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**Geochemistry of selenium, barium, and iodine in representative soils of the
Brazilian Amazon rainforest**

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Abstract

The Amazon rainforest is a heterogeneous ecosystem and its soils exhibit geographically variable concentrations of trace elements. In this region, anthropic activities - e.g., agriculture and mining - are numerous and varied, and even natural areas are at risk of contamination by trace elements, either of geogenic or anthropogenic

origin. A reliable dataset of benchmark values for selenium (Se), barium (Ba), and iodine (I) concentrations in soils is needed for use as a reference in research and public policies in the region. In this study, 9 selected sites in the Brazilian Amazon rainforest within areas represented by Oxisols and Ultisols were assessed for relevant soil physicochemical characteristics, along with the concentrations of total Se (Se_{Tot}), total Ba (Ba_{Tot}), and sequentially-extracted soluble Se (Se_{Sol}) and adsorbed Se (Se_{Ad}) in 3 different soil layers (0-20, 20-40, and 40-60 cm). In addition, organically bound-Se (Se_{Org}) and total I (I_{Tot}) concentrations in the surface layer (0-20 cm) were measured. Soil Se concentrations (Se_{Tot}) were considered safe and are likely a result of contributions of sedimentary deposits from the Andes. Available Se ($Se_{Sol} + Se_{Ad}$) accounted for 4.5% of Se_{Tot} , on average, while Se_{Org} in the topsoil accounted for more than 50% of Se_{Tot} . Barium in the western Amazon (State of Acre) and central Amazon (Anori, State of Amazonas) exceeded national prevention levels (PVs). Furthermore, the average I_{Tot} in the studied topsoil (5.4 mg kg^{-1}) surpassed the worldwide mean. Notwithstanding, the close relationship found between the total content of the elements (Se, Ba, and I) and soil texture (clay, silt, and sand) suggests their geogenic source. Finally, our data regarding Se_{Tot} , Ba_{Tot} , and I_{Tot} can be used to derive regional quality reference values for Amazon soils and also for updating prevention (PV) and investigation (IV) values established for selected elements by the Brazilian legislation.

Keywords: total concentration; availability; Amazon soils; trace elements; geogenic; Quality Reference Values.

1 INTRODUCTION

The Amazon region in Brazil comprises approximately 4,500,000 km² of tropical rainforest in a hot and humid climate. This vast ecosystem is highly diverse not only in terms of biota but also in morphology, soil types, lithology, and rainfall patterns.

It is also known that limited representative pedogeochemical data exist to characterize the region in its entirety (Lima et al., 2014; Matschullat et al., 2020). Soils from the Amazon rainforest were formed from both ancient and recent parent materials under advanced weathering. The inheritance of trace elements' contents from parent material can be modified by pedogenesis. Therefore, pedogenic processes contribute to the enrichment, depletion, and mobilization of elements, such as barium (Ba), iodine (I) and selenium (Se) in the soil profile, and consequently to soil diversity in the Amazon rainforest (Souza et al., 2018).

Even though the nature of the parent material has an important influence on the total elemental addition in soil systems, sometimes anthropogenic activities, such as mining, smelting, agriculture, industrial and waste disposal, may have a much greater influence on the occurrence and distribution of trace elements (TE). For this reason, it is important to identify TE origin concerning natural (geogenic) and/or anthropogenic sources in order to manage soil quality and reduce exposure risk from the long-term accumulation (Duplay et al., 2014). Thus, the geochemical similarity between surface and subsurface soil layers and also significant correlations between TE and other soil physicochemical attributes would indicate a dominant geogenic (or natural) origin of the studied elements, which is mostly related to the local variability of the parent materials, with less (or insignificant) influence from anthropogenic activities (Sahoo et al., 2019).

Selenium can be both hazardous and beneficial to plants, animals, and humans. The biogeochemical behavior of Se and its environmental impact on the soil-plant-human system has received wide attention in the last decades (Yang et al., 2022). Soil Se concentration is highly variable and dependent on site-specific characteristics such as soil type, geological and climatological settings (Nascimento et al., 2021). Therefore, Se variation in a particular environment reflects not only soil-forming processes but also

atmospheric deposition that can be influenced by the ocean, which is a sink for atmospheric Se (Feinberg et al., 2020). Total Se concentrations in Brazilian soils are reported to range from <0.09 to 5.97 mg kg^{-1} (Gabos et al., 2014; Matos et al., 2017; Silva Junior et al., 2017; Reis et al., 2017).

Total Se concentration in soil is an inaccurate predictor of its availability for crops. Therefore, to obtain information on Se potential for accumulation by plants and other organisms (i.e. solubility and bioavailability), a chemical extraction procedure has to be applied to understand the possible impacts on the soil ecosystem and the general environment. Selenium in different fractions displays various degrees of mobility and availability, based on its binding strength, and is reflected in its extractability from the soil solid phase (Feudis et al., 2019).

Another vital trace element in living systems is iodine (I), which is a component of thyroid hormone synthesis in humans and also very important for grazing animals, yet its essentiality to plants is still a matter of debate (Nascimento et al., 2022). Various effects of I on human health have been reported, with many of them being closely related not only to normal thyroid function but also to the physical and brain development of children (Powley et al., 2019; Wang et al., 2020). The average I content of worldwide soils is estimated as 2.8 mg kg^{-1} (Kabata-Pendias, 2011). Its accumulation in surface and subsurface soil horizons is affected by aerial deposition and biogenic concentration and the atmosphere is a basic source of I in soils. The ocean is the reservoir from which all of the atmosphere I is drawn (Kabata-Pendias, 2011; Fuge and Johnson, 2015). Limited data are available on I distribution in tropical soils and particularly under the Amazon rainforest. Since forest soils, in general, contain reasonable amounts of organic matter (OM), they could be an important terrestrial

reservoir of I, considering that OM content plays the most important role in soil I retention in the environment (Duborská et al., 2020).

Barium is a dense alkaline earth metal considered to be a non-essential element for organisms in general. Barium exposure may cause multiple deleterious effects in animals and humans, including damage to the cardiovascular, renal, respiratory, hematological, nervous, and endocrine systems and eventually resulting in death (Kravchenko et al., 2014; Lu et al., 2019). Barium is not very mobile in soil because it is easily precipitated as sulfates and carbonates, and also strongly adsorbed by clays. Its concentration in surface soils varies from 10 to 1500 $\mu\text{g kg}^{-1}$ (Kabata-Pendias, 2011). Evidence suggests the presence of hollandite ($\text{Ba}_2\text{Mn}_8\text{O}_{16}$) in soils of the southwestern Amazonia, which is the possible cause of the origin of soils with high Ba concentrations and the reason for the high accumulation of this element in Brazil nuts (Silva Junior et al., 2022).

The Brazilian National Environment Council established prevention values (PVs) in soil for Se as 5 mg kg^{-1} and Ba as 150 mg kg^{-1} . The PV is the maximum limit concentration of a given element in the soil, such that it is able to sustain its main environmental functions. The national legislation establishes 3 reference levels: 1-Quality reference (normal); 2-Prevention (needs attention); and, 3-Investigation (needs remediation) (CONAMA, 2009). For I there is no reference value established by the Brazilian legislation, but it is believed so far that I does not present a health risk of toxicity for the population at the natural levels occurring in Brazilian soils, and in fact, there is a widespread I deficiency throughout the country and prevalent particularly in the states of the legal Amazon (Cesar et al., 2020). For Se and Ba, on the other hand, there are reports showing levels that exceed the prevention value in certain locations,

although toxicity for organisms has not been reported (Biondi et al., 2011; Matos et al., 2017).

The present study had the objectives of 1) assessing the geochemistry and availability of Se, I, and Ba in soils from representative sites of the Brazilian Amazon; and, 2) comparing the total values reported for the above-mentioned elements with national quality reference values that establish the contamination levels for soils in Brazil. We hypothesize that the typical levels of these elements found in soils from the Amazon are not toxic for the environment considering the national guidelines and present a dominant geogenic source. Additionally, we reinforce the need to update the reference values established for these TE on regional and national scales. We further contribute by studying the major soil physical and chemical attributes that drive the variation in Se, Ba, and I concentrations and how they are interrelated on different sites and soil layers in the Brazilian Amazon rainforest.

2 MATERIALS AND METHODS

2.1 Study design

A total of 414 soil samples including three different soil layers (0–20, 20–40, and 40–60 cm) from 9 sites were used for physical and chemical soil characterization, and for evaluating total Ba, total Se, as well as soluble and adsorbed Se fractions. Moreover, for assessing organic-bound Se and total I (both extracted by tetramethylammonium hydroxide-TMAH) 138 topsoil (0–20 cm) samples were used, which were all collected in the same aforesaid sites. Correlation and regression analyses were performed to make inferences about soil environmental controls and relationships with Se, Ba, and I in soils.

2.2 Study area and soil sampling characterization

Soil samples were collected from nine sites belonging to the Amazon rainforest ecosystem in Brazil. Information about the sampling sites, soil classification, coordinates, altitude and Köppen climate classification is presented in **Table S1** of the supplementary material. In order to better understand the position of each site in the Amazon region, they were grouped taking the Amazon River mainstream as a reference: Northern Amazon: Caracaraí - state of Roraima (RR) and Laranjal do Jari – state of Amapá (AP); Southern Amazon: Itaúba - state of Mato Grosso (MT) and Porto Velho – state of Rondônia (RO); Western Amazon: Sena Madureira – state of Acre (AC:SM) and Xapuri – state of Acre (AC:XP); and Central Amazon: Anori – state of Amazonas (AM:AN), Itacoatiara – State of Amazonas (AM:AR) and Santarém – state of Pará (PA).

The dominant lithology in the region is formed by Pleistocene Detritic-Lateritic Cover, with pelitic and psammitic sediments from Cenozoic deposits in the Solimões Formation (Bernini et al., 2013) sandy sediments of Neogene age enriched in quartz in the Barreiras group (Gloaguen and Passe, 2017), and fine to medium sandstone, clayey, unconsolidated and eventually conglomeratic units (Tapajós and Trombetas Groups) covered by quaternary deposits in the Alter do Chão formation (Carvalho et al., 2014).

At each site, samples were taken at 15 points in the native Amazon rainforest, except for AM:AR, where 18 points were sampled in the Aruanã farm (Itacoatiara), a commercial Brazil nut plantation. Soil samples were collected between 2014 and 2017. The soil was sampled manually at each site with a soil auger (Sondaterra, Piracicaba, São Paulo State, Brazil) at three different depths (0–20, 20–40, and 40–60 cm) after removing surface litter material. The sampling method is described in details by Silva Junior et al. (2017).

