Revista Brasileira de Ciência do Solo

Division - Soil Use and Management | Commission - Soil and Water Management and Conservation

Geochemical background and geopedological interactions of selenium in soils from Piauí state, Northeastern Brazil

Gustavo de Sousa de Oliveira Leite[(1)], **Clístenes Williams Araújo do Nascimento**[(2)], **Rennan Cabral Nascimento**[(1)], **Cácio Luiz Boechat**[(2)], **Pâmalla Graziely Carvalho Morais**[(1)], **Paloma Cunha Saraiva**[(1)], **Lizandra de Sousa Luz Duarte**[(1)], **Jacqueline Sousa Paes Landim**[(1)] **and Yuri Jacques Agra Bezerra da Silva**[(1)*]

[(1)] Universidade Federal do Piauí, Departamento de Agronomia, Bom Jesus, Piauí, Brasil.
[(2)] Universidade Federal Rural de Pernambuco, Departamento de Agronomia, Recife, Pernambuco, Brasil.

*** Corresponding author:**
E-mail: yurijacques@ufpi.edu.br

Received: September 19, 2023

Approved: November 20, 2023

How to cite: Leite GSO, Nascimento CWA, Nascimento RC, Boechat CL, Morais PGC, Saraiva PC, Duarte LSL, Landim JSP, Silva YJAB. Geochemical background and geopedological interactions of selenium in soils from Piauí state, Northeastern Brazil. Rev Bras Cienc Solo. 2024;48:e0230110
https://doi.org/10.36783/18069657rbcs20230110

Editors: José Miguel Reichert and Maria Betânia Galvão dos Santos.

ABSTRACT: Although Selenium (Se) plays a role as a micronutrient for humans through vegetable consumption, it is also recognized as toxic when present in excessive quantities. Therefore, quantifying Se contents in soils can prevent diseases influenced by crop Se deficiency or excess. We aimed to measure background contents, establish quality reference values (QRV) for Se in soils from two Brazilian biomes (Cerrado and Caatinga), and assess how geopedological factors affect Se content and spatial variability. Two hundred and eight composite topsoil samples were analyzed for Se content, covering an area of about 251,578 km². Sampling sites were under the minimal anthropogenic influence to represent Se background contents. Selenium contents were determined by hydride generation atomic absorption spectroscopy (HGAAS), ranging from 0.002 to 4.78 mg kg^{-1}. Most soils had contents below the world average of 0.44 mg kg^{-1} but still above the soil content that causes human Se deficiency (0.125 mg kg^{-1}). Soils from Cerrado and Caatinga biomes showed similar average contents of Se, 0.41 and 0.47 mg kg^{-1}, respectively. Organic carbon content and soil particle size (clay fraction) were the main factors governing Se content in the soils. Our results contribute to understanding the Se content and spatial distribution in tropical soils and the factors governing them. They also provide a tool for agriculture and environmental decision-makers to plan public policies regarding the management of Se levels in these and similar tropical soils in the world.

Keywords: selenium deficiency, human health, guideline values, spatial variability.

INTRODUCTION

Selenium (Se) is a micronutrient for humans and animals but is also regarded as toxic in high concentrations. Thus, both the deficiency and the excess of Se in the body can lead to various disorders and diseases (WHO, 2009; Muthayya et al., 2012; Vasiliu and Dixon, 2018). Selenium deficiency has been observed in China, United States, United Kingdom, and sub-Saharan African countries, affecting as many as 0.5 to 1.0 billion people (Ullah et al., 2019; Belay et al., 2020; Ligowe et al., 2020). Recent studies have also suggested that Se may have a potentially repressive effect on the proliferation of AIDS (Ullah et al., 2019) and may be related to mortality risks in the case of SARS-CoV-2 virus infection (COVID-19) (Moghaddam et al., 2020).

Selenium assimilation by food consumption accounts for almost 80 % of human Se ingestion (Ullah et al., 2019). Selenium accumulation in grains, however, depends on plant type and Se content and chemical form in the soil (Banuelos et al., 2013; Natasha et al., 2018; Ullah et al., 2019). Particle size, organic matter content, acidity, redox potential, and rainfall also control Se distribution in soils (Sun et al., 2016; He et al., 2018; Nascimento et al., 2021). Selenium natural average content in the earth's crust is low, varying from 0.05 to 0.10 mg kg^{-1}, resulting in naturally Se-deficient soils (Lopes et al., 2017; Natasha et al., 2018; Ullah et al., 2019). Globally, Se content in soils ranges from 0.01 to 2.0 mg kg^{-1}, with an average of 0.44 mg kg^{-1} (Ullah et al., 2019). Soils containing less than 0.125 mg kg^{-1} are considered selenium-deficient (Tan et al., 2002; Song et al., 2020), whereas those containing more than 5 mg kg^{-1} are known as seleniferous soils (Wadgaonkar et al., 2018) and can reach up to 1,200 mg kg^{-1} (Fernández-Martínez and Charlet, 2009; He et al., 2018). Seleniferous soils often occur in small hotspots and are derived from Se-rich rocks such as black shales, carbonaceous limestones, carbonaceous cherts, mudstones and seleniferous coal, or result from anthropic sources (i.e., irrigation with Se-rich waters) (Winkel et al., 2012). This can be detrimental to animal and human health (Lopes et al., 2017; Wadgaonkar et al., 2018). Conversely, soils with low Se content can prompt Se deficiency in plants, ultimately resulting in humans lacking the element in their diet (Natasha et al., 2018; Ligowe et al., 2020).

Geochemical background is a relative measure to distinguish between the natural content of a given element and its anthropogenically-influenced contents in a set of soil samples (Matschullat et al., 2000). Therefore, determining background values is essential to establish soil guideline values and decide whether the land is contaminated or impoverished in each element. Selenium content in soils is well documented, particularly in countries such as China, where Se human deficiency was recently reported (Tan et al., 2016; He et al., 2018; Song et al., 2020; Xie et al., 2021). Studies aiming at quantifying and analyzing the spatial distribution of Se in Brazilian soils, on the other hand, are primarily limited to the Southeast and Midwest regions of the country (Silva et al., 2012; Gabos et al., 2014; Matos et al., 2017; Carvalho et al., 2019), with only one study carried out in Northeastern Brazil (Nascimento et al., 2021).

Background values are also a first step to establishing soil guidelines values (SGV). In Brazil, the SGV intended to protect soil quality is the quality reference value (QRV), which is of the 75th or 90th percentile of the element concentration in a sufficiently high data set (Conama, 2009). Therefore, the QRV is a benchmark to identify contamination or insufficient Se concentrations in a given area (Teng et al., 2008).

Our study area is a transition region between two Brazilian biomes - the Cerrado and the Caatinga. The region experiences intense urbanization in the north and agricultural activities in the southwest and south areas, focused on soybeans, corn, and cotton. Additionally, some parts of the region remain in their natural state and are protected by conservation units, resulting in a considerable variation in biogeoclimatic, pedological, and socioeconomic characteristics (Cepro, 2013; Seplan, 2015). This study aimed to establish the QRVs and assess the influence of geopedological characteristics on the content and spatial variability of Se in soils from Caatinga and Cerrado Biomes, northeastern Brazil.

MATERIALS AND METHODS

Study site

Our study area comprises the entire state of Piauí and covers a total area of 251,577.7 km² (16.1 % of the extension of the Brazilian Northeast) where 3,271,199 inhabitants reside (Cepro, 2013; IBGE, 2023) (Figure 1a). Parnaíba Sedimentary Basin comprises 81.5 % of the study area, with soils developed from Phanerozoic sedimentary rocks, such as sandstones, argillites, shales, siltstones, and limestones (Pfaltzgraff et al., 2010). The remaining area is part of the São Francisco (9.4 %) and Borborema (8.1 %) geological provinces, with a small portion in the Coastal province (IBGE, 2019, 2020) that cover a crystalline basement composed of metamorphic and igneous rocks (i.e., migmatites, orthogneisses, schists, granodiorites) with the occurrence of intercalated sandstones (IBGE, 2019, 2021; SGB, 2017) (Figure 1d). Area geomorphology comprises the Parnaíba Sedimentary Basin and is formed by dissected plateaus, flattened surfaces with isolated mountains, embedded valleys with structural steps and plateau edges. The area comprising the provinces of São Francisco and Borborema, which coincides with the crystalline basement, in the southeast and part of the extreme south of the state, the relief is characterized by flattened surfaces, trays, structural steps, and plateau edges (Pfaltzgraff et al., 2010).

