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Baseline

Determination of background geochemistry of an Amazon estuary: The Cuñaní Estuary – Amapá

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ABSTRACT

This study aims to determinate the background geochemistry values for 23 chemical elements on the Amapá coastline. To do so, 8 cores were sampled (≤70 cm) along the Cuñaní Estuary. The metal concentrations were measured by means of inductively coupled plasma mass spectrometry. In mg.kg-1, the background values for Ba, Sr, Y, Sc, V, Cr_2O_3, Co, Ni, Cu, Zn, Ga, As, Rb, Nb, Sn, Cs, Ta, W, Hg, Pb, Bi, Th, and U were, respectively, 392.41, 133.29, 29.22, 12.80, 109.13, 0.008, 13.82, 22.69, 19.73, 75.09, 19.50, 14.77, 94.81, 15.62, 3.38, 6.59, 1.05, 1.82, 0.04, 19.02, 0.27, 13.25, and 3.57. The background geochemistry values for the region are an important tool for monitoring the metal concentrations and serve as a baseline for comparison with possible incidents of contamination with these elements on the Amapá coast.

To develop guidelines for environmental legislation, it is necessary to establish background levels of heavy metal concentrations in sediments and soils to distinguish natural source levels from those from anthropogenic sources. The background geochemistry is intrinsically dependent on geological characteristics such as mineral composition, grain size distribution, and organic matter content. Geochemical and statistical methods are some normalization methods to determine the background values for heavy metals. These are the main approaches described in the literature for determining concentrations of geochemical reference levels (Dung et al., 2013; Gałuszka and Migaszewski, 2011).

Sedimentation processes preserve the sedimentological and geochemical characteristics in a coastal environment (Dai et al., 2007; Watson et al., 2013). Thus, studies with sedimentary cores are a very effective method for determining background values for metals (Ho et al., 2012; Xavier et al., 2017b). The Amapá coastal zone shows several particularities in climatological, geological and oceanographic patterns, the high sedimentation rates, and the macro-tidal regimes (Allison et al., 1996; Xavier et al., 2017a), and it is among coastal environments with little anthropic intervention. Within the Amapá coastal zone are three environmental protection areas: the Piratuba Lake Biological Reserve (3570 km^2), the Maracá-Jipióca Ecological Station (720 km^2), and the Cape Orange National Park (6190 km^2) (Xavier et al., 2017a), making it a strategic area for the study and determination of background geochemical levels, and an important tool in the characterization of inputs from natural or anthropogenic sources during the sedimentation process (Galuszka, 2007).

With this premise, the present study aims to determine the background geochemical levels for the 23 elements classified as heavy metals (Ba, Sr, Y, Sc, V, Cr_2O_3, Co, Ni, Cu, Zn, Ga, As, Rb, Nb, Sn, Cs, Ta, W, Hg, Pb, Bi, Th, U) in order to establish a tool for monitoring studies of these elements in the Amapá coastal zone and in future studies in the Amazon region.

The Cuñaní Estuary is located in the north of the Amapá coastal plain. This estuary is approximately 80 km in length and discharges around 108 tons/day of liquid and solid material. In addition, this es-