2.3 Soil physical and chemical characterization

Soil samples were dried at room temperature, ground, sieved (< 2 mm) and subjected to chemical and physical (textural) analysis. Soil pH was determined potentiometrically in water (pH H₂O) in the ratio 1:2.5 soil/solution. The exchangeable cations (Ca²⁺, Mg²⁺, and Al³⁺) were obtained by extraction in 1.0 mol L⁻¹ KCl. Sulfur was extracted (as S-sulfate) with monocalcium phosphate [Ca(H₂PO₄)₂, 500 mg L⁻¹ of P] in acetic acid (CH₃COOH, 2 mol L⁻¹, pH 2.2). Available P, Na, K, and micronutrients (Fe, Zn, Mn, and Cu) were obtained by extraction in Mehlich-1 (0.05 mol L⁻¹ HCl + 0.0125 mol L⁻¹ H₂SO₄; in 1:10 soil/solution ratio). Potential acidity (H + Al) was estimated indirectly through the SMP pH method (Shoemaker et al., 1961). Exchangeable aluminum (Al³⁺) was determined by titration with sodium hydroxide (0.025 mol L⁻¹ NaOH) using phenolphthalein as indicator (1.0% m v⁻¹ in ethanol). Phosphorus (P) was determined colorimetrically, potassium (K) by flame emission photometry, sulfur (S) by turbidimetry, and Ca, Mg, Zn, Fe, Mn, and Cu were determined by atomic absorption spectrometry (AAS). The organic matter content was determined by the oxidation of the organic matter in the soil with potassium dichromate solution (0.0667 mol L⁻¹ K₂Cr₂O₇) in the presence of H₂SO₄ (Carter and Gregorich, 2006). The Sum of bases (SB), cation exchange capacity at pH 7 (CEC_{Pot}), effective cation exchange capacity (CEC_{ef}), base saturation (BS%), and aluminum saturation (m%) were calculated based on the results of the chemical analyses. The particle size analysis (clay, silt, and sand) was performed according to the hydrometer method, as described by Embrapa (1997).

2.4 Determination of selenium, barium, and iodine

Total Se (Se_{Tot}) and Ba (Ba_{Tot}) analyses were performed in air-dried and < 2 mm sieved soil samples. A portion of each soil sample was finely ground (< 0.45 mm) using an agate ball mill (Retsch PM 400 mill). Soil samples (~0.2 g DW) were fully digested in 70% HF, 70% HNO₃, and 60% HClO₄ (TAG; Fisher Scientific UK Ltd), using perfluoroalkoxy (PFA) digestion vessels and a 48-place Teflon-coated graphite digester block (Model A3, Analysco Ltd, Chipping Norton, UK) (Chilimba et al., 2011). The digestion programs are detailed in **Table S4**.

Soluble (Se_{Sol}) and adsorbed (Se_{Ad}) Se were sequentially extracted with 0.01 mol L⁻¹ KNO₃ being used for the soluble fraction, and 0.015 mol L⁻¹ KH₂PO₄ for the adsorbed fraction (Ligowe et al., 2020).

The analytical determinations of Se_{Tot} , Se_{Sol} , Se_{Ad} , and Ba_{Tot} were performed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, X-Series II, Thermo Fisher Scientific).

The tetramethylammonium hydroxide (TMAH) extraction of soil to fractionate Se in the organic matter (Se_{Org}) and to extract total I (I_{Tot}) was performed as a “stand-alone” method, and therefore, performed in a single step of preparation following the extraction method proposed by Watts and Mitchell (2009). Samples from topsoil (0–20 cm) were selected because of the expected higher organic matter content and presence of Se and I linked to this layer. Analyses of all TMAH extracts were performed using ICP-MS (Thermo-Fisher Scientific X-series II).

Data for Se_{Tot} , Se_{Org} , I_{Tot} , and Ba_{Tot} concentration in soils are reported on a dry weight basis (DW) and expressed in mg kg⁻¹. Data for Se_{Sol} and Se_{Ad} are expressed in µg kg⁻¹. Additional details concerning the determination of Se, Ba, and I are presented in section 2 of the supplementary material.

2.5 Statistical analysis

A descriptive analysis of Se_{Tot} , Ba_{Tot} , Se_{Sol} , and Se_{Ad} (0–20, 20–40, and 40–60 cm layers), as well as Se_{Org} and I_{Tot} (0–20 cm layer) concentrations was carried out. Box plots were used to display data distribution and compare sites and layers. After verifying the significance of effects through ANOVA, the mean values for Se_{Tot} and Ba_{Tot} concentration in soils were compared among layers using Tukey's HSD test with the package `emmeans v 2.23` (Lenth, 2019) in R 3.6.2 (R Development Core Team, 2020). Logarithmic transformations were used whenever data did not meet statistical assumptions for the ANOVA. Generalized least squares (GLS) was used for the log-transforming of the I_{Tot} data, in order to allow the variance to be estimated separately for each site and to avoid heteroscedasticity of the residues, before proceeding to ANOVA (Cleasby and Nakagawa, 2011).

The data from the 0–20 cm layer was submitted to Spearman correlation analysis, which was performed for all 6 main variables studied (Se_{Tot} , Se_{Sol} , Se_{Ad} , Ba_{Tot} , Se_{Org} , and I_{Tot} , denoted as response variables) and other relevant soil physicochemical properties (denoted as explanatory variables). The following procedure was applied for each response variable: 1) Select explanatory variables to obtain a list of candidates for the multiple linear regression model based on the significance ($p \leq 0.05$) and correlation coefficient ($|r| \geq 0.4$) of each candidate in the Spearman correlation matrix (**Fig. S1** of the supplementary material); 2) For the multiple linear regression model, the raw data was submitted to log-transformation in order to attend parametric statistical assumptions (normality and homoscedasticity) whenever necessary, and the best combination of explanatory variables was obtained with regression by leaps and bounds approach using the branch and bound algorithm (Furnival and Wilson Junior, 2000; Zhang et al., 2014). The criteria used for the selection of best explanatory variables combination was the

minimum Mallow's Cp (equivalent to Akaike information criteria - AIC) (Darnius and Tarigan, 2018). The non-multicollinearity of the explanatory variables was checked with the variance inflation factor ($VIF < 5$) and removed from the regression equation whenever necessary. The Spearman correlation and multiple regression model analyses were performed using R 3.6.2 (R Development Core Team, 2021).

3 RESULTS AND DISCUSSION

3.1 Relevant soil physicochemical properties and classification

The soils from the 9 sites were classified according to the Brazilian Soil Classification System (SiBCS) (Santos et al., 2018) as follows: Yellow Latosol (LA), Red Latosol (LV), Red-Yellow Latosol (LVA), and Red-Yellow Argisol (PVA). They correspond to Anionic Acrudox, Typic Hapludox, Xanthic Hapludox, and Typic Hapludult, respectively, according to the US Soil Taxonomy (Soil Survey Staff, 2014), which would be generically represented by Oxisols and Ultisols (**Table S1**).

The topsoil samples (0-20 cm) showed acidic pH mostly and ranged from 3.2 to 6.1. Despite the considerable wide range, most sites had an average pH around 4, which is considered acidic (Alvarez et al., 1999). Organic matter concentration ranged from 0.75% to 3.8% with the highest average percentage observed at site AM:AR (2.6%) and lowest at site AP (1.2%), which is explained directly by their contrasting clay content. Soil texture, as an important physical factor used to distinguish soil classes, also reflected the great variability amongst the studied soils. With clay contents ranging from 12 to 85% and sand from 4 to 82%, the particle size analyses demonstrated that the dominant soil textures were clay and sandy loam (**Fig. 1**). For the cation exchange capacity of the soil (CEC_{Pot}), the highest average value by far was observed at site AM:AN (22.6 $cmol_c dm^{-3}$), but values ranged from 3.5 to 52.4 $cmol_c dm^{-3}$ over all the

sites and 7 out of 9 sites studied had average CEC_{Pot} lower than $10 \text{ cmol}_c \text{ dm}^{-3}$. The available elements P (ranging from 0.8 to 6.2 mg kg^{-1}) and S (ranging from 2.28 to 38 mg kg^{-1}) also presented a wide variation among the sites studied, but the averages for P are still considered very low ($< 4 \text{ mg kg}^{-1}$) given the clay percentage below 60% in most sites studied (Alvarez et al., 1999). Aluminum saturation (m) ranged from 0 to 96% and presented notably the lowest average in the site AP (7%), which was directly associated with the higher average pH observed in this site (**Fig. 1**).

Regarding the clay mineralogy, the typical soils from the Brazilian Amazon are dominated by kaolinite, gibbsite, iron oxides, and small amounts of 2:1 aluminosilicate clay minerals (Kitagawa and Moller, 1979). Using the estimation of the CEC of the clay for the soils from the 9 sites studied in the present research, we inferred about the predominant mineralogy of these soils. **Table S2** shows that the sites from the western Amazon (AC:SM, AC:XP) and AM:AN all presented values for CEC of the clay $\geq 27 \text{ cmol}_c \text{ kg}^{-1}$, and therefore the clay fraction mineralogy is dominated by 2:1 clay types (for example montmorillonite, vermiculite and illite eventually). For the other sites studied, the predominant clay mineralogy was reported to be dominated by 1:1 (kaolinite) and Fe and Al oxides, since the CEC of the clay was on average $< 27 \text{ cmol}_c \text{ kg}^{-1}$ (Lepsch et al., 2011). These results are in agreement with a previous report by Marques et al. (2002), who observed the presence of smectite, vermiculite, and hydroxy-interlayered smectite as a result of sedimentary additions, precipitation from solution, and transformation from primary 2:1 minerals in soils from the western Amazon. Matschullat et al. (2020) had also noticed such variability in Amazon basin soils and observed that soils from the Central Amazon basin seemed to be slightly more weathered than in the South and that the higher precipitation in the former region likely explained this finding. This is relevant, as higher precipitation in the Central Amazon

may impact plant-soil interactions and relative enrichment/depletion of trace elements in soils.

3.2 Total selenium and barium concentration in soil

Selenium concentrations (Se_{Tot}) in soils ranged from 0.05 to 2.5 mg kg⁻¹ (average of 0.8 mg kg⁻¹), which represented a considerable variation among the 9 sites studied (**Fig. 2**). Given the values of Se_{Tot} observed, even the highest concentrations are still lower than the prevention value (PV) of 5 mg kg⁻¹ established by the Brazilian National Environmental Council (CONAMA, 2009). Therefore, Se levels can be considered safe on these studied sites. Considering the soil classification coverage in the sites studied, the soils classified as LA (Yellow Latosol) presented the highest average Se concentration (1.25±0.52 mg kg⁻¹) and the IV (Red Latosol) presented the lowest average Se concentration (0.20±0.03 mg kg⁻¹) (**Fig. S2**). Such difference may be related to the particular mineralogy of each soil class and the CEC of the clay, which leads to lower Se retention when the CEC increases (**Table S3**).

Selenium (Se_{Tot}) in the topsoil layer (0–20 cm) was positively correlated with all three Se fractions studied (Se_{Sol} , Se_{Ad} , and Se_{Org}), as well as with I_{Tot} , S, and clay, and negatively correlated with Ba_{Tot} , K, and sand in the soils (**Table 1**). In the multiple regression, the best predictive equation ($R^2 = 0.81$) showed that the soil attribute contributing most to the model was clay (**Table 2**). Selenium concentration in soils from the Jequitinhonha Valley (MG), Brazil, correlated significantly and positively with Al_2O_3 ($r = 0.76$), Fe_2O_3 ($r = 0.57$), and clay ($r = 0.64$) and negatively with SiO_2 ($r = -0.76$) and sand ($r = -0.54$) (Matos et al., 2017). Therefore, clay mineralogy and its content are widely acknowledged as soil attributes playing an important role in Se retention.