According to the Köppen-Geiger classification system, three climatic types occur: Aw - Tropical with a dry season in winter and rains in summer; As - Tropical with a dry season in summer and rainfall in winter; and BSh - Hot semiarid (Alvares et al., 2013). Annual average rainfall in the state ranges from 600 to 2,000 mm yr^{-1} (Andrade Júnior et al., 2004). Vegetation is composed of species from Cerrado and Caatinga, a tropical dry forest (Figure 1b). Soils are predominately Ferralsols (*Latossolos*), Leptosols (*Neossolos Litólicos*), Arenosols (*Neossolos Quartzarênicos*), Fluvisols (*Neossolos Flúvicos*), Plinthosols (*Plintossolos*), and Acrisols (*Argissolos*) (IBGE, 2019, 2021).

The southwest region of the state, mainly comprised by Cerrado biome, is one of the most recent agricultural frontiers of Brazil (MATOPIBA), where high-tech agriculture has been expanding since the 1980s, with accelerated replacement of native vegetation and intensive use of agricultural inputs (Magalhães and Miranda, 2014; França et al., 2016; Souza et al., 2019). Areas located in the Caatinga biome have desert physiognomy, high average annual temperatures (23 to 27 °C), relative humidity often below 50 %, and low rainfall rates (between 500 and 700 mm annually), which results in marked limitations on land-use for agricultural purposes (Menezes et al., 2012).

Soil sampling and laboratory analyses

Two hundred and eight composite soil samples, consisting of five sub-samples each, were collected at a layer of 0.00-0.20 m in sites under minimal anthropogenic interference. Samples were air-dried, crushed, and passed through a 2.0 mm sieve (ABNT No. 50). Chemical analyses were carried out following Teixeira et al. (2017). The pH was determined in water at a ratio of 2:1. Exchangeable Ca and Mg contents were extracted with KCl 1.0 mol L^{-1} and determined by atomic absorption spectrometry, using a flame atomic absorption spectrometer (Flame AA). Exchangeable Al was extracted with KCl 1.0 mol L^{-1} and volumetrically determined with a diluted NaOH 1.0 mol L^{-1}. Potassium and available P contents were extracted using Mehlich-1, and determined by flame photometry and colorimetry, respectively. Potential acidity (H+Al) was determined by extraction with calcium acetate 0.5 mol L^{-1} at pH 7.0. Soil organic carbon was determined by the Walkley-Black method, adapted by Silva et al. (1999). Sum of bases (SB) and cation exchange capacity (CEC) were calculated from the values obtained from the sorptive complex. Particle size analysis was performed according to the methodology proposed by Gee and Or (2002). Sodium hydroxide (NaOH) at 1.0 mol L^{-1} was used as a chemical dispersant.

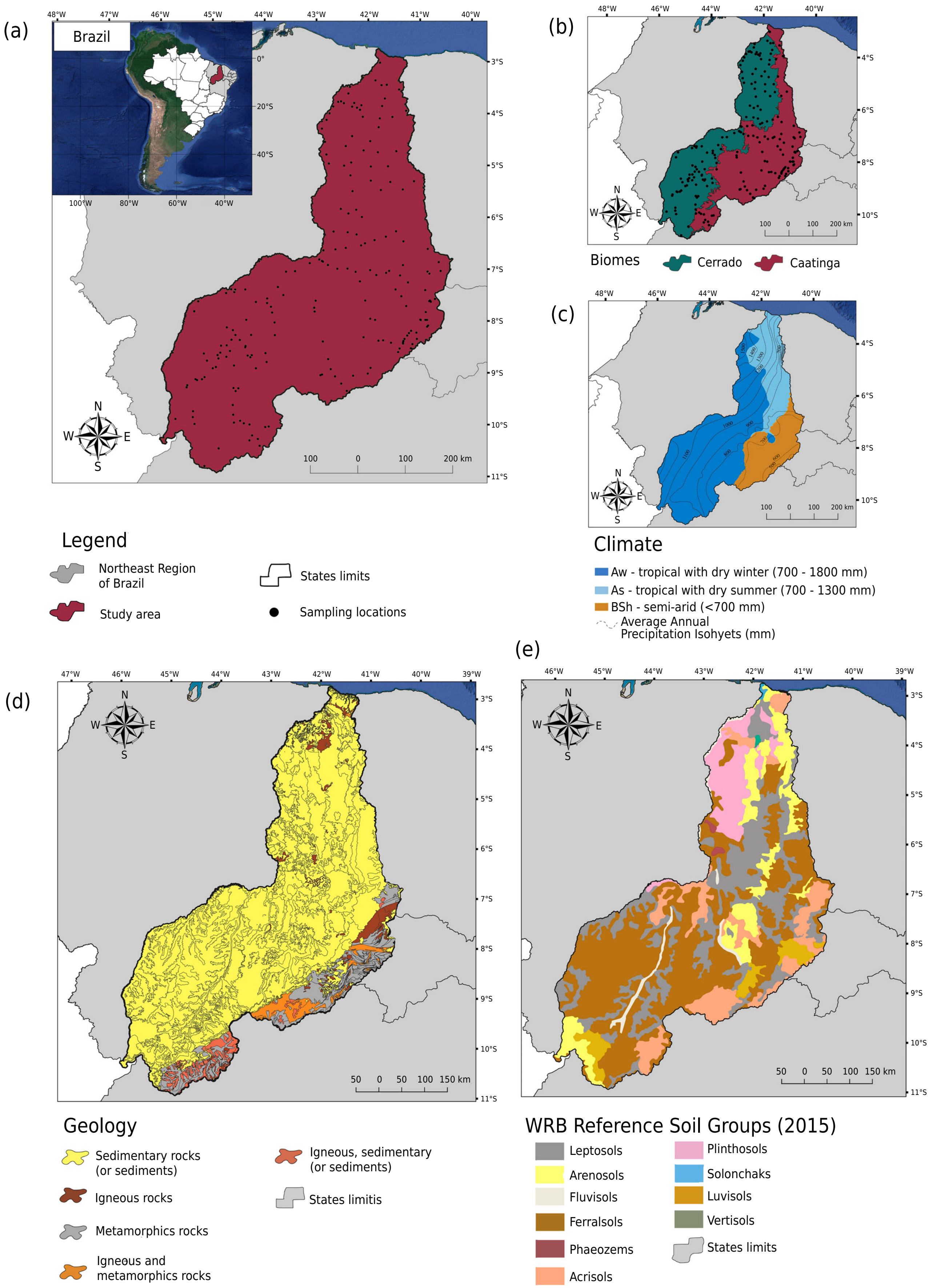

Figure 1. Geographical location of the Piauí State (a), map of the Cerrado and Caatinga biomes in the study area (b), climate map according to the Köppen-Geiger classification system (c), geological map (d), and soil map (e).

Selenium analysis and quality control

Selenium was extracted from soil samples by acid digestion according to method 3051A recommended by the U.S. Environmental Protection Agency (Usepa, 2007). Each sample was finely ground and passed through a stainless-steel sieve with a 0.15 mm mesh diameter. Subsequently, 0.5 g was added into the Teflon tube in a microwave for acid digestion (3:1, HNO_3, and HCl). Then, the extracts were filtered and transferred to certified volumetric flasks and completed with ultrapure water. Pre-reduction of Se in the extracts was done previously using HCl to generate Se hydrides. Selenium content determinations were made by hydride generation atomic absorption spectroscopy (HGAAS), using an atomic absorption spectrometer with a coupled hydride generator (FIAS 100/Flow Injection System) to reduce volatilization losses. Analytical quality was verified using a reference material (SRM 2709a, San Joaquin Soil) certified by the National Institute of Standards and Technology (NIST). Selenium recovery rates were considered acceptable (mean equal to 85 %). Selenium analysis was carried out in duplicate. Blanks were also analyzed. Quantification limit for Se was 0.002 mg kg^{-1}.

Statistical analysis

Selenium values were submitted to exploratory analysis to identify and eliminate outliers from the data set and perform descriptive statistics (mean, median, minimum and maximum values, standard deviation, skewness, and kurtosis). If the data did not follow a normal distribution, they were normalized by the Box-Cox transformation. Samples with Se values below the detection limit of quantification were not included in descriptive and geostatistical analyses (27 samples). Spearman correlation was used to obtain the correlation coefficient among selenium and soil physical and chemical properties. The 75th and 90th percentiles were calculated to establish the QRVs for Se. All statistical analysis was performed using the free statistical program "R" version 4.2.3., and the "ggplot2" package.

