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

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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 eighty 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$_2$O) 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)

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

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.
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 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.
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
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 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).
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).
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.

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REFERENCES


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
Leite et al. Geochemical background and geopedological interactions of selenium in...

Consuelo. Rafaello. In: Leite et al. Geochemical background and geopedological interactions of selenium in...


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


Instituto Brasileiro de Geografia e Estatística - IBGE. Macrocaracterização dos recursos naturais do Brasil: Províncias estruturais, compartimentos de relevo, tipos de solos, regiões


