppermost 2 cm of the sediment layer was targeted and stored for further analysis. Of the 78 samples, 8 were from the Ulla River's main channel, 22 were obtained from small tributaries, 12 from the estuary and 36 from the marine domain.

Once in the laboratory, the samples were oven dried at 45 ± 5 °C until constant weight, and sieved to separate gravel, sand, and fines (silt + clay). The <2 mm fraction (sand + silt + clay) was selected for analysis due to the significant variability in particle size distribution in the population. Although fine particles are known to play a significant role in the elemental composition of sediment (Laceby et al., 2017), Matys Grygar and Popelka (2016) recommend avoiding particle-size separation of a minor fraction of sediments because the coarser fraction does not only include sand-quartz, but also other minerals that can significantly affect the real contents of trace elements, particularly in fluvial immature sediments. The <2 mm fraction was homogenised by grinding in an agate mill.

In a clean laboratory, (Analytical Service for the Determination of Metals in the Marine Environment, IIM-CSIC), the samples were acid digested (total digestion with HNO_3, HCl and HF) on a hot plate. The digest was transferred into 50 mL volumetric flasks and brought to volume with Milli-Q water. Procedural blanks, certified reference materials and internal standards (0.1 mg L^{-1} of Ir and Ge) were used to verify the accuracy and precision of the analytical procedure. In the resulting solutions As, Cr, Cu, Ni, Pb and Zn were analysed by ICP-MS (Agilent 7900) and the composition of samples and reference material determined. The analysis of the reference material was in good agreement with the certified contents (see Table 1).

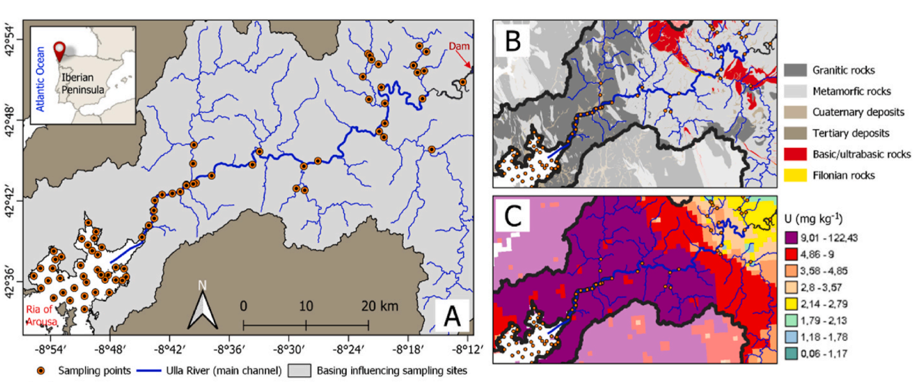

Fig. 1. Location map of the study area. (A) Fluvial network and location of sampling points (© Instituto Geográfico Nacional de España and Xunta de Galicia). (B) Lithology settings of the surveyed area (© Instituto Geológico y Minero de España - Xunta de Galicia). (C) Uranium in sediments by total extraction, WMS service of the Geochemical Atlas of Spain (© Instituto Geológico y Minero de España).

Table 1
Analysis of certified reference material MESS-4 (n = 4) from the National Research Council of Canada.

	As	Cr	Cu	Ni	Pb	U	Zn
Measured	20.7 ± 0.8	91.9 ± 4.1	32.8 ± 1.6	43.9 ± 3.9	22.1 ± 1.3	3.9 ± 0,2	150 ± 46
Certified	21.7 ± 2.8	94.3 ± 1.8	32.9 ± 1.8	42.8 ± 1.6	21.5 ± 1.2	3.4 ± 0,4	147 ± 6

All the steps of the process, i.e. sampling, handling, pre-treatment, treatment, and analysis of samples, were performed using trace metal clean techniques, as described by Howard and Statham (1993).