Spatial variability maps were constructed using the ordinary Kriging method as a geostatistical interpolator. Analysis was based on semivariogram analysis, which was adjusted by the spherical theoretical model (https://doi.org/10.1016/j.agsy.2018.01.030). The probability of areas presenting Se contents higher than the QRVs for the state of Piauí was spatially modeled by indicator kriging. Spatial statistical analysis procedures were performed using ArcGIS software (ESRI Inc., USA).

RESULTS AND DISCUSSION

Soils characterization

Soils of the Piauí state exhibit a medium texture, predominantly sandy (mean sand content: 710.0 g kg^{-1}; median: 740.6 g kg^{-1}), with low levels of SOC, ranging from 0.01 to 2.5 dag kg^{-1} (mean: 0.94; median: 0.67). Soil pH(H_2O) ranged from 3.1 to 8.6 (mean: 4.7 and median: 4.5) (Table 1). The CEC ranged from 0.03 to 34.53 $cmol_c$ dm^{-3}, indicating considerable variation among the soils. Extreme values for pH, P, Ca^{2+}, Mg^{2+}, and Al^{3+} were observed at some locations, showing high chemical variability in the study area. Fifty-five samples (26.4 %) showed higher Ca^{2+} content in comparison to the mean for the entire state (1.69 $cmol_c$ dm^{-3}), with 62 % of them located in the semiarid region (Caatinga biome), where conditions of lower acidity and less weathered soils prevail. Another 63 samples (30.3 %) had P content higher than the mean value (3.45 mg dm^{-3}). Most samples (79 %) were located in the Cerrado domain, where more acidic and weathered soils are commonly observed.

Selenium background and quality reference values

Selenium contents ranged from 0.002 to 4.78 mg kg^{-1}, with mean and median values equal 0.44 and 0.25 mg kg^{-1}, respectively (Figure 2). According to the human Se requirement proposed by Tan et al. (2002) and Song et al. (2020), 62 samples (30 %) were Se deficient (<0.125 mg kg^{-1}). Additionally, 14 samples (7 %) showed low Se levels (0.125-0.175 mg kg^{-1}), 60 samples (29 %) exhibited moderate Se levels (0.175-0.400 mg kg^{-1}), and 71 samples (34 %) contained high Se content (0.400-3.0 mg kg^{-1}). Only one sample showed excessive levels of Se (>3.0 mg kg^{-1}), exceeding the maximum limit set for Se in Brazilian soils by Conama (2009). Comparatively, most samples (72 %) had Se content below the world average of 0.44 mg kg^{-1}, in agreement with values reported in the literature for soils from other regions of Brazil (Gabos et al., 2014; Matos et al,. 2017; Carvalho et al., 2019; Nascimento et al., 2021).

Some values for Se in the soils exceed those reported by Nascimento et al. (2021) in two northeastern states of Brazil (Figure 2b). However, only a few sites showed Se levels above the upper limit of 1.35 mg kg^{-1} (11 samples). Compared with other regions in Brazil, our study indicates that the average Se content in soil is higher than that found in soils from Minas Gerais state (mean: 0.38 mg kg^{-1}; median: 0.29 mg kg^{-1}; n = 305) (Silva et al., 2012), Goiás and Minas Gerais States (mean: 0.04 mg kg^{-1}, n = 30; and 0.04 mg kg^{-1}, n = 60, respectively) (Carvalho et al., 2019), and São Paulo State (mean A horizon: 0.18 mg kg^{-1}; median: 0.10 mg kg^{-1}; n = 58) (Gabos et al., 2014). However, the average Se content in our study is lower than that observed in soils from the Jequitinhonha Valley region in Minas Gerais (Matos et al., 2017). This disparity may be attributed to the higher clay content of the Jequitinhonha Valley soils. Previous findings indicate that clay content affects soil Se contents (Lopes et al., 2017).

According to the global average Se content, the soils in the study area can generally be considered deficient in Se. Approximately 56 % of the sampled sites had moderate to high levels of Se (Tan et al., 2002) based on human needs, which is a widely referenced classification used in various studies (Ni et al., 2016; Song et al., 2020; Nascimento et al., 2021). While many sites have low Se contents, most samples (62 %) exceed the critical limit of soil Se deficiency, which is 0.125 mg kg^{-1} (Tan et al., 2002). Contents below that can induce endemic diseases such as Keshan disease (KSD) and Kashin Beck disease (KBD), which are linked to soil Se deficiency (Tan et al., 2002; Johnson et al., 2010; Du et al., 2018).

Table 1. Descriptive statistics of physical and chemical properties of the studied soils (n = 208)

Variables	Mean	Median	SD	Min	Max	Skewness	Kurtosis	p-value SW test
pH	4.70	4.50	±1.10	3.10	8.60	0.79	0.15	<0.0001
Ca^{2+} ($cmol_c$ dm^{-3})	1.69	0.34	±3.17	0.03	22.89	3.54	16.67	<0.0001
Mg^{2+}($cmol_c$ dm^{-3})	1.06	0.25	±2.58	0.01	19.72	4.60	23.68	<0.0001
K^+ ($cmol_c$ dm^{-3})	0.19	0.12	±0.18	0.01	1.26	2.51	9.27	<0.0001
P (mg dm^{-3})	3.45	2.08	±13.52	0.15	194.03	13.46	186.53	<0.0001
Al^{3+} ($cmol_c$ dm^{-3})	0.72	0.60	±0.60	0.00	4.80	1.80	9.06	<0.0001
H+Al ($cmol_c$ dm^{-3})	3.78	2.88	±3.28	0.40	17.50	1.69	3.31	<0.0001
CEC ($cmol_c$ dm^{-3})	3.67	1.76	±5.33	0.03	34.53	3.66	15.51	<0.0001
SB ($cmol_c$ dm^{-3})	2.94	0.73	±5.45	0.03	33.93	3.53	14.47	<0.0001
SOC (dag kg^{-1})	0.94	0.67	±0.72	0.01	2.50	0.71	-0.76	<0.0001
Sand (g kg^{-1})	710.0	740.6	±150.60	188.90	948.2	-0.91	0.52	<0.0001
Clay (g kg^{-1})	182.6	177.0	±94.30	3.00	508.0	0.81	0.95	<0.0001
Silt (g kg^{-1})	107.4	55.5	±125.30	0.35	608.65	1.71	2.44	<0.0001

SD: standard deviation; Min: minimum; Max: maximum; SW: Shapiro-Wilk normality test; CEC: effective cation exchange capacity; SB: sum of bases; SOC: soil organic carbon.