Comparatively, in a previous study conducted with soils from Eastern Amazon, the range of Se concentrations were lower than the values observed in the present study (Fernandes et al., 2018). Selenium concentrations reported in soils from the northeastern region in Brazil by Nascimento et al. (2021) were related to the degree of weathering and contents of organic matter and clay, with Gleysols presenting the highest mean Se concentration because of the reducing soil conditions that lead to organic matter accumulation. Gabos et al. (2014) observed a range of Se concentrations more similar to the ones obtained in the present study, despite having a much lower mean concentration. On the other hand, Matos et al. (2017) reported a wider range of Se concentrations. The authors also noticed that the average concentration slightly increased from the A horizon (1.1 mg kg^{-1}) to the B horizon (1.2 mg kg^{-1}), which was also a behavior observed for Se in some sites in the present study (**Table 3**).

Barium (Ba_{Tot}) presented overall concentrations ranging from 8 to 765 mg kg^{-1} , with a relatively low average (107 mg kg^{-1}), which indicated the presence of abnormally high concentrations in the sites from western Amazon (AC:SM and AC:XP). The site AC:XP (western Amazon) presented the highest median concentration and the site with the lowest median concentration was MT (southern Amazon). In terms of distribution in depth, the sites did not present significant difference between the layers studied, except for the site AC:XP where the concentrations decreased from the top to the bottom, which reflected a quite homogenous distribution of Ba as a function of soil depth (**Fig. 3**). On the other hand, for spatial distribution, Ba in soils of the Amazon rainforest is not homogeneous but rather concentrated in "nuggets", which might explain the wide range of concentrations within the sites studied (McBride et al., 2014). The Ba_{Tot} concentrations presented wide variation between and within soil classes as noticed by the difference between PVA (Red-Yellow Argisol) - with an average of

206±134 mg kg⁻¹ - and the other 3 soil classes, which presented average values more than 6-fold lower than the first (**Fig. S2**). The Red-Yellow Argisol was the class with the highest estimated clay activity (higher clay CEC) (39.1±26.3 cmol_c kg⁻¹) and therefore, the predominant mineralogy type was 2:1 (**Table S3**). Such high clay CEC may explain the higher Ba_{Tot} because of the higher retention of Ba cations by these soils.

Barium (Ba_{Tot}) in the 0-20 cm soil layer was positively correlated with Se_{Sol}, K, Al, CEC_{ef}, Zn, and silt; and negatively correlated with all the main response variables studied (Se_{Tot}, Se_{Ad}, Se_{Org}, and I_{Tot}) and other soil attributes such as OM, S, and clay (**Table 1**). In the multiple regression equation ($R^2 = 0.87$), the greatest positive contribution was given by the CEC_{ef} value, which means that negatively charged geocolloids in the soil contribute to the retention of Ba in the studied sites. The positive contribution of silt in the equation might be an indication that less weathered soils such as those from the State of Acre (AC:XP and AC:SM) tend to have higher total Ba concentrations (**Table 2**). Barium demonstrates low affinity to soil organic matter, which is due to the low affinity of the Ba²⁺ cation for the binding sites of organic compounds, explaining the negative correlation found in our results (Magalhães et al., 2011).

There are no quality reference values for contaminants established specifically for soils from the Amazon region, which should be derived for each state or sub-region at least. Background levels of Ba_{Tot} above the prevention and investigation values established by CONAMA (2009) were reported by Biondi et al. (2011) in soils from the State of Pernambuco, raising concerns on the need of research to investigate these values at regional levels to update the national standards (**Table 3**). In the present study, in some cases such as the soils from the State of Acre (AC:SM and AC:XP) and the

State of Amazonas (AM:AN), the average soil Ba concentrations were higher than the prevention level established by the Brazilian Legislation (150 mg kg^{-1}), yet these findings may not necessarily represent contamination for these soils. Again, this demonstrates the need to update and create reference values that are more representative for the region, based on studies considering properly the pedology and geochemical specificities of the soils from the Amazon biome.

High concentrations of Ba_{Tot} found in soils from the Amazon rainforest (i.e. anomalous values higher than the prevention level in the western Amazon) are presumably not harmful to the native plants or other organisms, considering that concentrations above 600 mg kg^{-1} have been reported to reduce slightly the production of soybean in an Entisol (Melo et al., 2011) and that we observed only a few samples above this value. Although Ba_{Tot} concentrations can serve as a reference for general Ba status in soils, correlations between Ba_{Tot} in soil and plant uptake seem to be poor because Ba solubility in soils is low and dependent on several soil properties (Melo et al., 2014).

Another environmental factor that demonstrates influence on the heterogeneous distribution of Se and Ba in soils from the Amazon is the rainfall intensity since the weathering is connected with the precipitation and soil moisture (Matschullat et al., 2020). An elemental enrichment/depletion in different subregions of the Amazon was observed as the abundance of Se and Ba in the studied sites reflected this variation. We observed higher Se/lower Ba concentrations in the sites from central Amazon and higher Ba/lower Se concentrations in the sites from western Amazon (**Fig. 2 and 3**). Additionally, the significative and often high correlations observed between Se and Ba concentrations and other soil physical and chemical properties for soils with different parent materials is attributed to the pedogenic process, indicating that the observed

anomalies (higher Ba_{Tot} in the western amazon) and particular geographical distribution (higher Se_{Tot} in sites from Central Amazon and closer to Amazon main river stream) are strictly related to geogenic control (Souza et al., 2018; Sahoo et al., 2019).

3.3 Soluble and adsorbed soil selenium

Extractable Se in the soil ($Se_{Sol} + Se_{Ad}$) decreased from the topsoil (0–20 cm) to the deepest layer (40–60 cm), with a few exceptions, and also presented a wide variation among sites and layers studied. For Se_{Sol} , the absolute concentrations ranged from 1.7 $\mu\text{g kg}^{-1}$ to 20.3 $\mu\text{g kg}^{-1}$ with an average value of 6.7 $\mu\text{g kg}^{-1}$. The Se_{Ad} data ranged from 4.4 $\mu\text{g kg}^{-1}$ to 50.8 $\mu\text{g kg}^{-1}$ with an average value of 17.3 $\mu\text{g kg}^{-1}$. The results also confirmed that Se_{Ad} in the soil was higher than Se_{Sol} in the sites studied (**Fig. 4**). Remarkably, despite not having the highest total soil Se, the available fraction (soluble + adsorbed) was higher for the site AP (**Fig. 4**), which coincides with the site with the highest average soil pH observed (**Fig. 1**). These findings confirmed that soil pH plays a major role in Se availability for plants, which is not necessarily related to total soil Se concentration. In the same context, a high accumulation of Se in Brazil nuts was previously observed in the same site (Silva Junior et al., 2017), which was already attributed to the direct effect of pH in the availability of soil Se.

The relative concentrations extracted by KNO_3 and KH_2PO_4 were quite variable among sites and layers studied. Moreover, it is important to mention that while the relative occurrence in the soluble (KNO_3) fraction decreased from the topsoil to the deepest layer on average (35.9% > 28.6% > 25.7%), the relative occurrence in the adsorbed (KH_2PO_4) fraction increased from the 0–20 cm to the 40–60 cm layer (64.1% < 71.4% < 74.3%) (**Fig. 4**). Such results reflected the behavior of Se in tropical soils and its relationship with the geocolloidal surface charges. It is possible to deduce that

because of the lower and decreasing amount of negative charges in soil colloids in deeper layers, Se may be transferred from the Se_{Sol} pool to the Se_{Ad} pool due to the increasing positive charges provided by Fe and Al oxides in the clay fraction.

The overall average percentage of extractability in soils from the Amazon (available = Se_{Sol} + Se_{Ad} fractions) ranged from 1.1% to 10.6% (mean = 4.5%). The extractability was generally higher for the topsoil (0-20 cm) than for the deeper layers studied (20-40 and 40-60 cm) (**Fig. S3**). Considering the highly weathered soils from the Brazilian Amazon rainforest, the predominance of Fe and Al oxides (gibbsitic and goethitic soils) combined with low pH (acidic soils) (Souza et al., 2018) are likely to play a major role in Se adsorption, controlling the soluble and adsorbed fractions, particularly in deeper layers where there is low organic matter content.

The Se_{Sol} and Se_{Ad} in the topsoil (0-20 cm) presented different behavior in terms of correlated variables. Despite Se_{Sol} being dependent on the Se_{Ad} fraction, the first one is more dynamic and responds faster to external influences. For example, while Se_{Sol} was positively related to soil pH, the Se_{Ad} was not. The Se_{Sol} data was also positively correlated to Ca. The multiple regression model for Se_{Sol} considered pH as the only significant variable and explained only 27% of the variation in Se_{Sol} contents. Moreover, Se_{Ad} was positively related to S and clay and negatively related to K and Al. Clay had a major positive contribution to Se_{Ad} while K contributed negatively to the regression model, which explained 62% of the variation in Se_{Ad} contents in the soils studied (**Table 1 and 2**).

Zhang et al. (2019) presented available soil Se as the sum of soluble and exchangeable Se fractions. Moreover, they showed significant correlations between Se in soil and Se in plant tissues (grain, leaf, and roots) in their experiment. The bioavailable form of Se in soil (soluble and adsorbed/exchangeable) is the most

dynamic and important pool of Se in terms of environmental cycling. The Se represented by the more mobile fractions (soluble and adsorbed) in the present study demonstrated a pool that can be lost more easily through leaching for example (Zhai et al., 2019), than when compared with a fraction more strongly bound to clay such as the organic-bound fraction.

3.4 TMAH extractable selenium and iodine

Concentrations of Se_{Org} in soil samples studied (0–20 cm layer) ranged from 0.05 to 1.6 mg kg⁻¹ (average 0.5 mg kg⁻¹) (**Fig. 5**). The Se_{Org} in soil comprised in general more than 50% of the Se_{Tot} in the topsoil of the sites studied.

Long et al. (2018) observed values for the organic Se fraction in the 0-20 cm layer of 4 sites in China, ranging from 30–40% from the total Se, which is below the values observed in our present study, but it still supports the significant association between Se and organic matter. The mechanism behind this association is the capacity of the plants to take up available Se from the soil, bioconcentrate the locally available Se in their tissues and return it as organic Se after its death and decomposition in the soil (Pilon-Smits, 2019).

The Se_{Org} was highly correlated with Se_{Tot} in soil ($r = 0.95$), which reflects its major importance and association with Se content behavior in soils from Amazon. Among the soil physicochemical attributes, Se_{Org} was positively correlated to S and clay, and negatively correlated to K and sand. The multiple regressions followed the same pattern ($R^2 = 0.79$), with the greatest contribution provided by clay (**Table 1 and 2**). Organic matter plays a key role in Se retention and partitioning between solid and liquid phases by forming organo-mineral associations that may protect adsorbed Se

from leaching and/or create anoxic zones (aggregates) where Se is immobilized after its reduction (Tolu et al., 2014).