2.3. Statistical treatment

The essayed background estimation is a bivariate technique used to calculate the correlation between a target element (dependent variable) and a reference (lithogenic) element (independent variable) through iterative linear least squares regression (Birch, 2017). Empirical background functions derived from regression have been shown to effectively reduce grain size bias (Matys Grygar and Popelka, 2016). Although this procedure is widely used in background estimation of sediment cores with identifiable preindustrial layers, it has also been successfully used previously to estimate the natural pattern in surface sediments (Álvarez-Vázquez et al., 2018, 2022). In this approach, the background is expressed as a linear function according to equation (1):

$$[EL]_{BG} = a[RE] + b \qquad \text{Eq. 1}$$

where $[EL]_{BG}$ stands for the theoretically (empirically) estimated background content of a given target element, *[RE]* represents the measured content of a reference element, *a* is the slope, and *b* is the intercept. In this case, only linear shapes with intercept $\neq 0$ will be considered, but different functions (e.g. power-function or logarithmic) could produce comparable or better results (Álvarez-Vázquez et al., 2020; Matys Grygar and Popelka, 2016). The function is adjusted by applying successive regressions on the database, deleting unusual residuals in each step until no unusual residuals are identified in the regression subset (iterative approach). Any case with a studentized residual greater than 2 in absolute value is considered an unusual residual.

All statistical data processing in this work was performed using the Statgraphics Centurion 18 software (Statgraphics Technologies, Inc.).

2.4. Normalization

The natural composition of sediments can vary due to several factors such as mineralogy (parent geology), particle size distribution (Loring, 1991) or organic matter content (Dung et al., 2013). Other processes such as weathering dynamics and post-depositional processes can also play a role (Matys Grygar et al., 2023). "Normalization is the attempt to compensate for the natural variability of trace metals in sediments so that any anthropogenic metal contributions may be detected and quantified" (Loring, 1991). Herut and Sandler (2006) state the necessity of normalization by any physical (e.g. particle size) or chemical factor (e.g. reference element) when trying to detect anomalous anthropogenic contents in sediments. It is important to note that procedures to estimate background by normalization do not automatically detect anthropogenic disturbances in sediments but content anomalies (i.e. deviations from the background) that may be caused by natural factors or not.

Among the many methods for data normalization, geochemical methods rely on the use of a conservative element as a normalizer or reference element. Many elements have been proposed as reference elements when estimating trace element backgrounds, such as Al, Be, Cs, Eu, Fe, Ga, K, Li, Rb, Sc, Si, Sm, Ti, Zr (Dung et al., 2013; Jickells and Rae, 1997; Salomons and Förstner, 2012), and others. The selection of a reference element is a critical task in order to correct factors that produce natural variability (Matys Grygar and Popelka, 2016). For example, Dung et al. (2013) assert that Al is inefficient in sediments with variable feldspar content, early diagenetic processes can affect Fe, and Li resulted in being more efficient than Al in sediments from glacial erosion of crystalline rocks. In the fluvial environment (Morava River, Czech Republic), Bábek et al. (2015) found that Ti was more appropriate for normalizing than Al and Rb. Moreover, Matys Grygar and Popelka (2016) assert that an appropriate reference element needs to be chosen for each element of interest. This means that, in the same study over the same geographical area, multiple possibilities of reference elements have to be considered to properly estimate the background of any target element under study. In this work, U will be empirically tested as a reference element to see if it can be offered as another possibility when searching for the best reference element in the background estimation of trace element contents in sediments.

3. Results and discussion

3.1. Uranium as reference element (normalization)

In the framework of (geo)chemical normalization, linear regression stands out as a method of selecting a suitable reference element to normalize grain size and composition variability. According to Loring (1991), linear geochemical normalization must to fulfil the following requirements.

(i) Significant granulometry variation between the samples

In this study, all samples predominantly presented a particle size below 2 mm. Dry sieving was performed to quantify the sand fraction (particle size between 2 and 0.063 mm) and the fine fraction (silt + clay, particle size <0.063 mm). To illustrate particle-size heterogeneity, the average abundance of the fine fraction was 49.4 ± 47.4%, with a relative standard deviation of 96.0%. The range of fines abundance varied from samples where the total passed the 0.063 mm mesh (100%) to samples where the fine fraction was below 0.5% of the bulk mass.