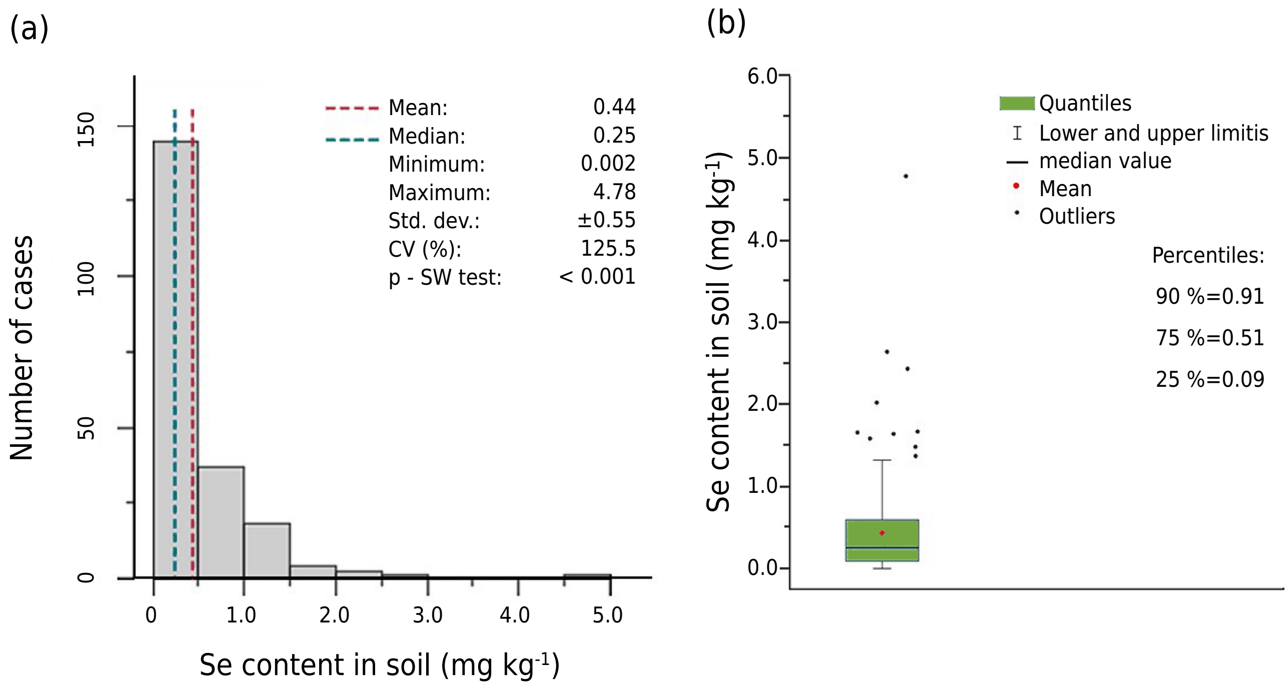

Figure 2. Descriptive statistics of Se content in soils from Piauí State: (a) histogram of the frequency distribution; and (b) box-plot with quartiles/percentiles and outliers.

The 75th and 90th percentiles were equal to 0.51 and 0.91 mg kg^{-1}, respectively (Figure 2b). Based on the 75th percentile, the Se QRV was higher than those calculated for other soils in Northeastern Brazil, such as Paraíba and Rio Grande do Norte states (0.19 mg kg^{-1}) (Nascimento et al., 2021) and Southeastern Brazil, such as São Paulo (0.25 mg kg^{-1}) (Cetesb, 2005) and Minas Gerais (0.50 mg kg^{-1}) (Copam, 2011). Most of the soils in the study area are derived from sedimentary rocks, which may explain the higher Se background value compared to other Northeastern Brazilian states with a predominance of crystalline rocks (IBGE, 2021).

Spatial distribution of Se in the study area

High variability in Se content in the area is evident (Figure 3a), with two natural hotspots observed in the eastern and southwestern regions. These areas are likely to surpass the 75th percentile (0.51 mg kg^{-1}) but have a low probability of exceeding the 90th percentile (0.91 mg kg^{-1}) (Figures 3b and 3c). Center-south, southeast, and north areas of the state exhibit the lowest Se levels (Figure 3a). Similar variability of Se in soils has been reported globally (Lopes et al., 2017; Natasha et al., 2018).

Distribution of Se-rich soils on a large scale is closely related to the geological context (Liao et al., 2020). Imran et al. (2020) and Nascimento et al. (2021) demonstrated that lithology controls Se content and affects its distribution in the soils. However, in our study, both high and low Se values occurred in the same geological environment of sedimentary rocks, indicating that other soil factors control the Se content in both hotspots.

Several studies have linked the soil Se content to wet deposition, particularly by rainfall (Suess et al., 2019; Pearson et al., 2019; Uchiyama et al., 2019). For example, Nascimento et al. (2021) found that Se deficiency is prevalent in semiarid areas, whereas regions experiencing annual rainfall exceeding 700 mm, typically exhibit elevated Se contents. Indeed, one of the hotspots for Se is in the most humid region of the state (southwestern hotspot), which coincides with the Cerrado biome, where the mean annual rainfall ranges from 800 to 1,200 mm yr^{-1} (Figure 1b). However, Se contents above the global average also occurred in the semiarid region (Figure 3), some sites in the eastern hotspot and also in other areas of the southeastern part - a region situated in the domain of the Caatinga biome, where the mean annual precipitation is less than 700 mm yr^{-1} (Figure 1b).

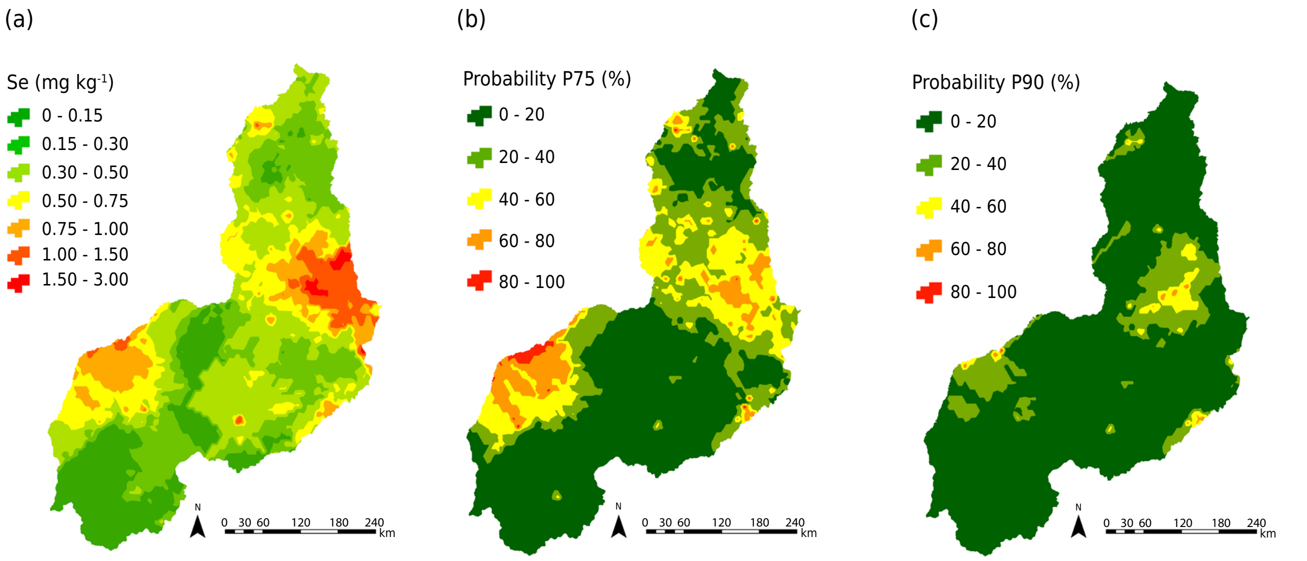

Figure 3. Spatial variability of selenium content (a) and the probability of quality reference value occurrence (b and c) in the surface soil layer of the Piauí State. P75(%): 75th percentile = 0.51 mg kg^{-1}; P90(%): 90th percentile = 0.91 mg kg^{-1}.

Relationship between geology, soil properties and Se contents

Mean and median Se contents in soils derived from sedimentary rocks (Figure 1d) were 0.45 and 0.24 mg kg^{-1}, respectively. In contrast, soils developed from metamorphic and igneous rocks had average and median Se contents of 0.39 and 0.28 mg kg^{-1}, respectively. Nascimento et al. (2021) and Liao et al. (2020) also reported higher mean Se values in soils derived from sedimentary rocks. However, we found no significant difference in the Se mean contents between soil parent materials (Figure 4). Also, no statistical difference was found between Se contents in the soils of the two biomes (Figure 5). Mean and median Se contents in the soils from Cerrado were 0.41 and 0.23 mg kg^{-1}, respectively, while the mean and median Se values for the Caatinga were 0.47 and 0.26 mg kg^{-1}, respectively (Figure 5).

Selenium contents above the global average were found in Ferralsols (*Latossolos*) and Arenosols (*Neossolos Quartzarênicos*) (Figure 6), although no significant difference in Se content was observed among different soil orders (Figure 7). Ferralsols (*Latossolos*), the predominant soils in the study area, are often acidic and highly weathered. These soils contain significant Fe and Al oxides and hydroxides contents (Gomes et al., 2004). It also leads to the predominance of clay mineral complexes with soil organic substances, enhancing the adsorption of Se, particularly in the inorganic selenite form (Se^{4+}). This Se form has low mobility in acidic soils (Kabata-Pendias and Pendias, 2000; Coppin et al., 2009; Natasha et al., 2018).

Average Se content in Arenosols was higher than the global average, probably because the mean value can be skewed by extreme values (outliers), which we observed in the Se distribution of these particular soils (Figure 6). In this specific case, three soil samples were situated in the hotspot (east part), which could account for the higher Se contents in sandy soils. Conversely, sandy soils typically exhibit low Se contents (Lopes et al., 2017).