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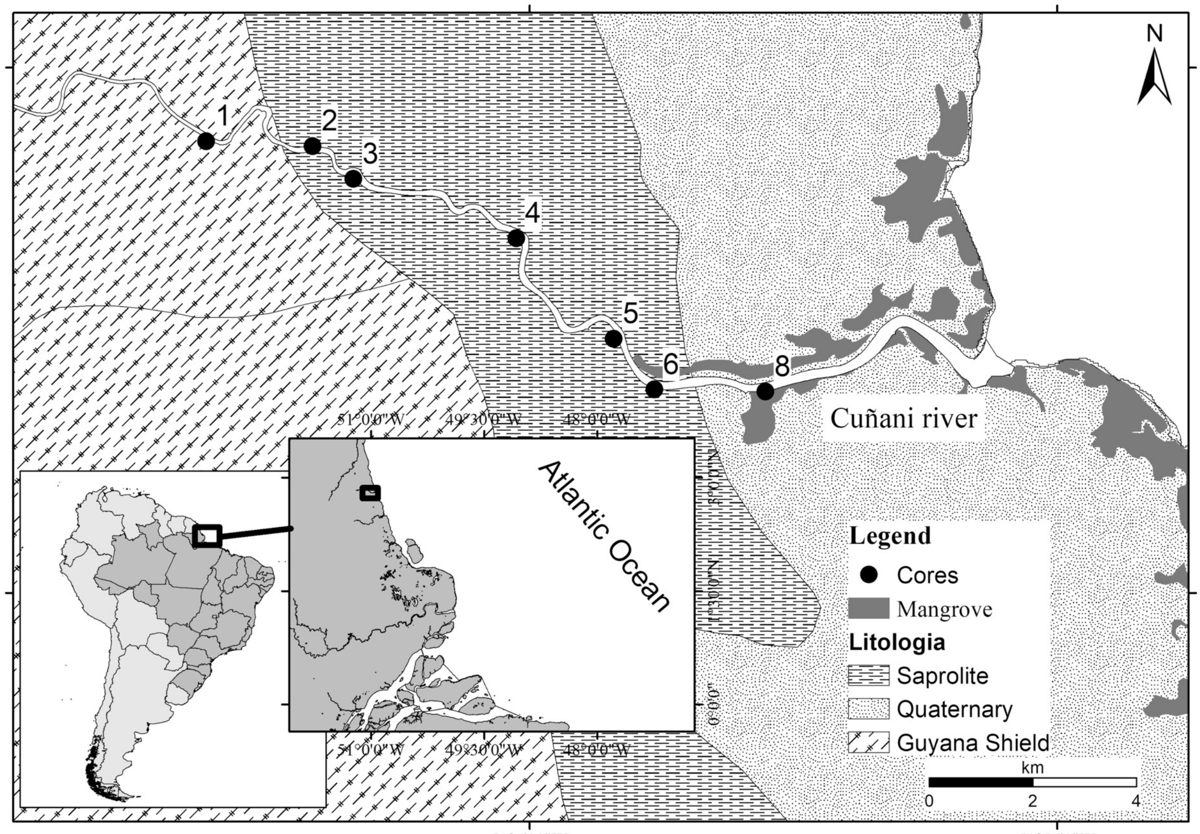

Fig. 1. Location of Cunaní estuary with the sample points along of estuarine system.

Table 1
Mathematical formule and classification for Enrichement Factor, Contamination Factor, Geoaccumulation Index and Potential Ecological Risk.

	Mathematical formule	Classification
Enrichment Factor (Szefer et al., 1998)	$EF = \frac{(C\,/\,Al)sample}{(C\,/\,Al)background}$ Where Csample is the metal concentrations in sample and Cbackground is metal background regional value	< 1 indicates no enrichment, < 3 is minor, 3–5 is moderate, 5–10 is moderately severe, 10–25 is severe, 25–50 is very severe and > 50 is extremely severe
Contamination Factor (Hakanson, 1980)	$CF = \frac{C_{metal}}{C_{Backgroung}}$ Where Cmetal is the metal concentration in sample and Cbackground is the metal background regional value	< 1 refers to low contamination; 1 ≤ CF < 3 means moderate contamination; 3 ≤ CF ≤ 6 indicates considerable contamination; and CF > 6 indicates very high contamination
Geoacumullation index (Müller, 1969)	$I_{geo} = \log_2 \frac{Cn}{1.5\,x\,Bn}$ Where Cn is the metal concentration e Bn is the metal background regional value	≤0 – unpolluted; 0 < Igeo < 1 – unpolluted to moderately polluted; 1 < Igeo < 2 – moderately polluted; 2 < Igeo < 3 - moderately to strongly polluted; 3 < Igeo < 4 - strongly polluted; 4 < Igeo < 5 - strongly polluted to extremely polluted; Igeo > 5 – extremely polluted.
Potential Ecological Risk (Hakanson, 1980)	$E_r^i = T_f^i \times C_f^i$ Where Eir is the coefficient of ecological risk potential e *Cfi* is the accumulating coefficient of element *i* and *Tif* is the toxic-response factor of element *I* (which reflects its toxicity levels and the sensitivity of bioorganism to it). The toxic-response factors for common heavy metals Zn = 1; Cr = 2; Co = Cu = Pb =5, Ni = 6, As = 10, Hg = 40.	E_r^i < 40 – low ecological risk; 40 ≤ E_r^i < 80 – moderate ecological risk; 80 ≤ E_r^i < 600 – considerable ecological risk; 160 ≤ E_r^i < 320 – very high ecological risk

Table 2
Descriptive statistic of heavy metals results of Cuñaní Estuary. All concentrations in mg.kg − 1.