(ii) Statistically significant correlation between the reference element and grain size distribution, and between the reference element and target elements

The correlation between the U contents in the bulk sample (<2 mm) and the abundance of the fine fraction (<0.063 mm) was checked using Spearman rank correlation, and it presented a significant non-zero correlation at the 99% confidence level (p-value <0.01). Moreover, all the studied trace elements presented good correlation with U (Spearman rank correlation), with p-values below 0.01, indicating a statistically significant non-zero correlation at the 99% confidence level.

(iii) Both reference element and target element have to be accurately measured

The accuracy of the analytical procedure was evaluated by analysing the reference material MESS-4 (National Research Council of Canada), and the measured contents were in good agreement with the certified value. The results are presented in Table 1.

It is commonly acknowledged that any possible reference element has to fulfil two other requisites.

(iv) To behave conservatively

To assess this condition, the contents of U were compared with those of Al, the most commonly used reference element (Birch, 2020; Herut and Sandler, 2006), particularly in the NW Iberian Peninsula (Prego et al., 2008; Rubio et al., 2000). Aluminium is considered conservative, a proxy for fine-grained material, and being in percentage contents in sediments, its abundance is believed to be significantly unaffected by a hypothetical human input (contamination). The databases for both elements (Al and U) presented standardized skewness and kurtosis within the range +2 to −2, thus, they respond to a normal distribution. Moreover, they are strongly correlated, presenting a statistically significant non-zero correlation at the 99% confidence level (P-value <0.01 with a Pearson product moment correlation of 0.69, and a Spearman rank correlation of 0.68; n = 78). According to this good correlation, U seems to be at least as good reference element as Al in sediment background assessment.

(v) Not to be significantly affected by human alterations (e.g. contamination)

Along with the good correlation with Al, the measured contents of U (average 4.5 ± 2.0 mg kg^{-1}, median 4.5 mg kg^{-1}) are slightly higher than the global reference of the upper continental crust (2.7 mg kg^{-1}, Rudnick and Gao, 2014), and also higher than the composition of the Earth's crust (2.0 mg kg^{-1}, Emsley, 2011). However, they are similar to the Clarke value (3–4 mg kg^{-1}; Cuney, 2009), and similar to U contents in granite reported around the world (an average of about 5 mg kg^{-1}; Brindha and Elango, 2013). Moreover, the Geochemical Atlas of Spain (Locutura et al., 2012) has reported U contents in the area above 8 mg kg^{-1} in soils (fraction <2 mm), floodplain sediments (<0.063 mm) and stream sediments (<0.150 mm). The higher contents reported in the area by the Geochemical Atlas of Spain are particularly related to alkaline, calc-alkaline granitoids, and gneisses in the bedrock (see Fig. 1B and C). In a nearby granitic reach in the same geographical area (Miño River) background contents of U in sediments (fine fraction, <0.063 mm) were estimated to be higher, i.e. 8.7 ± 1.9 mg kg^{-1} (Álvarez-Vázquez et al., 2021). According to the measured contents, there is no suspicion of a significant variation of anthropogenic origin in the U contents, particularly when contamination sources are mainly U-mining and processing, nuclear facilities, weapons, and erosion of agricultural soils with intensive use of fertilizers (Wang et al., 2017; Li and Zhang, 2012; Todorov and Ilieva, 2006). None of these potential sources of anthropogenic U was detected in the area.

3.2. Regression and background estimation

In order to perform linear least squares regression between two variables, it is necessary to assume that both datasets follow a normal distribution. However, this can be a common challenge, as the presence of distinct lithologies or contamination can cause deviations from normality and/or result in poly-modal distributions (Matys Grygar et al., 2023; Álvarez-Vázquez et al., 2020). Poly-modality can hinder or compromise regression results if the different modes are not identified and separated. As previously observed, the data for U contents in this study follow a normal distribution. After conducting an initial statistical exploration of the target element contents, it was found that only Pb exhibited a standardised skewness and kurtosis within the range of +2 to −2. This can also be observed in the probability plots presented in Fig. 2.