The highest Se contents observed in the southwestern portion of the state (Figure 3a) are probably due to the higher SOC and clay contents and soil acidity conditions found in these locations (Coser et al., 2018). Selenium is more mobile and bioavailable under alkaline conditions (Fordyce et al., 2010). Thus, areas where soil pH ranges from

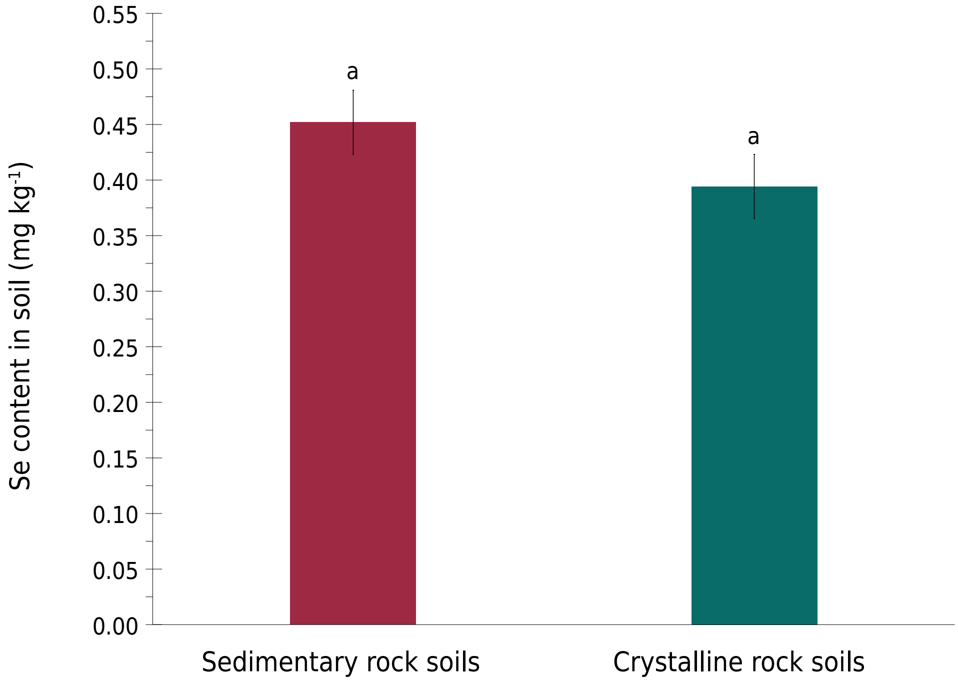

Figure 4. Selenium average content in soils with different parent materials of the Piauí State. Means with the same letter do not differ statistically by Fisher-Snedecor's F test (p-value = 0.09) ($p<0.05$) and Student's t-test (p-value = 0.74). Sedimentary rock soils (n = 155); crystalline rock soils (n = 53).

acidic to neutral conditions favor the adsorption of inorganic forms of Se on the surface of colloidal soil particles, such as selenite (Se^{4+}) and selenide (Se^{2-}) (Fordyce, 2007). Furthermore, soils with high contents of oxyhydroxide and organic matter tend to exhibit low Se mobility, which directly affects the total Se content and its availability (Lopes et al., 2017). In contrast, in the central-south region of the state, there are predominantly low to deficient Se levels (ranging from <0.125 to 0.175 mg kg^{-1}). In this region, soil acidity conditions are similar to those observed in the southwestern part. However, the SOC and clay contents decrease. The lowest Se levels found in the extreme south of the state coincide with areas where soils with low SOC and clay values prevail, corroborating what is commonly reported in the literature (Natasha et al., 2018).

Selenium content correlated significantly and positively with the SOC (0.33; $p<0.01$) and the silt and clay contents (0.15 and 0.24; $p<0.05$). The most significant correlation occurred between Se contents and SOC contents (weak positive). There was no significant correlation between Se and the other soil physical and chemical properties (data not shown).

A significant positive correlation between Se content and SOC is reported by Silva et al. (2012), Gabos et al. (2014), and Nascimento et al. (2021) in topsoils from Brazil. Organic matter is a relevant pool of Se retention due to the direct interaction between inorganic forms of Se, such as selenite, and clay minerals, such as clay-sized Fe and Al oxides, forming Se-metal-humus complexes (Coppin et al., 2009; Fernández-Martínez and Charlet, 2009). However, some studies also found no correlation between Se contents and organic matter in Colorado (Statwick and Sher, 2017) and Cerrado soils from Central-West and Southeast Brazil (Carvalho et al., 2019).

Clay fraction is also an important component influencing Se content in the soils due to the high adsorption of Se(IV) (selenite) on clay minerals and iron oxides, compared to Se(VI) (selenate) (Natasha et al., 2018). Negative correlation between Se and sand content can be explained by the low specific surface area and the few surface charges found in this fraction, which limits the adsorption of Se (Kämpf et al., 2009).

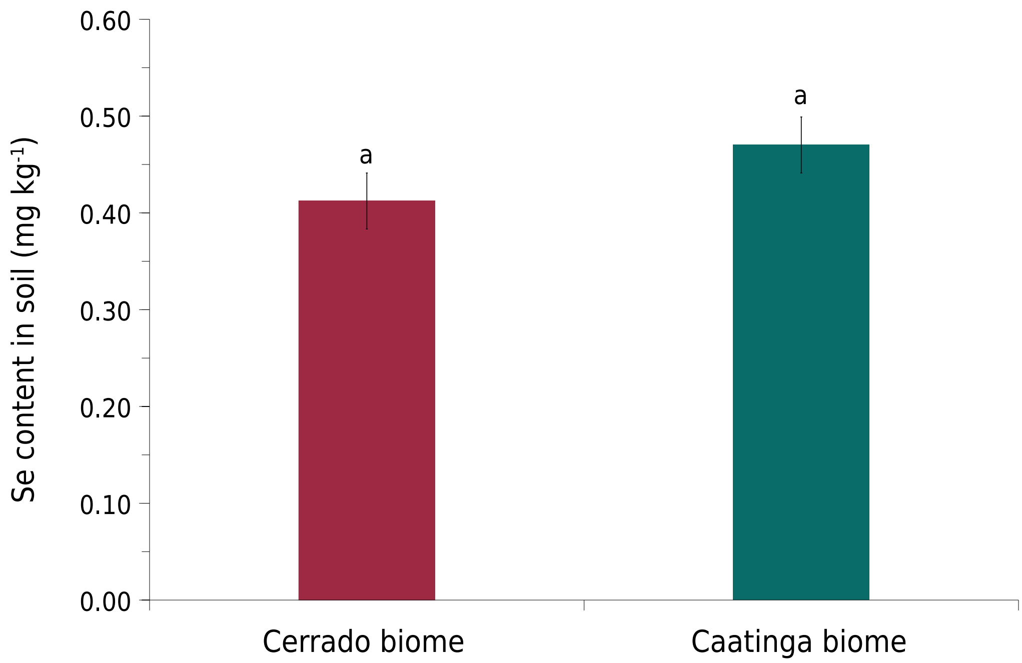

Figure 5. Mean values of Se content in the soil in different bioclimatic contexts from Piauí State, Brazil. Means with the same letter do not differ statistically by Fisher-Snedecor's F test (p-value = 0.37) and Student's t-test (p-value = 0.27) (p<0.05). Cerrado biome (n = 118); Caatinga biome (n = 90); Crystalline rock soils (n = 53).