For I_{Tot} in soil samples, the concentrations ranged from 0.7 to 14.2 mg kg⁻¹ (0–20 cm) with an overall average of 5.4 mg kg⁻¹ (**Fig. 5**). Considering the soil classes, I_{Tot} presented similar behavior of Se, with the highest average for the LA (Yellow Latosol) - 7.78±2.84 mg kg⁻¹ - and the lowest average for the LV (Red Latosol), with 2.28±0.34 mg kg⁻¹ (**Table S3 and Fig. S2**). Such behavior may be related to the clay mineral type and CEC of the clay fraction (Hong et al., 2012), which was twice as great in the LV when compared with the LA soils. Such results reinforce that the higher the CEC of the clay, the lower the possibility of retention of I anions in soil colloids of the Amazon biome.

Roulier et al. (2019) reported a wider range of I concentrations among sites in the 0–40 cm layer of French forest soils (**Table 3**). Their results confirmed that OM, Fe and Al (hydr)oxides produced greater retention of I in the soil and they stated that the fate of I in forest soils depends not only on soil properties but also on vegetation and climatic conditions. Many I_{ex} concentrations are of similar magnitude as those seen in I-deficient areas where goiter has been reported, e.g. in the UK, Sri Lanka, China, and Morocco (Fordyce et al., 2000; Johnson et al., 2002; Fordyce et al., 2003; Bowley et al., 2017) (**Table 3**). However, it should be emphasized that the presence of endemic goiter is not always clearly related to the occurrence of deficient I in the environment (Stewart et al., 2003).

Iodine (I_{Tot}) in the 0–20 cm layer presented a remarkable positive correlation with all Se fractions (Se_{Tot} , Se_{Sol} , Se_{Ad} , and Se_{Org}), which does not mean that the geochemistry of both elements are directly interrelated but simply because their dynamic in the soil is controlled by similar soil physical and chemical attributes. Also,

OM, S, and clay presented positive correlation with I_{Tot} . Negative correlations were observed for Ba_{Tot} , K, and sand (**Table 1**). The greatest contribution to the regression equation ($R^2 = 0.79$) was provided by clay followed by S and sand contents. Negative contributions were provided by K and OM (**Table 2**). There is a contrast between the results of the present research and those reported by relevant studies in the literature, which usually observe associations between I and both soil organic matter and pH. For example, Bowley et al. (2019) found a significant positive correlation between soil organic matter and I concentrations ($r = 0.64$, $p = 0.004$) and a significant negative correlation between soil pH and I ($r = -0.58$, $p = 0.011$) in soils from Northern Ireland. The dynamics of I in the soils from Amazon are not completely understood yet, but the results showed that I_{Tot} is affected by soil texture (clay and sand) and its abundance may be controlled by soil mineralogy, having a primary geogenic source, besides the input from atmospheric deposition (Fuge and Johnson, 2015).

The highest Se_{Org} and I_{Tot} concentrations were observed for the site AM:AR (central Amazon), where also the highest organic matter and clay content were seen. On the other hand, the lowest Se_{Org} and I_{Tot} concentrations were observed at AC:XP (western Amazon), the site with the lowest available S concentration and also one of the lowest clay contents (< 25%) (**Fig. 1**). Thus, we assume that clay and OM partly determine the abundance of both I and Se in the topsoil. Additionally, the remarkable correlation between I_{Tot} and Se_{Org} (**Table 1**) suggests that the availability of both elements to plants may be controlled by similar soil physicochemical attributes (Bowley et al., 2017).

4 CONCLUSIONS

Selenium (Se_{Tot}) concentrations observed in soils from the sites studied are within the safe range according to the Brazilian legislation (< 5 mg kg⁻¹). Total

concentrations vary widely among the sites studied, and the higher concentrations observed for sites in central Amazon, which are closer to the mainstream of the Amazon river, indicate a geogenic origin and an influence of sedimentary deposits from the Andes, the South American mountain system (*cf.* Silva Junior et al., 2017).

The available Se fraction (soluble + adsorbed) accounted for only 4.5% of the Se_{Tot} on average, which indicates a very low risk of loss via leaching and environmental contamination in the soils from the Amazon rainforest. The Se_{Org} in the topsoil is the fraction with a higher contribution for total Se, and therefore, essential for its cycle in Amazonian ecosystems.

For Ba_{Tot} , levels higher than the prevention value of the Brazilian legislation ($> 150 \text{ mg kg}^{-1}$) were observed in sites of the western and central Amazon, where the dominant mineralogy of the clay fraction is 2:1 and the CEC of the clay tends to be higher. Barium (Ba_{Tot}) presents homogeneous distribution in depth, which indicates a major contribution of geogenic sources in its soil concentration, but rather heterogeneous spatial distribution within and between the sites studied.

The average I_{Tot} in the topsoil was above the world soil average (2.8 mg kg^{-1}). Iodine (I_{Tot}) concentration is affected by soil texture (clay and sand) and its abundance may be controlled by soil mineralogy, having a primary geogenic source, besides the input from atmospheric deposition. Yet, the dynamic of I in soils from Amazon is not completely understood and needs further research.

Finally, our findings are very useful for creating a regional dataset concerning Se_{Tot} , Ba_{Tot} , and I_{Tot} in Amazon soils, so as to derive local quality reference values as well as to support an update of prevention and investigation values for soil TE currently established by the Brazilian legislation, which should also be set on a regional scale.

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References

Alvarez, V.V.H.R.F., Novais, N.F., Barros, R.B., Cantarutti, A., Lopes, S., 1999. Interpretation of soil analysis results. In: Ribeiro, A.C., PTG, Guimarães (Eds.), Recommendations for Use of Amendments and Fertilizers in Minas Gerais, Brazil, 5^a ed, pp. 25–32 Viçosa. (In Portuguese).

Bernini, T.A., Pereira, M.G., Anjos, L.H.C. dos, Perez, D.V., Fontana, A., Calderano, S.B., Wadt, P.G.S., 2013. Quantification of aluminium in soil of the solimões

formation, Acre state, Brazil. *Rev. Bras. Ciência do Solo* 37, 1587–1598.

<https://doi.org/10.1590/S0100-06832013000600015>

Biondi, C.M., Nascimento, C.W.A. do, Fabricio Neta, A. de B., 2011. Teores naturais de Bário em solos de referência do Estado de Pernambuco. *Rev. Bras. Ciência do Solo* 35, 1819–1826. <https://doi.org/https://doi.org/10.1590/S0100-06832011000500036>

Bowley, H.E., Mathers, A.W., Young, S.D., Macdonald, A.J., Ander, E.L., Watts, M.J., Zhao, F.J., McGrath, S.P., Crout, N.M.J., Bailey, E.H., 2017. Historical trends in iodine and selenium in soil and herbage at the Park Grass Experiment, Rothamsted Research, UK. *Soil Use Manag.* 33, 252–262. <https://doi.org/10.1111/sum.12343>

Bowley, H.E., Young, S.D., Ander, E.L., Crout, N.M.J., Watts, M.J., Bailey, E.H., 2019. Iodine bioavailability in acidic soils of Northern Ireland. *Geoderma* 348, 97–106. <https://doi.org/10.1016/j.geoderma.2019.04.020>

Carter, M.R., Gregorich, E.G., 2006. *Soil Sampling and Methods of Analysis*, 2^o. ed, CRC Press. Canadian Society of Soil Science, 1224 p.

Carvalho, J. da S., Tomasella, J., Shiraiwa, S., Araujo, R.L.C. de, 2014. Stratigraphic aspects of the Alter do chão formation in the northern region of Manaus, based on geoelectric information. *Rev. Bras. Geofis.* 32, 61–70. <https://doi.org/10.22564/rbgf.v32i1.397>

Cesar, J.A., Santos, I.S., Black, R.E., Chrestani, M.A.D., Duarte, F.A., Nilson, E.A.F., 2020. Iodine status of Brazilian school-age children: A national cross-sectional survey. *Nutrients* 12, 1–15. <https://doi.org/10.3390/nu12041077>

Chilimba, A.D.C., Young, S.D., Black, C.R., Rogerson, K.B., Ander, E.L., Watts, M.J., Lammel, J., Broadley, M.R., 2011. Maize grain and soil surveys reveal suboptimal dietary selenium intake is widespread in Malawi. *Sci. Rep.* 1–9. <https://doi.org/10.1038/srep00072>

Cleasby, I.R., Nakagawa, S., 2011. Neglected biological patterns in the residuals. *Behav. Ecol. Sociobiol.* 65, 2361–2372. <https://doi.org/10.1007/s00265-011-1254-7>

Darnius, O., Tarigan, G., 2018. Simulation method of model selection based on Mallows' Cp Criteria in linear regression. *J. Phys. Conf. Ser.* 1116, 1–6. <https://doi.org/10.1088/1742-6596/1116/2/022008>

Duborská, E., Bujdoš, M., Uršák, M., Matúš, P., 2020. Iodine fractionation in agricultural and forest soils using extraction methods. *Catena* 195, 104749. <https://doi.org/10.1016/j.catena.2020.104749>

Duplay, J., Semhi, K., Mey, M., Messina, A., Quaranta, G., Huber, F., Aubert, A., 2014. Geogenic versus anthropogenic geochemical influence on trace elements contents in soils from the Milazzo Peninsula. *Chemie der Erde* 74, 691–704. <https://doi.org/10.1016/j.chemer.2014.04.006>

Empresa Brasileira de Pesquisa Agropecuária – Embrapa. Manual de métodos de análise de solo. 2.ed. Rio de Janeiro, 1997. 212p.

Feinberg, A., Stenke, A., Peter, T., Winkel, L.H.E., 2020. Constraining atmospheric selenium emissions using observations, global modeling, and bayesian inference. *Environ. Sci. Technol.* 54, 7146–7155. <https://doi.org/10.1021/acs.est.0c01408>

Fernandes, A.R., Santos, E.S., de Souza Braz, A.M., Birani, S.M., Alleoni, L.R.F., 2018. Quality reference values and background concentrations of potentially toxic elements in soils from the Eastern Amazon, Brazil. *J. Geochemical Explor.* 190, 453–463. <https://doi.org/10.1016/j.gexplo.2018.04.012>

Feudis, M. De, D’Amato, R., Businelli, D., Guiducci, M., 2019. Fate of selenium in soil: A case study in a maize (*Zea mays* L.) field under two irrigation regimes and fertilized with sodium selenite. *Sci. Total Environ.* 659, 131–139. <https://doi.org/10.1016/j.scitotenv.2018.12.200>

Fordyce, F.M., Johnson, C.C., Navaratna, U.R.B., Appleton, J.D., Dissanayake, C.B., 2000. Selenium and iodine in soil, rice and drinking water in relation to endemic goitre in Sri Lanka. *Sci. Total Environ.* 263, 127–141. [https://doi.org/10.1016/s0048-9697\(00\)00684-7](https://doi.org/10.1016/s0048-9697(00)00684-7)

Fordyce, F.M., Stewart, A.G., Ge, X., Jiang, J.-Y., Cave, M., 2003. Environmental Controls in IDD: A Case Study in the Xinjiang Province of China. *Br. Geol. Surv. Tech. Rep.* CR/01/045N.

Fuge, R., Johnson, C.C., 2015. Iodine and human health, the role of environmental geochemistry and diet, a review. *Appl. Geochemistry* 63, 282–302. <https://doi.org/10.1016/j.apgeochem.2015.09.013>

Furnival, G.M., Wilson Junior, R.W., 2000. Regressions by leaps and bounds. *Technometrics* 42, 69–79.