The figure shows that departures from normality appear to be caused by a limited number of extreme values. For example, a single record of 4.9 g kg^{-1} completely distorts the probability plot of Pb (Fig. 2C). To separate the main mode and check if this mode conforms to a normal distribution, an iterative deletion of outliers was performed until no outliers were found in the data distribution. In this case, outliers represent values outside the Turkey inner fences (i.e. median±1.5IQR). After deleting outliers, the majority of the data remained in the new dataset, from 82% of samples (As) to 96% (Pb). The data distribution of the six target elements in the dataset without outliers presented standardized skewness and kurtosis within the range of +2 to −2 indicating a non-significant departure from normality. Therefore, it can be assumed that both data series (i.e. reference element and the main mode of target elements) are normally distributed.

After assessing normality, background functions were calculated using linear least squares regression with U as the independent variable and target elements (As, Cr, Cu, Ni, Pb and Zn) as the dependent variables. The regression was performed on the complete dataset, including outliers, and adjusted iteratively by deleting unusual residuals in each step until none were detected. Unusual residuals are observations with studentized residuals >2 in absolute value, indicating a measured content differing more than two standard deviations from the model. The resulting background functions and graphical plots are presented in Fig. 3.

The background functions allow for the estimation of theoretical trace element baselines in each observation based on the measured content of the reference element. This allows for the calculation of significant differences between the measured content of the trace element and the reference baseline. When a significant difference is observed, it is defined as enrichment, which is the difference between the current

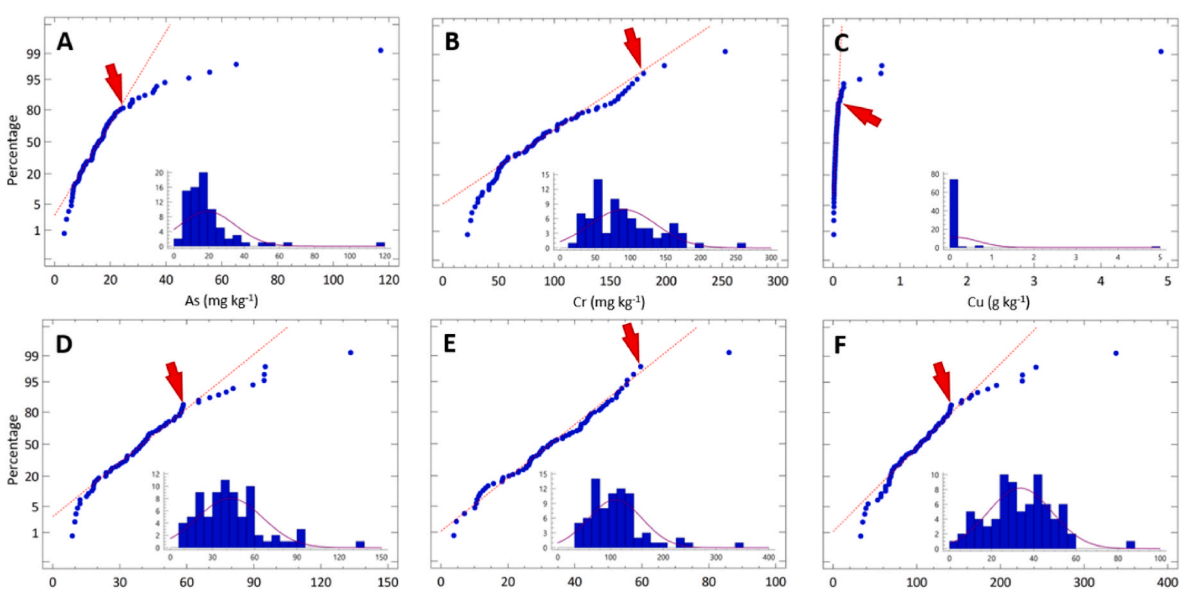

Fig. 2. Exploratory normal probability plots and frequency histograms. Arrows indicate high changes in the trend of the data distribution.