Elements	Minimum–Maximum	Mean and standard deviation
Ba	275.00–450.00	384.71 ± 41.95
Sr	109.60–144.30	133.23 ± 6.71
Y	16.00–34.90	30.07 ± 2.92
Sc	6.00–18.00	13.51 ± 3.03
V	54.00–151.00	115.27 ± 24.55
Cr_2O_3	0.005–0.012	0.009 ± 0.002
Co	9.10–19.00	14.61 ± 2.43
Ni	12.30–28.50	22.29 ± 4.00
Cu	6.00–26.50	19.60 ± 5.20
Zn	46.00–93.00	75.05 ± 11.17
Ga	9.50–26.60	19.34 ± 4.53
As	7.10–22.10	15.72 ± 2.50
Rb	53.20–142.70	106.43 ± 22.52
Nb	7.80–18.90	15.45 ± 2.09
Sn	1.00–4.00	3.24 ± 0.77
Cs	2.60–11.10	7.53 ± 2.25
Ta	0.60–1.50	1.10 ± 0.13
W	0.80–2.90	1.87 ± 0.41
Hg	0.02–0.07	0.04 ± 0.01
Pb	8.60–27.10	20.34 ± 4.57
Bi	0.10–0.50	0.33 ± 0.09
Th	7.10–17.70	13.63 ± 2.27
U	1.70–4.50	3.48 ± 0.37

tuarine system is considered an importer of organic matter and sediment (Paulo et al., 2017) (Fig. 1). The Cuñaní Estuary is influenced by macro-tidal, asymmetrical, semi-diurnal tides with longer ebb periods. The climate is hot and humid, with two climatic periods: (i) the dry season from September to November, with precipitation around 50 mm per month; and (ii) the rainy season from February to March, with precipitation > 250 mm per month. The average annual temperature ranges from 24 °C to 26 °C, and relative humidity varies from 80 to 90% (Paulo et al., 2017).

As for geological characteristics, the Cuñaní Estuary is on the Guiana Shield, which is composed of granite rocks of the Archean and Cenozoic ages, with medium to coarse quartz granulation with mica and feldspar. Most of these granitic rocks are under heavy weathering, forming saprolites, predominantly clayey, and reddish-yellow or white in color (Paulo et al., 2017).

In addition to the Guiana Shield, Pleistocene deposits ranging in age from 30,000 to 80,000 years AP are present in the estuarine area. These deposits register two lithostratigraphy units: i) sandy terraces and sandy-clay terraces, both with intense oxidation, and ii) fluvium-marine and fluvium-estuarine plain deposits, the latter registering fine-grained sediments (silt and clay) (Bezerra et al., 2015).

For this study, eight sedimentary cores of approximately 70 cm depth were recovered along the Cuñaní Estuary (Fig. 1). In the laboratory, these cores were longitudinally sectioned and subsampled at 10 cm intervals, totaling 41 samples. The determination of metals followed the method Codes Lithogeochem Standard Package (W2 and WHG-1 standards), with the support of inductively coupled plasma mass spectrometry, performed in the Acme Analytical Laboratory (Canada).

The Al-normalized methodology was used to determine the values of the background geochemistry. This method consists of a regression analysis of metal concentrations by the aluminum values registered in the samples, assuming a 95% confidence level and significance of $p > .0001$ (Loring and Rantala, 1992; Roach, 2005). The background values were calculated by the averaging of all values within the 95% confidence level of regression analysis (Ho et al., 2012).

After determination of background geochemical values, the Enrichment Factor, Contamination Factor, Geoaccumulation Index, and Potential Ecological Risk were calculated for analysis of the subsurface distribution of geochemical anomalies to determine the influence of natural and anthropic sources (Table 1).