Gabos, M.B., Alleoni, L.R.F., Abreu, C.A., 2014. Background levels of selenium in some selected Brazilian tropical soils. *J. Geochemical Explor.* 145, 35–39. <https://doi.org/10.1016/j.gexplo.2014.05.007>

Gloaguen, T.V., Passe, J.J., 2017. Importance of lithology in defining natural background concentrations of Cr, Co, Ni, Pb and Zn in sedimentary soils, northeastern Brazil. *Chemosphere* 186, 31–42. <https://doi.org/10.1016/j.chemosphere.2017.07.134>

Hong, C., Weng, H., Jilani, G., Yan, A., Liu, H., Xue, Z., 2012. Evaluation of iodide and iodate for adsorption-desorption characteristics and bioavailability in three types of soil. *Biol. Trace Elem. Res.* 146, 262–271. <https://doi.org/10.1007/s12011-011-9231-6>

Johnson, C.C., Strutt, M.H., Hmeurras, M., Mounir, M., 2002. Iodine in the environment of the high atlas mountain area of Morocco. *Br. Geol. Surv. Comm. Report*, CR/02/196N.

Kabata-Pendias, A., 2011. Trace elements in soils and plants, 4^o. ed, CRC Press. Taylor & Francis, Boca Raton.

Kitagawa, V., Moller, M.R.F., 1979. Clay mineralogy of some typical soils in the Brazilian Amazon region. *Pesqui. Agropecuária Bras.* 14, 201–228.

Kravchenko, J., Darrah, T.H., Miller, R.K., Lyerly, H.K., 2014. A review of the health impacts of barium from natural and anthropogenic exposure. *Environ. Geochem. Health* 36, 797–814. <https://doi.org/10.1007/s10653-014-9622-7>

Lenth, R. (2019). Emmeans: Estimated marginal means, aka least-squares means. R Package Version 1.3.2. Retrieved from <http://CRAN.R-project.org/package=emmeans>.

Ligowe, I.S., Young, S.D., Ander, E.L., Kabambe, V., Chilimba, A.D.C., Bailey, E.H., Lark, R.M., Nalivata, P.C., 2020. Selenium biofortification of crops on a Malawi Alfisol under conservation agriculture. *Geoderma* 369, 114315. <https://doi.org/10.1016/j.geoderma.2020.114315>

Lima, M., Cruz, S., Diniz, H., Almeida, F. De, Poellmann, H., 2014. On the geology, mineralogy and geochemistry of the bauxite-bearing regolith in the lower Amazon basin: Evidence of genetic relationships. *J. Geochemical Explor.* 146, 58–74. <https://doi.org/10.1016/j.gexplo.2014.07.021>

Long, Z., Yuan, L., Hou, Y., Bañuelos, G.S., Liu, Y., Pan, L., Liu, X., Yin, X., 2018. Spatial variations in soil selenium and residential dietary selenium intake in a selenium-

rich county, Shitai, Anhui, China. *J. Trace Elem. Med. Biol.* 50, 111–116.
<https://doi.org/10.1016/j.jtemb.2018.06.019>

Lu, Q., Xu, X., Liang, L., Xu, Z., Shang, L., Guo, J., Xiao, D., Qiu, G., 2019. Barium concentration, phytoavailability, and risk assessment in soil-rice systems from an active barium mining region. *Appl. Geochemistry* 106, 142–148.
<https://doi.org/10.1016/j.apgeochem.2019.05.010>

Magalhães, M.O.L., Amaral Sobrinho, N.M. do, Zonta, E., Lima, L. da S., Paiva, F.S.D. de, 2011. Mobilidade de bário em solo tratado com sulfato de bário sob condição de oxidação e redução. *Quim. Nova* 34, 1544–1549.
<https://doi.org/https://doi.org/10.1590/S0100-40752011000900012>

Marques, J.J., Teixeira, W.G., Schürze, D.G., Curi, N., 2002. Mineralogy of soils with unusually high exchangeable Al from the western Amazon Region. *Clay Miner.* 37, 651–661. <https://doi.org/10.1180/0009855023740067>

Matos, R.P., Lima, V.M.P., Windmöller, C.C., Nascentes, C.C., 2017. Correlation between the natural levels of selenium and soil physicochemical characteristics from the Jequitinhonha Valley (MG), Brazil, in: *Journal of Geochemical Exploration*. Elsevier B.V., pp. 195–202. <https://doi.org/10.1016/j.gexplo.2016.11.001>

Matschullat, J., Martins, G.C., Enzweiler, J., von Fromm, S.F., van Leeuwen, J., de Lima, R.M.B., Schneider, M., Zurba, K., 2020. What influences upland soil chemistry

in the Amazon basin, Brazil? Major, minor and trace elements in the upper rhizosphere.

J. Geochemical Explor. 211, 106433. <https://doi.org/10.1016/j.gexplo.2019.106433>

McBride, M.B., Shayler, H. a, Spliethoff, H.M., Mitchell, R.G., Marquez-Bravo, L.G., Ferenz, G.S., Russell-Anelli, J.M., Casey, L., Bachman, S., 2014. Concentrations of lead, cadmium and barium in urban garden-grown vegetables: The impact of soil variables. Environ. Pollut. 194, 254–61. <https://doi.org/10.1016/j.envpol.2014.07.036>

Melo, L.C.A., Alleoni, L.R.F., Carvalho, G., Azevedo, R.A., 2011. Cadmium- and barium-toxicity effects on growth and antioxidant capacity of soybean (*Glycine max* L.) plants, grown in two soil types with different physicochemical properties. J. Plant Nutr. Soil Sci. 174, 847–859. <https://doi.org/10.1007/s10261-010-0250-0>

Melo, L.C.A., Silva, E.B. da, Alleoni, L.R.F., 2014. Transfer of cadmium and barium from soil to crops grown in tropical soils. Rev. Bras. Ciência do Solo 38, 1939–1949. <https://doi.org/10.1590/s0100-06632014000600028>

Nascimento, V.L., Souza, B.C.O.Q., Lopes, G., Guilherme, L.R.G., 2022. On the role of iodine in plants: a commentary on benefits of this element. Frontiers in Plant Science. Available at <https://www.frontiersin.org/articles/10.3389/fpls.2022.836835/full>. (Accessed 16 February 2022).

Nascimento, C.W.A. do, Silva, F.B.V. da, Neta, A. de B.F., Biondi, C.M., Lins, S.A. da S., Júnior, A.B. de A., Preston, W., 2021. Geopedology-climate interactions govern the spatial distribution of selenium in soils: A case study in northeastern Brazil. Geoderma

399, 115119. <https://doi.org/10.1016/j.geoderma.2021.115119>

National Environment Council - CONAMA, 2009. Resolution No. 420, 2009. Available online at: http://conama.mma.gov.br/?option=com_sisconama&task=arquivo.download&id=601, (Accessed 15 February 2022, in Portuguese).

Pilon-Smits, E.A.H., 2019. On the ecology of selenium accumulation in plants. *Plants* 8, 197. https://doi.org/10.1007/978-3-319-56249-0_11

R Development Core Team, 2020. R: a Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria, Version 3.6.2.

Reis, A.R. dos, El-Ramady, H., Santos, E.F., Gratão, P.L., Schomburg, L., 2017. Overview of selenium deficiency and toxicity worldwide: affected areas, selenium-related health issues, and case studies, in: *Selenium in Plants, Molecular, Physiological, Ecological and Evolutionary Aspects*. pp. 209–230. <https://doi.org/10.1007/978-3-319-56249-0>

Roulier, M., Coppin, F., Bueno, M., Nicolas, M., Thiry, Y., Della Vedova, C., Février, L., Pannier, F., Le Hécho, I., 2019. Iodine budget in forest soils: Influence of environmental conditions and soil physicochemical properties. *Chemosphere* 224, 20–28. <https://doi.org/10.1016/j.chemosphere.2019.02.060>

Sahoo, P.K., Dall'Agnol, R., Salomão, G.N., da Silva Ferreira Junior, J., da Silva, M.S., Martins, G.C., e Souza Filho, P.W.M., Powell, M.A., Maurity, C.W., Angelica, R.S., da Costa, M.F., Siqueira, J.O., 2019. Source and background threshold values of potentially toxic elements in soils by multivariate statistics and GIS-based mapping: a high density sampling survey in the Parauapebas basin, Brazilian Amazon. *Environ. Geochem. Health* 42, 255–282. <https://doi.org/10.1007/s10653-019-00345-z>

Santos, H.G., Jacomine, P.K.T., dos Anjos, L.H.C., de Oliveira, V.Á., Lumbrreras, J.F., Coelho, M.R., de Almeida, J.A., Araujo Filho, J.C. de, Oliveira, J.B. de, Cunha, T.J.F., 2018. Sistema brasileiro de classificação de solos 5^a edição revista e ampliada. Brasília: Embrapa, 2018. 187p. Available at: <https://www.embrapa.br/solos/busca-de-publicacoes/-/publicacao/1107206/sistema-brasilero-de-classificacao-de-solos>. Accessed on February 7, 2022.

Shoemaker, H.E., McLean, E.O. Part, P.F., 1961. Buffer methods for determining lime requirement of soils with appreciable amounts of extractable aluminum. *Soil Sci. Soc. Am. J.* 25, 274–277. <https://doi.org/10.2136/sssaj1961.03615995002500040014x>

Silva Junior, E.C. da, Duran, N.M., de Lima Lessa, J.H., Ribeiro, P.G., de Oliveira Wadt, L.H., da Silva, K.E., de Lima, R.M.B., Batista, K.D., Guedes, M.C., de Oliveira, R.C., de Carvalho, H.W.P., dos Reis, A.R., Lopes, G., Guimarães Guilherme, L.R., 2022. Unraveling the accumulation and localization of selenium and barium in Brazil nuts using spectroanalytical techniques. *J. Food Compos. Anal.* 106, 104329. <https://doi.org/10.1016/j.jfca.2021.104329>

Silva Junior, E.C., Wadt, L.H.O., Silva, K.E., Lima, R.M.B., Batista, K.D., Guedes, M.C., Carvalho, G.S., Carvalho, T.S., Reis, A.R., Lopes, G., Guilherme, L.R.G., 2017. Natural variation of selenium in Brazil nuts and soils from the Amazon region. *Chemosphere* 188, 650–658. <https://doi.org/10.1016/j.chemosphere.2017.08.158>

Soil Survey Staff. 2014. *Keys to Soil Taxonomy*, 12th ed. USDA-Natural Resources Conservation Service, Washington, DC.