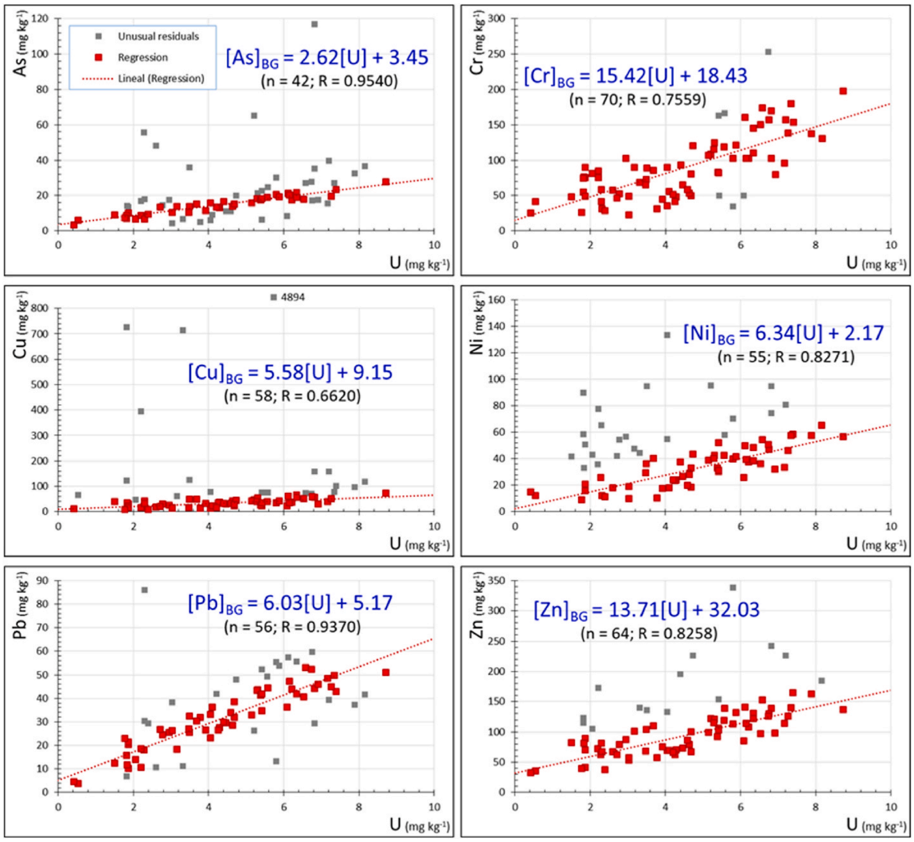

Fig. 3. Regression plots displaying the calculated background functions, represented by regression equations, along with the number of samples involved in the regression model (n) and the Pearson's correlation coefficient (R).

sediment metal contents and the baseline levels (Birch, 2017).

3.3. Background assessment

According to the samples used in the regression analysis between target elements and U (shown in the regression points in Fig. 3), the background contents can be estimated as follows: 14.3 ± 5.5 mgAs kg^{-1}, 84.5 ± 39.7 mgCr kg^{-1}, 33.5 ± 15.2 mgCu kg^{-1}, 33.2 ± 14.6 mg Ni kg^{-1}, 31.1 ± 12.6 mgPb kg^{-1}, and 94.0 ± 32.5 mgZn kg^{-1}. Additional statistical details can be found in Table 2.

Comparison with several references was included in Table 2. Arsenic's estimated background was higher compared to the general reference of the upper continental crust (UCC; Rudnick and Gao, 2014) and the Earth crust composition (EC; Emsley, 2011). However, it was relatively similar to the reference of the Geochemical Atlas of Spain (GAS; Locutura et al., 2012) and the average content in Galician sedimentary soils (GS; Macías Vázquez and Calvo de Anta, 2008).