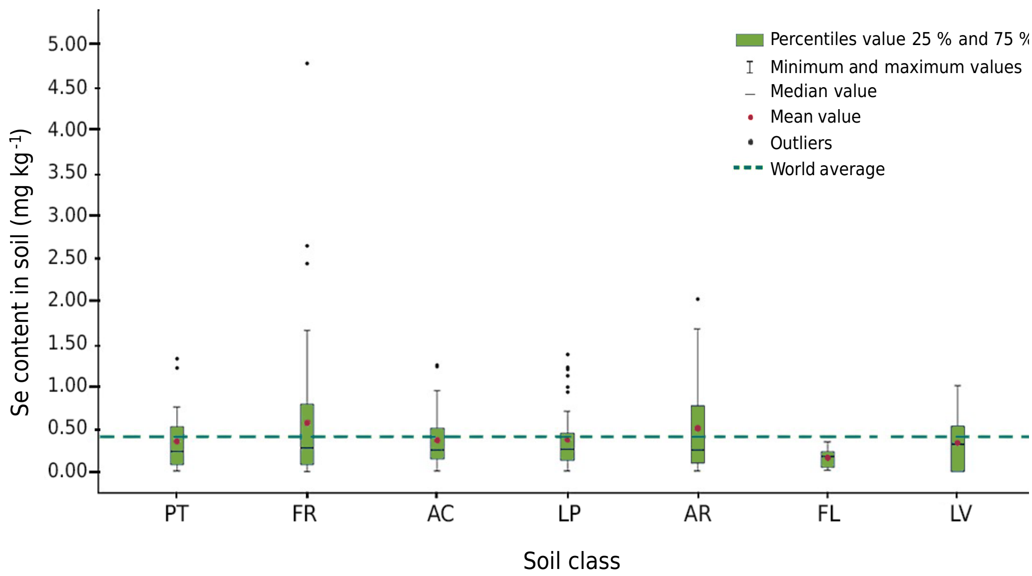

Figure 6. Distribution of Se contents according to the predominant soil classes in the state of Piauí, Brazil. PT: Plinthosols (*Plintossolos*) (n = 21); FR: Ferralsols (*Latossolos*) (n = 68); AC: Acrisols (*Argissolos*) (n = 42); LP: Leptosols (*Neossolos Litólicos*) (n = 45); AR: Arenosols (*Neossolos Quartzarênicos*) (n = 19); FL: Fluvisols (*Neossolos Flúvicos*) (n = 6); LV: Luvisols (*Luvissolos*) (n = 7).

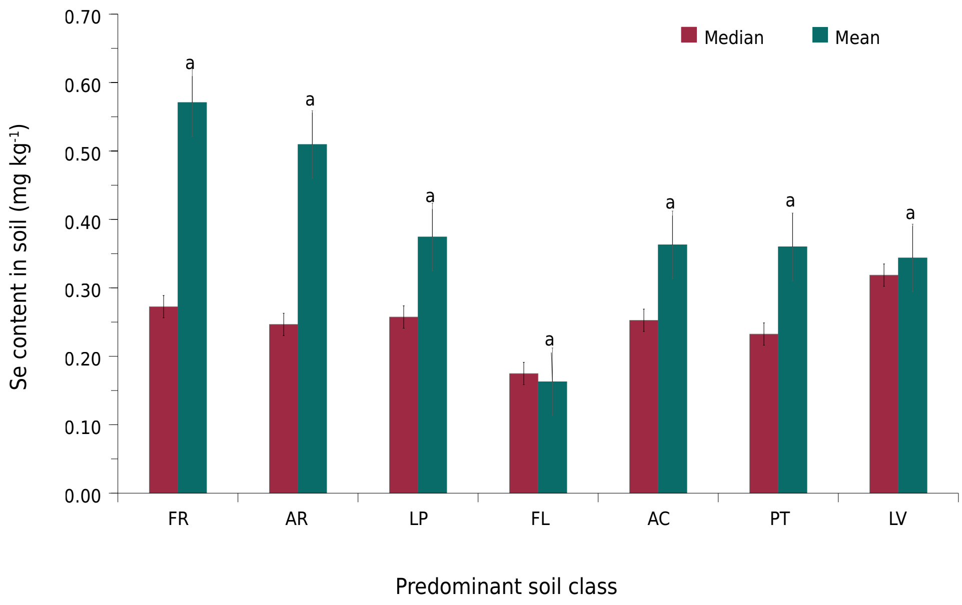

Figure 7. Mean and median values of Se content (± standard error) in the predominant soil types in the study area, according to the WRB reference soil groups. Values followed by the same letter do not differ statistically by the Kruskal-Wallis test ($p<0.05$). FR: Ferralsols (*Latossolos*) (n = 68); AR: Arenosols (*Neossolos Quartzarênicos*) (n = 19); LP: Leptosols (*Neossolos Litólicos*) (n = 45); FL: Fluvisols (*Neossolos Flúvicos*) (n = 6); AC: Acrisols (*Argissolos*) (n = 42); PT: Plinthosols (*Plintossolos*) (n = 21); LV: Luvisols (*Luvissolos*) (n = 7).

CONCLUSION

Background Se contents in the soils of the studied area ranged from deficient to high. While no areas were posing serious risks due to high Se contents, sites with Se contents too low to adequately supply crops deserve attention owing to human and animal health problems related to Se deficiency. Selenium spatial distribution showed high natural variability over the studied area. Such Se mapping suggests areas where more profound evaluations are needed to assess the local factors governing Se accumulations. In contrast to other studies, pedological rather than geological and climatic factors are the key factors governing the content and spatial variability of Se in the soils of the Piauí state.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data to this article can be found online at https://doi.org/10.1016/j.agsy.2018.01.030.

ACKNOWLEDGEMENTS

This research was supported by the Coordination for the Improvement of Higher Education Personnel (CAPES) that provided a scholarship to the first author. This study was financed by the Brazilian National Research and Development Council - CNPq (Process Number: 404394/2016-7).

AUTHOR CONTRIBUTIONS

Conceptualization: Cácio Luiz Boechat (equal), Clístenes Williams Araújo do Nascimento (equal), Gustavo de Sousa de Oliveira Leite (equal) and Yuri Jacques Agra Bezerra da Silva (equal).

Formal analysis: Jacqueline Sousa Paes Landim (equal), Lizandra de Sousa Luz Duarte (equal), Pâmalla Graziely Carvalho Morais (equal) and Paloma Cunha Saraiva (equal)

Funding acquisition: Cácio Luiz Boechat (equal), Clístenes Williams Araújo do Nascimento (equal) and Yuri Jacques Agra Bezerra da Silva (equal).

Investigation: Jacqueline Sousa Paes Landim (equal) and Yuri Jacques Agra Bezerra da Silva (equal).

Methodology: Cácio Luiz Boechat (equal), Gustavo de Sousa de Oliveira Leite (equal), Jacqueline Sousa Paes Landim (equal), Lizandra de Sousa Luz Duarte (equal), Pâmalla Graziely Carvalho Morais (equal), Paloma Cunha Saraiva (equal), Rennan Cabral Nascimento (equal) and Yuri Jacques Agra Bezerra da Silva (lead).

Project administration: Yuri Jacques Agra Bezerra da Silva (lead).

Resources: Clístenes Williams Araújo do Nascimento (lead).

Supervision: Yuri Jacques Agra Bezerra da Silva (lead).

Validation: Rennan Cabral Nascimento (lead).

Writing – original draft: Gustavo de Sousa de Oliveira Leite (equal), Rennan Cabral Nascimento (equal) and Yuri Jacques Agra Bezerra da Silva (equal).

Writing – review & editing: Clístenes Williams Araújo do Nascimento (equal), Gustavo de Sousa de Oliveira Leite (equal), Rennan Cabral Nascimento (equal) and Yuri Jacques Agra Bezerra da Silva (equal).

REFERENCES

Andrade Júnior AS, Bastos EA, Silva CO, Gomes AAN, Figueredo Júnior LGM. Atlas climatológico do Estado do Piauí. Teresina: Embrapa Meio-Norte; 2004 [cited 2023 Nov 22]. Available from: http://www.infoteca.cnptia.embrapa.br/infoteca/handle/doc/885291.

Alvares CA, Stape JL, Sentelhas PC, Gonçalves JLM, Sparovek G. Köppen's climate classification map for Brazil. Meteorol Z. 2013;22:711-28. https://doi.org/10.1127/0941-2948/2013/0507

Banuelos GS, Lin ZQ, Yin X. Selenium in the environment and human health [internet]. Boca Raton: CRC Press; 2013 [cited 2023 Nov 22]. Available from: https://books.google.com.br/books?id=QC3MBQAAQBAJ&hl=pt-BR&lr=.

Belay A, Joy EJM, Chagumaira C, Zerfu D, Ander EL, Young SD, Bailey EH, Lark RM, Broadley MR, Gashu D. Selenium deficiency is widespread and spatially dependent in Ethiopia. Nutrients. 2020;12:1565. https://doi.org/10.3390/nu12061565

Carvalho GS, Oliveira JR, Curi N, Schulze DG, Marques JJ. Selenium and mercury in Brazilian Cerrado soils and their relationships with physical and chemical soil characteristics. Chemosphere. 2019;218:412-5. https://doi.org/10.1016/j.chemosphere.2018.11.099

Centro de Pesquisas Econômicas e Sociais do Piauí - Cepro. Piauí em números 10. ed. Teresina: Cepro; 2013 [cited 2023 Nov 21]. Available from: http://www.cepro.pi.gov.br/download/201310/CEPRO13_aab5263f9a.pdf.