Souza, J.J.L.L. de, Fontes, M.P.F., Gilkes, R., da Costa, L.M., de Oliveira, T.S., 2018. Geochemical signature of Amazon tropical rainforest soils. *Rev. Bras. Cienc. do Solo* 42, 1–18. <https://doi.org/10.1590/18069657rbc201700192>

Stewart, A.G., Carter, J., Parker, A., Alloway, B.J., 2003. The illusion of environmental iodine deficiency. *Environ. Geochem. Health* 25, 165–170. <https://doi.org/https://doi.org/10.1007/A:1021281822514>

Tolu, J., Thiry, Y., Buerge, M., Jolivet, C., Potin-Gautier, M., Le Hécho, I., 2014. Distribution and speciation of ambient selenium in contrasted soils, from mineral to organic rich. *Sci. Total Environ.* 479–480, 93–101. <https://doi.org/10.1016/j.scitotenv.2014.01.079>

Wang, Y., Cui, Y., Chen, C., Duan, Y., Wu, Y., Li, W., Zhang, D.D., Li, F., Hou, C., 2020. Stopping the supply of iodized salt alone is not enough to make iodine nutrition suitable for children in higher water iodine areas: A cross-sectional study in northern

China. *Ecotoxicol. Environ. Saf.* 188, 109930.
<https://doi.org/10.1016/j.ecoenv.2019.109930>

Watts, M.J., Mitchell, C.J., 2009. A pilot study on iodine in soils of greater Kabul and Nangarhar provinces of Afghanistan. *Environ. Geochem. Health* 31, 503–509.
<https://doi.org/10.1007/s10653-008-9202-9>

Watts, M.J., O'Reilly, J., Maricelli, A., Coleman, A., Anderson, E.L., Ward, N.I., 2010. A snapshot of environmental iodine and selenium in La Plata and San Juan provinces of Argentina. *J. Geochemical Explor.* 107, 87–93.
<https://doi.org/10.1016/j.gexplo.2009.11.002>

Yang, H., Yang, X., Ning, Z., Kwon, S.Y., Li, M.L., Tack, F.M.G., Kwon, E.E., Rinklebe, J., Yin, R., 2022. The beneficial and hazardous effects of selenium on the health of the soil-plant-human system: An overview. *J. Hazard. Mater.* 422, 126876.
<https://doi.org/10.1016/j.jhazmat.2021.126876>

Zhai, H., Xue, M., Du, Z., Wang, D., Zhou, F., Feng, P., Liang, D.L., 2019. Leaching behaviors and chemical fraction distribution of exogenous selenium in three agricultural soils through simulated rainfall. *Ecotoxicol. Environ. Saf.* 173, 393–400.
<https://doi.org/10.1016/j.ecoenv.2019.02.042>

Zhang, W., Wang, X., Chen, L., 2014. Improved leaps and bounds variable selection algorithm based on principal component analysis. *Chemom. Intell. Lab. Syst.* 139, 76–83. <https://doi.org/10.1016/j.chemolab.2014.09.017>

Zhang, M., Xing, G., Tang, S., Pang, Y., Yi, Q., Huang, Q., Huang, X., Huang, J., Li, P., Fu, H., 2019. Improving soil selenium availability as a strategy to promote selenium uptake by high-Se rice cultivar. *Environ. Exp. Bot.* 163, 45–54. <https://doi.org/10.1016/j.envexpbot.2019.04.008>

Table 1. Spearman correlation coefficients for data between main dependent variables studied: Total Se (Se_{Tot}), Total Ba (Ba_{Tot}), Soluble Se (Se_{Sol}), Adsorbed Se (Se_{Ad}), organic-bound Se (Se_{Org}), TMAH-I (I_{Tot}) and soil physical and chemical attributes from the layer 0-20 cm, selected from the correlation matrix ($p \leq 0.05$; $|r| \geq 0.4$) (Figure S1).

		Response variables					
		Se_{Tot}	Ba_{Tot}	Se_{Sol}	Se_{Ad}	Se_{Org}	I_{Tot}
Explanatory Variables	Se_{Tot}	-	-0.57**	0.44**	0.81**	0.95**	0.93**
	Ba_{Tot}	-0.57**	-	-	-0.44**	-0.45**	-0.60**
	Se_{Sol}	0.44**	-	-	0.74**	-	0.43**
	Se_{Ad}	0.81**	-0.44**	0.74**	-	0.79**	0.78**
	Se_{Org}	0.95**	-0.45**	-	0.79**	-	0.88**
	I_{Tot}	0.93**	-0.60**	0.43**	0.78**	0.88**	-
	pH	-	-	0.55**	-	-	-
	K	-0.57*	0.57**	-	-0.66**	-0.59*	-0.59**
	Ca	-	-	0.41**	-	-	-
	Al	-	0.50**	-	-0.40**	-	-
	CEC_{ef}	-	0.75**	-	-	-	-
	OM	0.44**	-0.50**	-	-	-	0.43**
	Zn	-	0.60**	-	-	-	-

S	0.70**	-0.49**	-	0.49**	0.65**	0.70**
Clay	0.84**	-0.51**	-	0.53**	0.78**	0.82**
Silt	-	0.63**	-	-	-	-
Sand	-0.55**	-	-	-	-0.63**	-0.47**

Obs.: Data from the site PA (Santarém-Pará) were excluded from the correlation matrix because of a lack of information about texture (clay, silt, and sand). *Correlation is significant at the 0.05 level; **Correlation is significant at the 0.01 level.

Table 2. Multiple regression equations for the relationship between the studied elements and fractions (Response variables) and other soil properties in the topsoil (0-20 cm) pre-selected via Spearman correlation (Table 1) and further variable selection performed via branch and bound algorithm

Response variables	Regression equation	R^2	RSE
$\log Se_{Tot}$	$= -3.51 - 0.40\log(K) - 0.46\log(OM) + 0.34\log(S) + 1.20\log(\text{clay})$	0.81	0.42
$\log Ba_{Tot}$	$= 2.57 + 0.61\log(K) - 0.21\log(Al) + 0.73\log(CEC_{ef}) - 0.61\log(OM) + 0.18\log(Zn) - 0.30\log(S) - 0.47\log(\text{clay}) + 0.60\log(\text{silt})$	0.87	0.48
Se_{Sol}	$= -7.83 + 3.0(\text{pH})$	0.27	3.41
$\log Se_{Ad}$	$= 2.44 - 0.36\log(K) - 0.26\log(Al) + 0.48\log(\text{clay})$	0.62	0.37
$\log Se_{Org}$	$= -0.66\log(K) + 0.28\log(S) + 0.71\log(\text{clay}) - 0.20\log(\text{sand})$	0.79	0.41
$\log I_{Tot}$	$= -1.38 - 0.39\log(K) - 0.26\log(OM) + 0.31\log(S) + 0.95\log(\text{clay}) + 0.12\log(\text{sand})$	0.79	0.34

Raw data were log-transformed in order to attend parametric statistics assumptions (homoscedasticity and normality) whenever necessary. Se_{Tot} = total Se (mg kg^{-1}); Ba_{Tot} = total Ba (mg kg^{-1}); Se_{Sol} = soluble Se ($\mu\text{g kg}^{-1}$); Se_{Ad} = adsorbed Se ($\mu\text{g kg}^{-1}$); Se_{Org} = organic bound-Se/Se-TMAH (mg kg^{-1}); I_{Tot} = total I (I-TMAH) (mg kg^{-1}); K = available potassium (mg kg^{-1}); S = available sulfur (mg kg^{-1}); Al = exchangeable aluminum ($\text{cmol}_c \text{kg}^{-1}$); Zn = available zinc (mg kg^{-1}); CEC_{ef} = effective cation exchange capacity

($\text{cmol}_c \text{ kg}^{-1}$); OM = organic matter (%); clay (%); silt (%) and sand (%). RSE = residual standard error.

Table 3. Information about total concentrations of Se, Ba, and I in different sites globally and their respective references

Element	Region/Country	Range of content and/or mean (mg kg^{-1})	Reference
Se	Northeast/Brazil	0.02-1.7 (0.3)	Nascimento et al. (2021)
Se	São Paulo/Brazil	< 0.1-1.6 (0.2)	Gabos et al. (2014)
Se	Minas Gerais/Brazil	< 0.3-5.97	Matos et al. (2017)
Se	Amazon/Brazil	0.05-2.5 (0.8)	This study (2022)
Se	Brazil (PV)*	5	CONAMA (2009)
Ba	Pernambuco/Brazil	4.4-2500	Biondi et al. (2011)
Ba	Pará/Brazil	0.90-126 (13.4)	Fernandes et al. (2018)
Ba	Amazon/Brazil	8-755	This study (2022)
Ba	Brazil (PV)*	150	CONAMA (2009)
I	UK	5.5 (median)	Fordyce et al. (2000)
I	Sri Lanka	3.1 (median)	Johnson et al. (2002)
I	China	1.0 (median)	Fordyce et al. (2003)
I	Morocco	2.1 (median)	Bowley et al. (2017)
I	La Pampa/Argentina	1.3–20.9	Watts et al. (2010)
I	San Juan/Argentina	0.1–10.5	Watts et al. (2010)
I	France	0.39–35.6 (7.11)	Roulier et al. (2019)
I	Amazon/Brazil	0.7-14.2	This study (2022)

*Prevention level (PV) established for soils in the country and reported by CONAMA (2009).