Chromium's estimated background content was similar to the aforementioned references (i.e. UCC, EC, and GAS) except for the average content in sedimentary Galician soils (GS), which was higher. This enrichment compared with the regional reference can be explained by the presence of metabasic rocks (amphibolite/green schist; Instituto de Estudos do Territorio, 2023) that produce sediments with significant Cr contents (Prego et al., 2014). This natural Cr enrichment was previously observed in certain rivers of the region, such as those draining the Cape Ortegal Geological complex, e.g. the "pristine" Das-Mestas River estuary (Ria of Cedeira) where average contents of 99.7 ± 4.6 mgCr kg^{-1} were reported (Álvarez-Vázquez et al., 2017). In the innermost part of the Ria of Arousa, particle size seems to represent a notable factor in Cr contents being higher in the <2 mm fraction than in fine (<0.063

Table 2
Some selected statistics of the background dataset (samples involved in the regression after deleting unusual residuals). Some references (Ref.) are provided for comparison.

	As	Cr	Cu	Ni	Pb	Zn
Average	14.3	85	33.5	33.2	31.1	94.0
Standard deviation	5.5	40	15.2	14.6	12.6	32.5
Median	13.9	81	32.9	33.1	31.1	91.2
Range	3.4–27.9	22–180	9.1–71.6	8.8–65.3	3.8–53.1	33–165
(Ref.) UCC[a]	4.8	92	28	47	17	67
(Ref.) EC[b]	1.5	100	50	80	14	75
(Ref.) GAS[c]	19	62	23	28	43	81
(Ref.) GS average[d]	14.8	22.9	14.7	29.2	21	48.3

(a) Composition of the upper continental crust (Rudnick and Gao, 2014).
(b) Earth crust composition (Emsley, 2011).
(c) Geochemical Atlas of Spain (Locutura et al., 2012).
(d) Galician sedimentary soils (Macías Vázquez and Calvo de Anta, 2008).

mm) sediments (Prego and Cobelo-García, 2003).

The background estimation for copper is similar (slightly higher) to the UCC and the GAS references. It is below but in the range of the EC reference. The average background content is more than double that of the average in sedimentary Galician soils (GS). Like Cr, this possible enrichment can be caused by the local lithology, Cu-mineralisations in headwater streams of the Ulla River (Instituto de Estudos do Territorio, 2023) where the amphibolite massif of Arinteiro is located, which is rich in Cu, Fe and Zn minerals. Those mineralisations have been reported to have Cu contents >150 mg kg^{-1} after the study of deep soil horizons in the Geochemical Atlas of Galicia (Guitián Ojea, 1992).

Nickel's average background content is similar to the aforementioned references (UCC, GAS, and GS), except for the Earth crust composition (EC) which is higher. The estimated background for lead is above the UCC and the EC. It is also moderately higher than the average reference of Galician sedimentary soils (GS) and similar to or slightly below the reference provided by the Geochemical Atlas of Spain (GAS).

The case of zinc is similar to that of Cr and Cu. Its estimated average background content is slightly higher than all the aforementioned references (UCC, EC, GAS and GS). In the aforementioned estuary of the Das-Mestas River, considered to be reliably unaffected by anthropogenic alterations in its sediment trace elements composition, Zn contents were measured to be 80.2 mg kg^{-1} (Álvarez-Vázquez et al., 2017). Moreover, in the Miño River (similar lithology, similar geographical area) Zn background in the < 2 mm fraction was estimated to be 91.7 mg kg^{-1} (unpublished data). Both rivers presented values similar to the background estimation in the Ulla River.

Uranium was discussed in section 3.1 as suitable reference element, fulfilling the criterion of being unaffected by human alterations. The good correlation of the regression background functions supports the reliability of the background estimation for the target elements. Moreover, the background-estimated contents were also discussed, and they are coherent with several references. When differences exist, they can be easily explained by the inherent variability of compositional data and natural factors like local anomalies in the lithology of the Ulla River basin.