The ranges and mean and standard deviation of metal concentration are shown in Table 2. Similar values were recorded by Oliveira et al. (2015) and Siqueira et al. (2018) in studies conducted on the Amazon coastal zone.

All heavy metals analyzed showed a strong correlation between the elements and the aluminum concentrations in the samples (Figs. 2 and 3). The concentrations inside of the 95% confidence were used for determination the background values for the Cuñaní Estuary (see Table 3).

The Enrichment Factor recorded variation from no enrichment (EF < 1) to enrichment (EF > 3). The Contamination Factor ranged from low contamination (CF < 1) to moderate contamination (1 > FC < 3). Lastly, the Geoaccumulation Index recorded variation from not polluted (Igeo > 0) to not polluted-to-moderately-polluted (0 > Igeo < 1) (Table 4). The Enrichment Factor and Contamination Factor values of less than three, and Geoaccumulation Index of < 1, are generally associated with geogenic signatures (Förstner and Wittmann, 2012; Hasan et al., 2013), as observed for the Cuñaní Estuary.

The Ecological Risk for Zn, Cr_2O_3, Co, Cu, Pb, Ni, As, and Hg ranged from 0.61 to 1.24, 1.25 to 3.00, 3.29 to 6.87, 1.52 to 6.72, 2.26 to 7.12, 3.25 to 7.54, 4.81 to 14.96, and 20.00 to 70.00, respectively. Among all elements, only mercury showed a moderate Ecological Risk.

Some Amazon rivers recorded limit of 0.20 ppm of mercury in yours superficial sediments and were classified as non-contaminated. (Pfeiffer and de Lacerda, 1988). The mercury concentrations recorded for the Cuñaní Estuary are similar to those on the Amazonian internal continental shelf; the authors also affirmed that these values are associated with the geological formation and the high organic matter percentages present in sediments located in the Amazon coastal zone (Siqueira et al., 2018).

Most of the background values registered for the Cuñaní Estuary were below those of Turekian and Wedepohl (1961), except for Ga, As, Y, Nb, Cs, Ta, and Th. The elements that showed values above those of Turekian and Wedepohl (1961) may be influenced by two factors: i) the rare earth elements may be influenced by the formation of the local geology, predominantly by granitic rocks, and ii) the heavy metals may