Companhia Ambiental do Estado de São Paulo - Cetesb. Valores orientadores para solo e água subterrânea no estado de São Paulo. São Paulo: Cetesb; 2014 [cited 2023 Nov 21]. Available from: https://cetesb.sp.gov.br/solo/wp-content/uploads/sites/18/2014/12/valores-orientadores-nov-2014.pdf.

Conselho Estadual de Política Ambiental - Copam. Deliberação Normativa Copam No. 166, de 29 de junho de 2011: Altera o Anexo I da Deliberação Normativa Conjunta COPAM CERH No. 2 de 6 de setembro de 2010, estabelecendo os Valores de Referência de Qualidade dos Solos. Diário do Executivo Minas Gerais; 2011 [cited 2023 Feb 9]. Available from: http://www.siam.mg.gov.br/sla/download.pdf?idNorma=18414.

Conselho Nacional do Meio Ambiente - Conama. Resolução No. 420, de 28 de dezembro de 2009: Dispõe sobre critérios e valores orientadores de qualidade do solo quanto à presença de substâncias químicas e estabelece diretrizes para o gerenciamento ambiental de áreas contaminadas por essas substâncias em decorrência de atividades antrópicas. Brasília, DF: Ministério do Meio Ambiente; 2009 [cited 2023 Nov 21]. Available from: http://conama.mma.gov.br/?option=com_sisconama&task=arquivo.download&id=601

Coppin F, Chabroullet C, Martin-Garin A. Selenite interactions with some particulate organic and mineral fractions isolated from a natural grassland soil. Eur J Soil Sci. 2009;60:369-76. https://doi.org/10.1111/j.1365-2389.2009.01127.x

Coser TR, Figueiredo CC, Jovanovic B, Moreira TN, Leite GG, Cabral Filho SLS, Kato E, Malaquias JV, Marchão RL. Short-term buildup of carbon from a low-productivity pastureland to an agrisilviculture system in the Brazilian savannah. Agr Syst. 2018;166:184-95. https://doi.org/10.1016/j.agsy.2018.01.030

Du Y, Luo K, Ni R, Hussain R. Selenium and hazardous elements distribution in plant-soil-water system and human health risk assessment of Lower Cambrian, Southern Shaanxi, China. Environ Geochem Hlth. 2018;40:2049-69. https://doi.org/10.1007/s10653-018-0082-3

Fernández-Martínez A, Charlet L. Selenium environmental cycling and bioavailability: a structural chemist point of view. Rev Environ Sci Bio. 2009;8:81-110. https://doi.org/10.1007/s11157-009-9145-3

Fordyce F. Selenium geochemistry and health. Ambio. 2007;36:94-7. https://doi.org/10.1579/0044-7447(2007)36[94:sgah]2.0.co;2

Fordyce FM, Brereton N, Hughes JC, Luo W, Lewis J. An initial study to assess the use of geological parent materials to predict the Se concentration in overlying soils and in five staple foodstuffs produced on them in Scotland. Sci Total Environ. 2010;408:5295-305. https://doi.org/10.1016/j.scitotenv.2010.08.007

França LCJ, Silva JBL, Lisboa GS, Lima TP, Ferraz FT. Elaboração de carta de risco de contaminação por agrotóxicos para a Bacia do Riacho da Estiva, Brasil. Floresta Ambient. 2016;23:463-74.https://doi.org/10.1590/2179-8087.141415

Gabos MB, Alleoni LRF, Abreu CA. Background levels of selenium in some selected Brazilian tropical soils. J Geochem Explor. 2014;145:35-9. https://doi.org/10.1016/j.gexplo.2014.05.007

Gee GW, Or D. Particle size analysis. In: Dane JH, Topp GC, editors. Methods of soil analysis: Part 4 Physical methods. 4th ed. Madison: Soil Science Society of America; 2002. p. 255-78. https://doi.org/10.2136/sssabookser5.4.c12

Gomes JBV, Curi N, Motta PEF, Ker JC, Marques JJGSM, Schulze DG. Análise de componentes principais de atributos físicos, químicos e mineralógicos de solos do bioma cerrado. Rev Bras Cienc Solo. 2004;28:137-53. https://doi.org/10.1590/S0100-06832004000100014

He Y, Xiang Y, Zhou Y, Yang Y, Zhang J, Huang H, Shang C, Luo L, Gao J, Tang L. Selenium contamination, consequences and remediation techniques in water and soils: A review. Environ Res. 2018;164:288-301. https://doi.org/10.1016/j.envres.2018.02.037

Imran M, Akhtar MS, Mehmood A, Rukh S, Khan A, Zhikun C, Mujtaba G. Soil selenium transformation across different parent materials in Pothwar uplands of Pakistan. Arab J Geosci. 2020;13:1098. https://doi.org/10.1007/s12517-020-06111-1

Instituto Brasileiro de Geografia e Estatística - IBGE. Levantamento geológico do Brasil. IBGE; 2021 [cited 2023 Nov 22]. Available from: https://www.ibge.gov.br/geociencias/downloads-geociencias.html.

Instituto Brasileiro de Geografia e Estatística - IBGE. Censo Demográfico 2022; 2023. IBGE; 2023 [cited 2023 Nov 21]. Available from: https://censo2022.ibge.gov.br/panorama/.

Instituto Brasileiro de Geografia e Estatística - IBGE. Macrocaracterização dos recursos naturais do Brasil: Províncias estruturais, compartimentos de relevo, tipos de solos, regiões fitoecológicas e outras áreas. Rio de Janeiro: IBG; 2019 [cited 2020 Nov 5]. Available from: https://biblioteca.ibge.gov.br/visualizacao/livros/liv101648.pdf.

Instituto Brasileiro de Geografia e Estatística - IBGE. Organização do território: Malhas territoriais. IBGE; 2020 [cited 2023 Nov 22]. Available from: https://www.ibge.gov.br/geociencias/organizacao-do-territorio/malhas-territoriais.html.

Johnson CC, Fordyce FM, Rayman MP. Symposium on "Geographical and geological influences on nutrition" Factors controlling the distribution of selenium in the environment and their impact on health and nutrition. Proc Nutr Soc. 2010;69:119-32. https://doi.org/10.1017/S0029665109991807

Kabata-Pendias A, Pendias H. Trace elements in soils and plants. 3rd ed. Boca Raton: CRC Press; 2000. Available from: http://base.dnsgb.com.ua/files/book/Agriculture/Soil/Trace-Elements-in-Soils-and-Plants.pdf.

Kämpf N, Curi N, Marques JJ. Óxido de alumínio, silício, manganês e titânio. In: Melo VF, Alleoni LRF, editors. Química e mineralogia do solo. Viçosa, MG: Sociedade Brasileira de Ciência do Solo; 2009. p. 573-610.

Liao Q, Cui X, Huang S, Huang B, Ren J, Gu X, Fan J, Xu H. Element geochemistry of selenium-enriched soil and its main sources in Jiangsu Province. Geology in China. 2020;47:1813-25. https://doi.org/10.12029/gc20200617

Ligowe IS, Phiri FP, Ander EL, Bailey EH, Chilimba ADC, Gashu D, Joy EJM, Lark RM, Kabambe V, Kalimbira AA. Selenium deficiency risks in sub-Saharan African food systems and their geospatial linkages. P Nutr Soc. 2020;79:457-67. https://doi.org/10.1017/S0029665120006904

Lopes G, Ávila FW, Guilherme LRG. Selenium behavior in the soil environment and its implication for human health. Cienc Agrotec. 2017;41:605-15. https://doi.org/10.1590/1413-70542017416000517

Magalhães LA, Miranda EE. MATOPIBA: Quadro natural. Campinas: Embrapa Territorial; 2014. (Nota técnica 5). Available from: https://www.embrapa.br/busca-de-publicacoes/-/publicacao/1037412/matopiba-quadro-natural.