Figure Captions

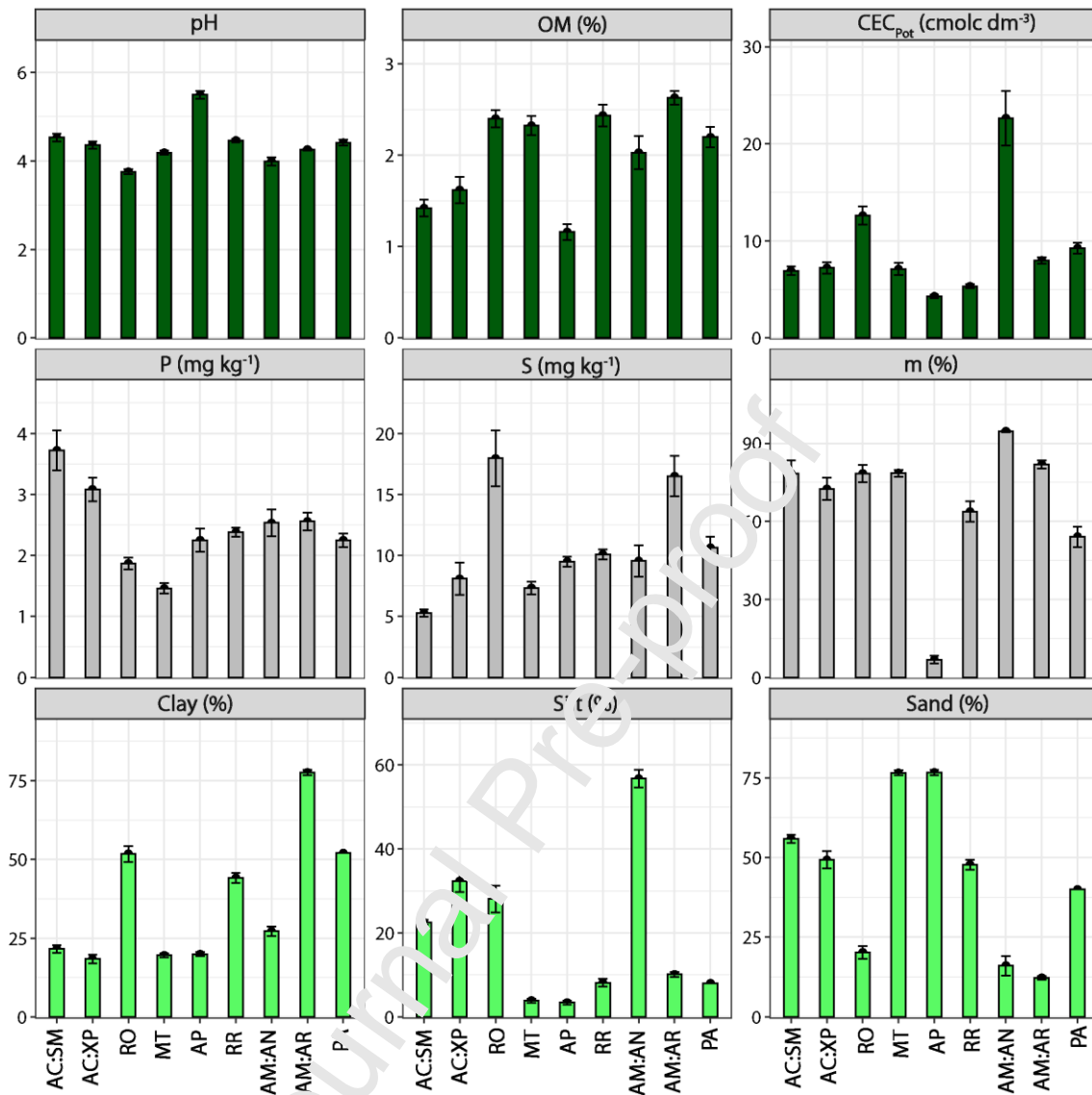


Fig. 1. Relevant physicochemical soil attributes in the topsoil (0-20 cm). The sites are identified as AC:SM = Acre-Sena Madureira; AC:XP = Acre-Xapuri; RO = Porto Velho-Rondônia; MT = Itaúba-Mato Grosso; AP = Laranjal do Jari-Amapá; RR = Caracará-Roraima; AM:AN = Amazonas-Anori; AM:AR = Amazonas-Aruanã farm (Itacoatiara); PA = Santarém-Pará. Bar plots contain average values for each site, and error bars represent the standard error of the mean (SEM, $n = 15$; AM:AR, $n = 18$).

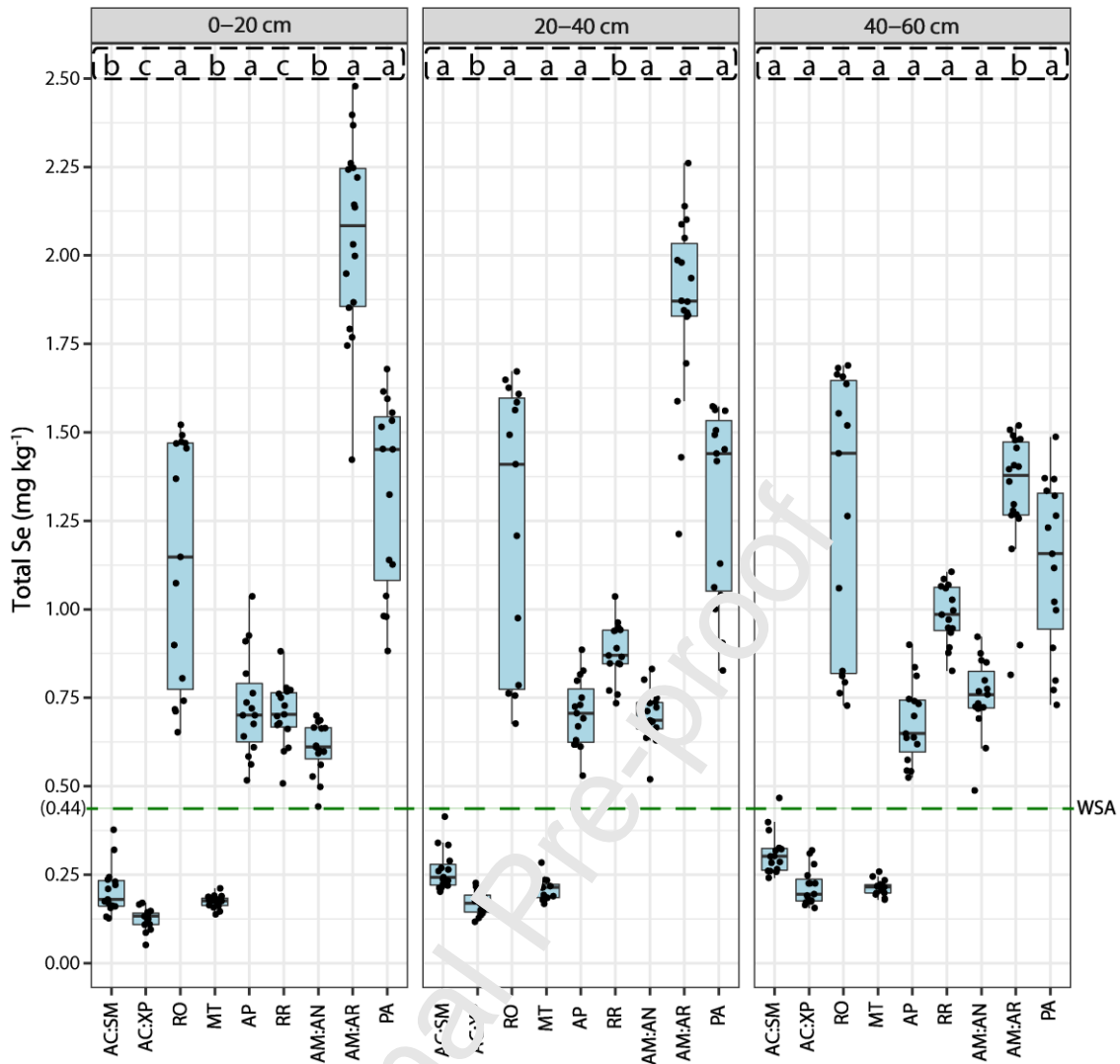


Fig. 2. Raw data of total soil Se (Se_{Tot}) concentration in samples collected at three different depths (0-20, 20-40, and 40-60 cm) on different sites of the Amazon rainforest (AC:SM = Acre-Sena, Madureira; AC:XP = Acre-Xapuri; RO = Porto Velho-Rondônia; MT = Itaúba-Mato Grosso; AP = Laranjal do Jari-Amapá; RR = Caracaraí-Roraima; AM:AN = Amazonas-Anori; AM:AR = Amazonas-Aruanã farm; PA = Santarém-Pará. Random horizontal noise was added to the points (raw observations) to facilitate visualization. The letter on top of each site indicates the result of Tukey's HSD test ($p = 0.05$) following a significant ANOVA ($p < 0.001$) for Se concentration, comparing the different layers for each site. Data for the site AC:SM were log-transformed before

ANOVA to attend statistical assumptions. WSA = world soil average for Se (0.44 mg kg^{-1}) provided by Kabata-Pendias (2011).

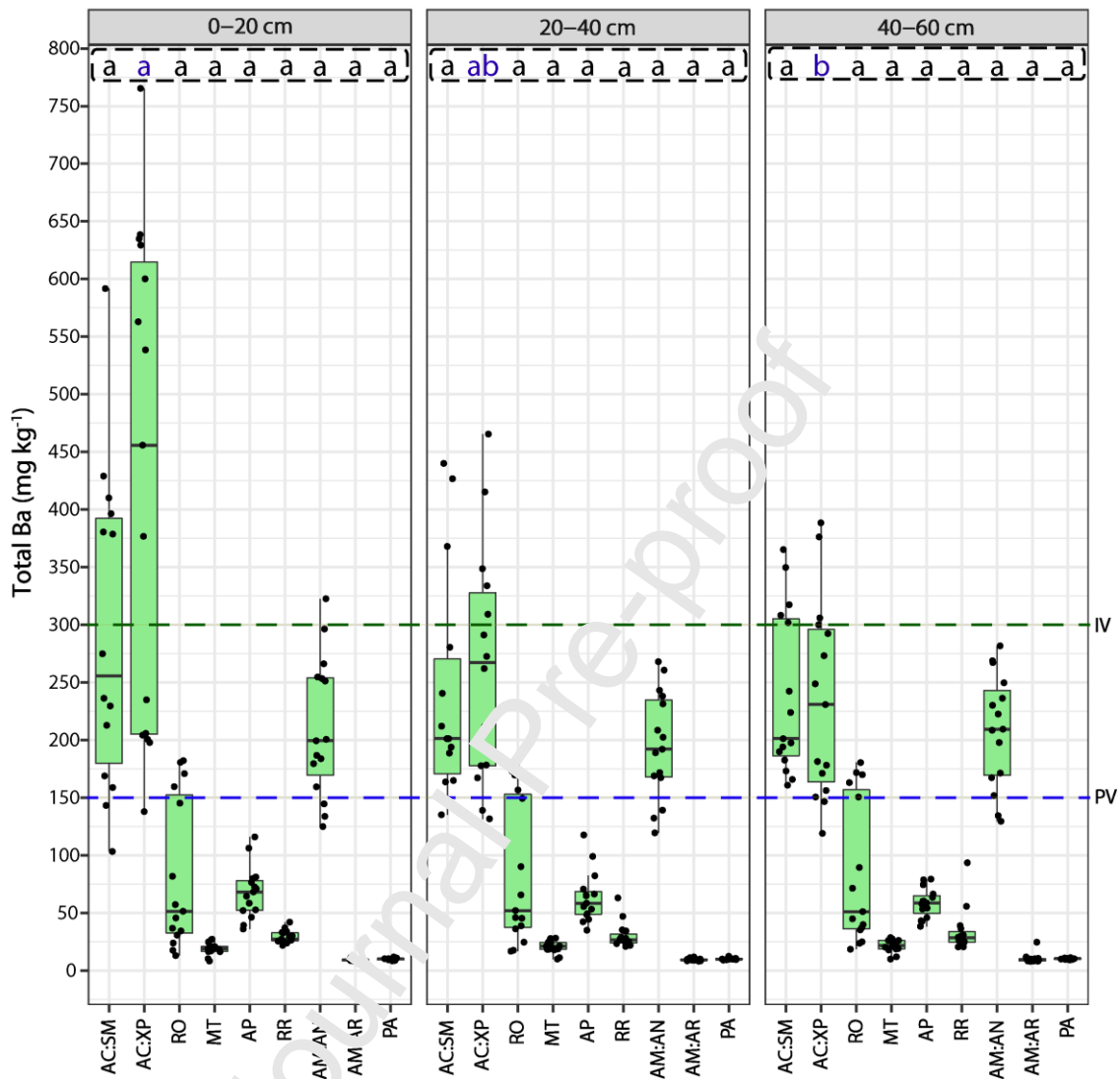


Fig. 3. Raw data of total soil Ba (Ba_{Tot}) concentration distribution in samples collected at three depths (0-20, 20-40, and 40-60 cm) in different sites of the Amazon rainforest (AC:SM = Acre-Sena Madureira; AC:XP = Acre-Xapuri; RO = Porto Velho-Rondônia; MT = Itaúba-Mato Grosso; AP = Laranjal do Jari-Amapá; RR = Caracaraí-Roraima; AM:AN = Amazonas-Anori; AM:AR = Amazonas-Aruanã farm; PA = Santarém-Pará. Random horizontal noise was added to the points (raw observations) to facilitate visualization. Data for the site AC:XP were log-transformed before ANOVA to attend statistical assumptions. The letter on top of the site AC:XP indicates the result of

Tukey's HSD test ($p = 0.05$) following a significant ANOVA ($p < 0.001$) for Se concentration, comparing the different layers for each site. For all other sites, there was no significant difference between the layers studied. PV and IV are Prevention and Investigation level (agricultural systems) for Ba in Brazil, provided by CONAMA (2009).