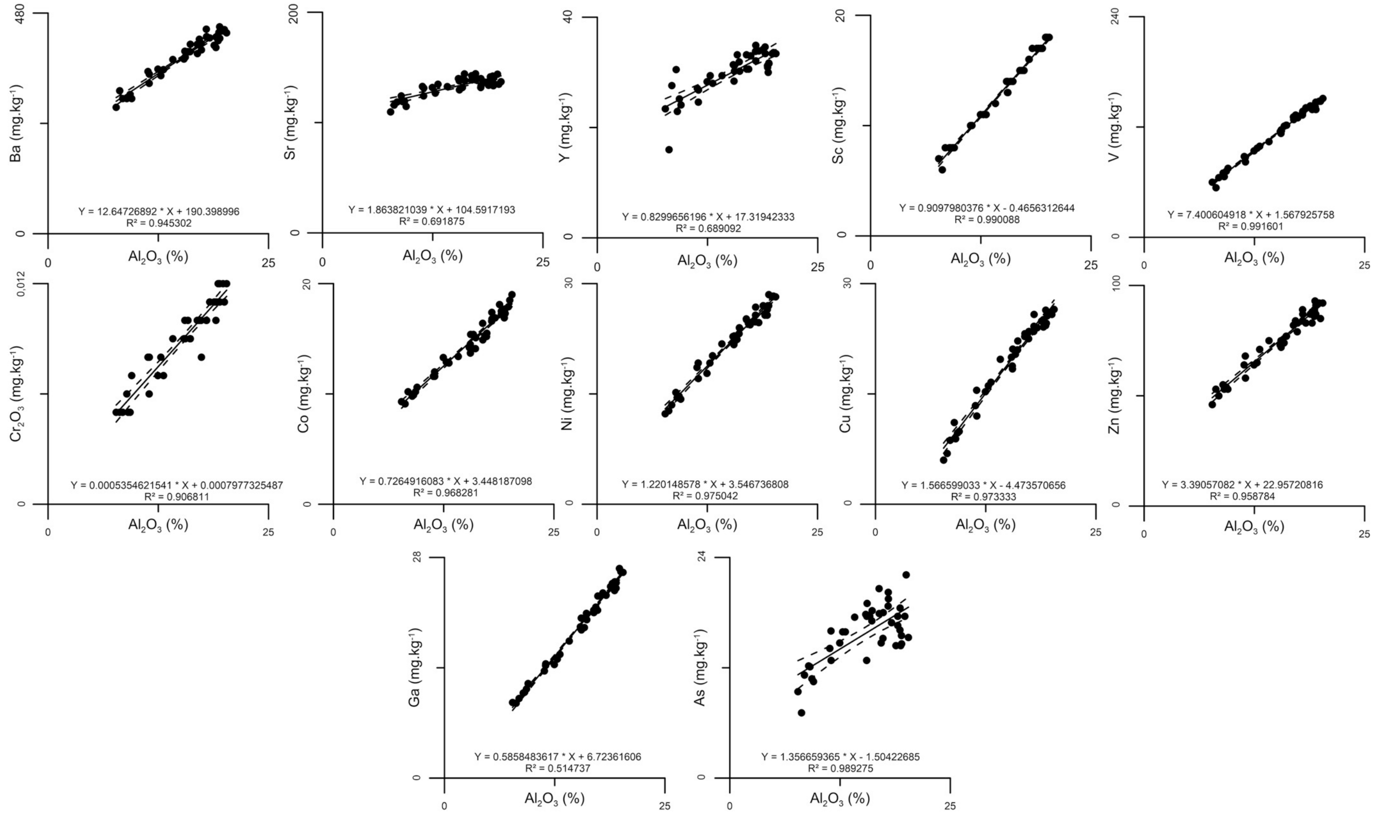

Fig. 2. Al-normalized results with 95% confidence for Ba, Sr, Y, Sc, V, Cr2O3, Co, Ni, Cu, Zn, Ga, As for Cuñani estuary.