Matos RP, Lima VMP, Windmöller CC, Nascentes CC. Correlation between the natural levels of selenium and soil physicochemical characteristics from the Jequitinhonha Valley (MG), Brazil. J Geochem Explor. 2017;172:195-202. https://doi.org/10.1016/j.gexplo.2016.11.001

Matschullat J, Ottenstein R, Reimann C. Geochemical background - Can we calculate it? Environ Geol. 2000;39:990-1000. https://doi.org/10.1007/s002549900084

Menezes RSC, Sampaio EVSB, Giongo V, Pérez-Marin AM. Biogeochemical cycling in terrestrial ecosystems of the Caatinga Biome. Braz J Biol. 2012;72:643-53. https://doi.org/10.1590/S1519-69842012000400004

Moghaddam A, Heller RA, Sun Q, Seelig J, Cherkezov A, Seibert L, Hackler J, Seemann P, Diegmann J, Pilz M, Bachmann M, Minich WB, Schomburg L. Selenium deficiency is associated with mortality risk from COVID-19. Nutrients. 2020;12:2098. https://doi.org/10.3390/nu12072098

Muthayya S, Hall J, Bagriansky J, Sugimoto J, Gundry D, Matthias D, Prigge S, Hindle P, Moench-Pfanner R, Maberly G. Rice fortification: An emerging opportunity to contribute to the elimination of vitamin and mineral deficiency worldwide. Food Nutr Bull. 2012;33:296-307. https://doi.org/10.1177%2F156482651203300410

Nascimento CWA, Silva FBV, Fabricio Neta ADB, Biondi CM, Lins SAS, Almeida Júnior AB, Preston W. Geopedology-climate interactions govern the spatial distribution of selenium in soils: A case study in northeastern Brazil. Geoderma. 2021;399:115119. https://doi.org/10.1016/j.geoderma.2021.115119

Natasha, Shahid M, Niazi NK, Khalid S, Murtaza B, Bibi I, Rashid MI. A critical review of selenium biogeochemical behavior in soil-plant system with an inference to human health. Environ Pollut. 2018;234:915-34. https://doi.org/10.1016/j.envpol.2017.12.019

Ni R, Luo K, Tian X, Yan S, Zhong J, Liu M. Distribution and geological sources of selenium in environmental materials in Taoyuan County, Hunan Province, China. Environ Geochem Hlth. 2015;38:927-38. https://doi.org/10.1007/s10653-015-9772-2

Pearson C, Howard D, Moore C, Obrist D. Mercury and trace metal wet deposition across five stations in Alaska: Controlling factors, spatial patterns, and source regions. Atmos Chem Phys. 2019;19:6913-29. https://doi.org/10.5194/acp-19-6913-2019

Pfaltzgraff PAS, Torres FSM, Brandão RL. Geodiversidade do estado do Piauí. Recife: CPRM; 2010. Available from: https://rigeo.cprm.gov.br/jspui/bitstream/doc/16772/1/Geodiversidade_PI.pdf.

Secretaria de Planejamento do Piauí - Seplan. Piauí: Pilares de crescimento e inclusão social - Avaliação ambiental e social. Teresina: Seplan; 2015. Available from: https://www.docdroid.net/yU3tnVK/docsalvaguardasrevisada-23set2015-pdf.

Serviço Geológico do Brasil - SGB. GeoSGB - Litoestratigrafia dos estados: Piauí. SGB; 2017 [cited 2023 Nov 22]. Available from: https://geosgb.sgb.gov.br/.

Silva AC, Torrado PV, Abreu Júnior JS. Métodos de quantificação da matéria orgânica do solo. Rev Universidade de Alfenas. 1999;5:21-6.

Silva J, Silva JD, Brustoline CR, Ferreira VP, Santos Junior L, Mello JWV, Michereff Filho M. Teor natural de selênio em solos do estado de Minas Gerais. In: FertBio – A responsabilidade socioambiental da pesquisa agrícola; 2012 Sep 17-21; Maceió, Alagoas. Maceió: Sociedade Brasileira de Ciência do Solo; 2012. Available from: https://www.alice.cnptia.embrapa.br/bitstream/doc/944159/1/0000000553FERTBIOJuscimar.pdf.

Song T, Cui G, Su X, He J, Tong S, Liu Y. The origin of soil selenium in a typical agricultural area in Hamatong River Basin, Sanjiang Plain, China. Catena. 2020;185:104355. https://doi.org/10.1016/j.catena.2019.104355

Souza KB, Silva JBL, Matias SSR, Almeida KNS, Lisboa GS, Ratke RF. Mudança no uso e ocupação do solo na bacia hidrográfica do rio Uruçuí-Preto, Piauí. Braz J Develop. 2019;5:25490-511. https://doi.org/10.34117/bjdv5n11-211

Statwick J, Sher AA. Selenium in soils of western Colorado. J Arid Environ. 2017;137:1-6. https://doi.org/10.1016/j.jaridenv.2016.10.006

Suess E, Aemisegger F, Sonke JE, Sprenger M, Wernli H, Winkel LH. Marine versus continental sources of iodine and selenium in rainfall at two European high-altitude locations. Environ Sci Technol. 2019;53:1905-17. https://doi.org/10.1021/acs.est.8b05533

Sun GX, Meharg AA, Li G, Chen Z, Yang L, Chen SC, Zhu YG. Distribution of soil selenium in China is potentially controlled by deposition and volatilization? Sci Rep-Uk. 2016;6:20953. https://doi.org/10.1038/srep20953

Tan J, Zhu W, Wang W, Li R, Hou S, Wang D, Yang L. Selenium in soil and endemic diseases in China. Sci Total Environ. 2002;284:227-35. https://doi.org/10.1016/S0048-9697(01)00889-0

Tan LC, Nancharaiah YV, van Hullebusch ED, Lens PNL. Selenium: environmental significance, pollution, and biological treatment technologies. Biotechnol Adv. 2016;34:886-907. https://doi.org/10.1016/j.biotechadv.2016.05.005

Teixeira PC, Donagemma GK, Fontana A, Teixeira WG. Manual de métodos de análise de solo. 3. ed. rev e ampl. Brasília, DF: Embrapa; 2017.

Teng Y, Ni S, Wang J, Niu L. Geochemical baseline of trace elements in the sediment in Dexing area, South China. Environ Geol. 2008;57:1649-60. https://doi.org/10.1007/s00254-008-1446-2

United States Environmental Protection Agency - Usepa. Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils, and oils. Usepa; 2007 [cited 2020 Dec 20]. Available from: https://www.epa.gov/sites/default/files/2015-12/documents/3051a.pdf.

Uchiyama R, Okochi H, Ogata H, Katsumi N, Nakano T. Characteristics of trace metal concentration and stable isotopic composition of hydrogen and oxygen in “urban-induced heavy rainfall” in downtown Tokyo, Japan; The implication of mineral/dust particles on the formation of summer heavy rainfall. Atmos Res. 2019;217:73-80. https://doi.org/10.1016/j.atmosres.2018.10.017

Ullah H, Liu G, Yousaf B, Ali MU, Irshad S, Abbas Q, Ahmad R. A comprehensive review on environmental transformation of selenium: Recent advances and research perspectives. Environ Geochem Hlth. 2018;41:1003-35. https://doi.org/10.1007/s10653-018-0195-8

Vasiliu M, Dixon DA. Selenium. In: White WM, editor. Encyclopedia of geochemistry: A comprehensive reference source on the chemistry of the earth. Cham: Springer; 2018. p. 1326-8. https://doi.org/10.1007/978-3-319-39312-4

Wadgaonkar SL, Nancharaiah YV, Esposito G, Lens PNL. Environmental impact and bioremediation of seleniferous soils and sediments. Crit Rev Biotechnol. 2018;38:941-56. https://doi.org/10.1080/07388551.2017.1420623

Winkel LHE, Johnson CA, Lenz M, Grundl T, Leupin OX, Amini M, Charlet L. Environmental selenium research: From microscopic processes to global understanding. Environ Sci Technol. 2012;46:571-9. https://doi.org/10.1021/es203434d

World Health Organization - WHO. Global prevalence of vitamin A deficiency in populations at risk 1995-2005: WHO global database on vitamin A deficiency. Switzerland: WHO Press; 2009. Available from: https://apps.who.int/iris/handle/10665/44110.

Xie M, Sun X, Li P, Shen X, Fang Y. Selenium in cereals: Insight into species of the element from total amount. Compr Rev Food Sci F. 2021;20:2914-40. https://doi.org/10.1111/1541-4337.12748