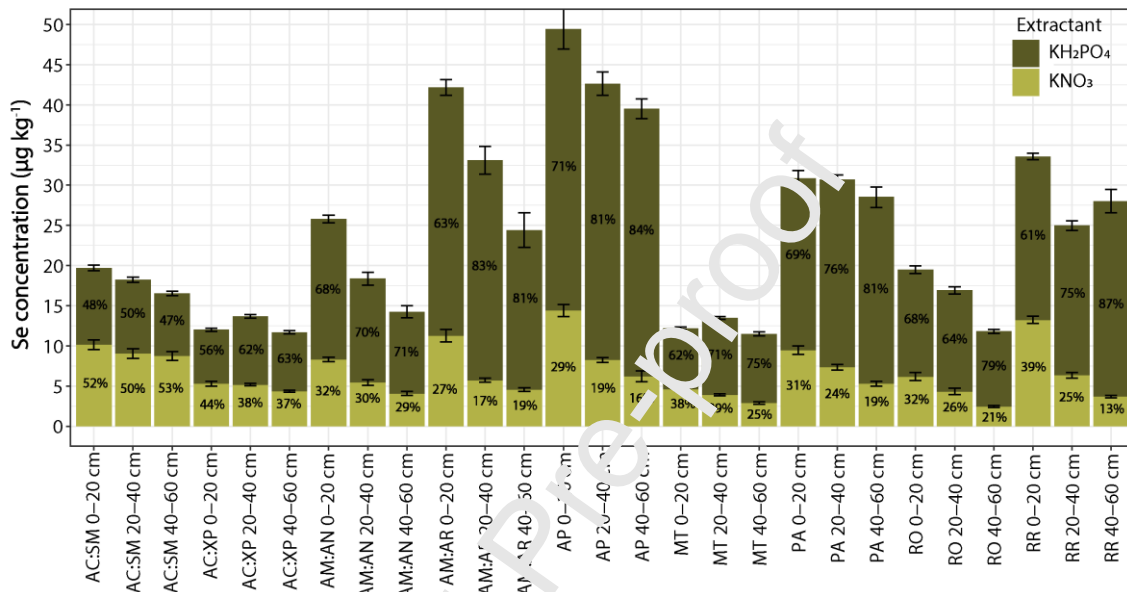


Fig. 4. Average concentration of Se_{S_e} (KNO_3) and Se_{Ad} (KH_2PO_4) with information of relative contribution of each extractant (%) for soil samples from different sites in the Amazon rainforest and different layers studied (0-20, 20-40, and 40-60 cm). Each site is identified by: AC:SM (Serra Madureira, State of Acre); AC:XP (Xapuri, State of Acre); AM:AN (Anori, State of Amazonas); AM:AR (Aruanã farm-Itacoatiara, State of Amazonas); AP (Laranjal do Jari, State of Amapá); MT (Itaúba, State of Mato Grosso); PA (Santarém, State of Pará); RO (Porto Velho, State of Rondônia) and RR (Caracaráí, State of Roraima). The vertical bar plot presents the standard error of the mean for each extractant (SEM, $n = 15$; AM:AR, $n = 18$).

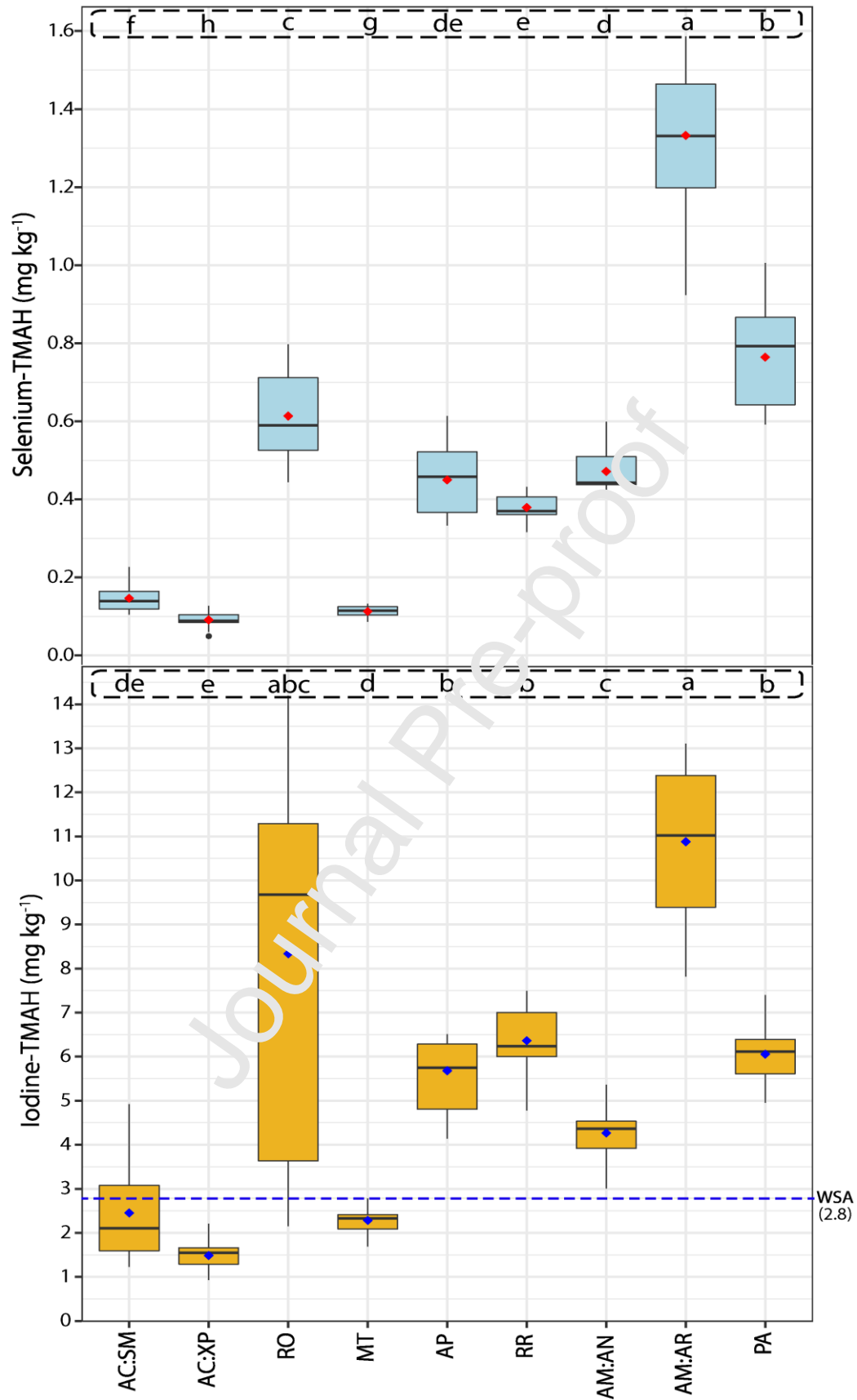


Fig. 5. Se_{Org} and I_{Tot} concentration in the topsoil (0-20 cm) layer on different sites of the Amazon rainforest represented as Box-and-whisker plot (median value line within box,

mean value as a rhombus). Sites are identified as follow: AC:SM = Acre-Sena Madureira; AC:XP = Acre-Xapuri; RO = Porto Velho-Rondônia; MT = Itaúba-Mato Grosso; AP = Laranjal do Jari-Amapá; RR = Caracaraí-Roraima; AM:AN = Amazonas-Anori; AM:AR = Amazonas-Aruanã farm; PA = Santarém-Pará. Data were log-transformed before proceeding to ANOVA, subsequently applying Tukey's HSD test for mean comparison among sites. WSA = world soil average for I (2.8 mg kg^{-1}) provided by Kabata-Pendias (2011).

Declaration of interests

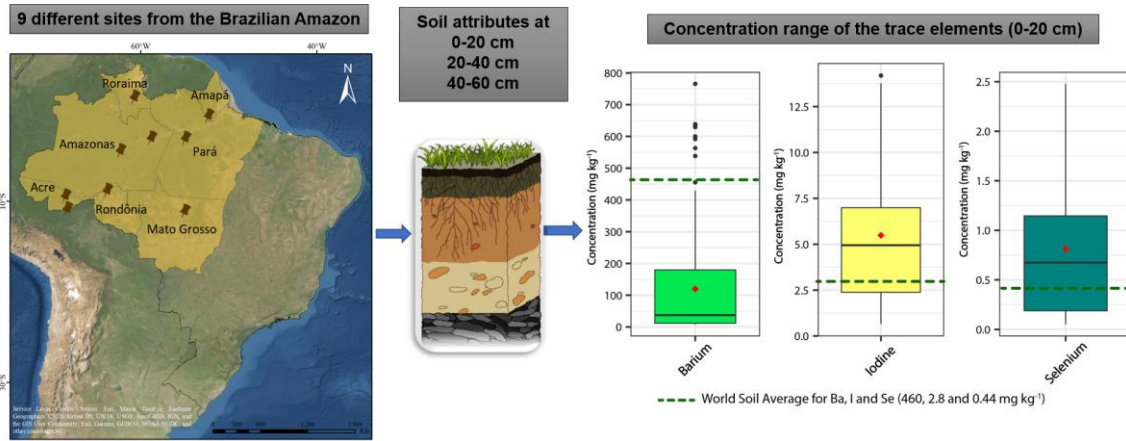
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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CREDIT AUTHOR STATEMENT

Ediu Junior: Conceptualization, Investigation, Formal analysis, Data curation and writing the original draft; **Lúcia Wadt:** Methodology, writing - review & editing; **Kátia Silva:** Resources, writing - review & editing; **Roberval Lima:** Resources; **Karine Batista:** Resources, writing - review & editing; **Marcelino Guedes:** Resources; **Raimundo Junior:** Resources; **André Reis:** Supervision, helped in review & editing; **Guilherme Lopes:** Conceptualization, Data Curation; **Martin Broadley:** Supervision, Project administration, Resources; **Scott Young:** Supervision, Project administration, Resources; **Luiz Guilherme** is the senior author and collaborated in the supervision, funding acquisition, conceptualization, writing - review & editing.



Graphical abstract

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Highlights

- Soil Se concentrations are considered safe on the sites studied ($< 5 \text{ mg kg}^{-1}$);
- Ba_{Tot} reaches concentrations that exceed the prevention level ($> 150 \text{ mg kg}^{-1}$);
- Average I_{Tot} in topsoil (5.43 mg kg^{-1}) was above the world average;
- Available Se ($\text{Se}_{\text{Sol}} + \text{Se}_{\text{Ad}}$) accounted for 4.5% of the Se_{Tot} on average;
- Statistical analyses suggest dominant geogenic source of Se, Ba, and I in soils.

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