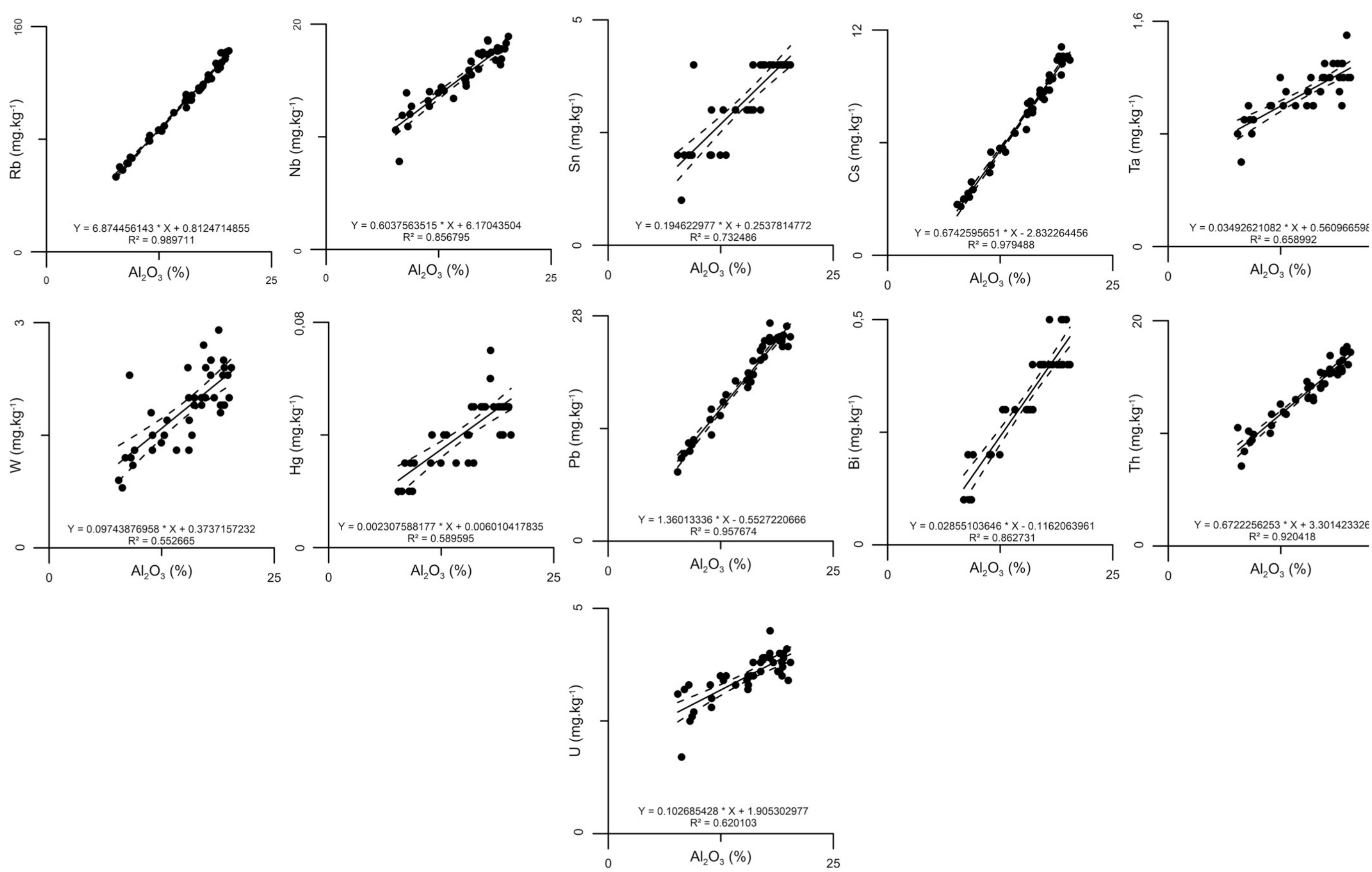

Fig. 3. Al-normalized results with 95% confidence for Rb,Nb, Sn, Cs, Ta, W, Hg, Pb, Bi, Th, U for Cuñani estuary.

Table 3
Heavy metals background geochemical records for the Cuñaní estuary.

Element	Background geochemical
Ba	392.41
Sr	133.29
Y	29.22
Sc	12.8
V	109.13
Cr_2O_3	0.008
Co	13.82
Ni	22.69
Cu	19.73
Zn	75.09
Ga	19.50
As	14.77
Rb	94.81
Nb	15.62
Sn	3.38
Cs	6.59
Ta	1.05
W	1.82
Hg	0.04
Pb	19.02
Bi	0.27
Th	13.25
U	3.57

be influenced by the amount of organic matter, with moderate correlations between carbon concentration and the elements Ga ($r^2 = 0.55$; $p > .001$), Cs ($r^2 = 0.54$; $p > .001$), Ta ($r^2 = 0.57$; $p > .001$), Th ($r^2 = 0.54$; $p > .001$) and strong correlations between carbon and As ($r^2 = 0.73$; $p > .001$) and Y ($r^2 = 0.73$; $p > .001$). Amazonian estuarine environments show retention characteristics of fine sediment and organic matter due to the presence of the mangrove environment along the Amazonian coastal region (Anthony et al., 2010), as observed in the Cuñaní River Estuary.

The background values determined in this study will be fundamental to assisting in the monitoring and identification of the possible sources contributing to the concentrations of metals in the Amapá coastal region. It is important to expand the studies of metals for the region because it is necessary to understand the behavior of these metals in this area, and to incorporate more data to obtain a better reading of reference levels for the region.

CRediT authorship contribution statement

Diego de Arruda Xavier: Writing - original draft, Formal analysis.**Valdenira Ferreira dos Santos:**Project administration, Resources.**Artur Gustavo Oliveira de Miranda:**Investigation.**José Francisco Berrêdo:**Conceptualization, Supervision.

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.

Table 4
The minimium, maximum, mean and standard deviation values for Enrichment Factor, Contamination Factor and Geoccumulation Index for Cuñaní Estuary. The mean and standard deviation values are inside of parenthesis.