As previously mentioned, the geochemical background has to be defined at a certain level of uncertainty because the background is not a unique number but a population (Matschullat et al., 2000) that "should be defined with statistical reliability" (Birch, 2017). As the background comprises a population of varying content data, once the background population is identified and characterized, it is possible to set thresholds or limits above which (or below which) a measured content can be considered to significantly differ from the background and receive more attention.

The set of samples involved in the regression background functions can be additionally utilized to define thresholds, i.e. elemental contents above which any content can be defined as anomalous. The background functions together with the calculation of the local enrichment factors (see e.g. Matys Grygar and Popelka, 2016), are sufficient to perform the environmental assessment at the local scale. However, thresholds can be interesting (more than centrality statistics) to compare different works from different areas. Some distinct exploratory approaches to thresholds were estimated, and results are included in Table 3. The first (PPs) comes from a visual inspection of probability plots (arrows in Fig. 2), the threshold (upper mode limit) is identified by breaks (gaps) or trend changes in the cumulative distribution (Matys Grygar et al., 2023; Reimann et al., 2018; Sinclair, 1991). The second (Median + 1.5IQR) is a non-parametric technique that responds to the Tukey upper fence (IQR represent the interquartile range, quartile 3 - quartile 1), and the values included in Table 3 are the result of the exploratory analysis presented in section 3.2. This approach has been employed (e.g.) by Reimann et al. (2018). The third and last one is based on the empirical rule and assumes normal distribution of the background mode, the average + 2SD represent a value below that is expected the 97.5% of the data in the background subset. The included values were calculated from the set of samples participating in the regression after the iterative deletion of unusual residuals (as explained in section 3.2). All the approaches provided similar values.

Table 3
Upper thresholds of the background estimate (in mg kg^{-1}), which were determined using alternative methods. These methods include identifying breaks or trend changes in probability plots (PPs), a non-parametric approach according to Tukey inner fences (Median+1,5IQR), and using the empirical rule on the samples of the regression subset (BG+2SD). The reference of Galician sedimentary soils (GS) is provided for comparison.

	As	Cr	Cu	Ni	Pb	Zn
PPs[(a)]	24.5	180	86.4	57.9	59,6	141
Median+1,5IQR	26.7	154	78.2	74.9	60.2	180
BG+2SD	25.3	163	63.9	62.4	56.4	159
GS (average+2SD)	39.4	46.9	36.8	61.9	27.9	93.8

(a) The approach is exploratory and should be considered with caution.

4. Concluding remarks

Uranium has shown potential as a reference element for assessing the composition of trace element contents in river-estuary-ria sediments, particularly in catchments dominated by granitic lithology. It has performed well across a range of particle sizes, from immature sand-sized sediments in headwaters small streams to well-developed fine sediments in the nearby coastal area. Uranium's relationships with local lithology and successful performance across varying particle sizes suggest it should be considered as a factor to minimize provenance, maturity and dilution effects that can impair accurate estimation of a reference (background) baseline.

The background estimation for six trace elements (As, Cr, Cu, Ni, Pb, and Zn) revealed natural contents ranging from 3 to 29 mgAs kg^{-1}, 22–180 mgCr kg^{-1}, 9–72 mgCu kg^{-1}, 9–65 mgNi kg^{-1}, 4–53 mgPb kg^{-1} and 33–165 mgZn kg^{-1}. The significant variability, of about one order of magnitude between the extremes, provides an indication of the dispersion of data even at local scale. Uranium's ability to minimize these differences by relating contents through background functions supports its suitability as a reference element to estimate background levels of different elements of interest. Uranium has shown potential as reference element for background estimation of trace element contents in sediment, especially in granitic catchments, but it is important to note that it is not the only option and suitability should be assessed for each dataset and element of interest.

However, this study was performed in a single river basin with predominantly granitic lithology. Further research is necessary to determine if these results can be extrapolated to other areas, especially in complex basins with diverse lithologies. Nonetheless, no reference element should be used without empirical verification of its suitability.

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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