Element	Enrichment Factor	Contamination Factor	Geoaccumulation Index
Ba	0.43–0.78 (0.53 ± 0.07)	0.70–1.15 (0.98 ± 0.11)	−1.10- -0.39 (−0.63 ± 0.17)
Sr	0.40–0.86 (0.55 ± 0.09)	0.82–1.08 (1.00 ± 0.05)	−0.87- -0.47 (−0.59 ± 0.07)
Y	0.42–0.93 (0.56 ± 0.09)	0.50–1.19 (1.03 ± 0.10)	−1.45- -0.33 (−0.56 ± 0.15)
Sc	0.46–0.59 (0.55 ± 0.01)	0.47–1.41 (1.06 ± 0.24)	−1.68- -0.09 (−0.57 ± 0.36)
V	0.49–0.58 (0.55 ± 0.01)	0.49–1.38 (1.06 ± 0.22)	−1.60- -0.12 (−0.56 ± 0.35)
Cr_2O_3	0.46–0.74 (0.59 ± 0.04)	0.63–1.50 (1.13 ± 0.22)	−1.26–0.00 (−0.46 ± 0.32)
Co	0.50–0.70 (0.56 ± 0.04)	0.66–1.37 (1.06 ± 0.18)	−1.19- -0.13 (−0.54 ± 0.25)
Ni	0.47–0.60 (0.52 ± 0.03)	0.54–1.26 (0.98 ± 0.18)	−1.47- -0.26 (−0.65 ± 0.29)
Cu	0.32–0.58 (0.51 ± 0.04)	0.30–1.34 (0.99 ± 0.26)	−2.30- -0.16 (−0.69 ± 0.47)
Zn	0.45–0.69 (0.53 ± 0.05)	0.61–1.24 (1.00 ± 0.15)	−1.29- -0.28 (−0.61 ± 0.23)
Ga	0.47–0.55 (0.51 ± 0.02)	0.49–1.36 (0.99 ± 0.12)	−1.62- -0.14 (−0.66 ± 0.38)
As	0.40–0.76 (0.57 ± 0.08)	0.48–1.50 (1.06 ± 0.17)	−1.64–0.00 (−0.53 ± 0.25)
Rb	9.56–0.63 (0.59 ± 0.01)	0.56–1.51 (1.12 ± 0.24)	−1.42–0.00 (−0.47 ± 0.34)
Nb	0.43–0.80 (0.53 ± 0.06)	0.55–1.29 (1.04 ± 0.13)	−1.59- -0.31 (−0.62 ± 0.21)
Sn	0.29–1.00 (0.50 ± 0.11)	0.30–1.18 (0.96 ± 0.23)	−2.34- -0.34 (−0.71 ± 0.38)
Cs	0.39–0.70 (0.58 ± 0.07)	0.39–1.68 (1.14 ± 0.34)	−1.93–0.17 (−0.51 ± 0.52)
Ta	0.39–0.85 (0.57 ± 0.09)	0.57–1.43 (1.05 ± 0.12)	−1.39- -0.07 (−0.54 ± 0.18)
W	0.37–1.13 (0.54 ± 0.08)	0.44–1.59 (1.03 ± 0.23)	−1.77–0.09 (−0.61 ± 0.35)
Hg	0.37–0.78 (0.54 ± 0.08)	0.50–1.75 (0.98 ± 0.24)	−1.58–0.22 (−0.60 ± 0.35)
Pb	0.47–0.63 (0.55 ± 0.02)	0.45–1.42 (1.07 ± 0.24)	−1.73- -0.07 (−0.55 ± 0.37)
Bi	0.00–0.82 (0.58 ± 0.11)	0.00–1.85 (1.17 ± 0.39)	−2.02- 0.30 (−0.39 ± 0.46)
Th	0.48–0.82 (0.55 ± 0.04)	0.54–1.34 (1.03 ± 0.17)	−1.49- -0.17 (−0.58 ± 0.26)
U	0.38–0.90 (0.53 ± 0.08)	0.48–1.26 (0.98 ± 0.10)	−1.66- -0.25 (−0.64 ± 0.16)

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