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Distribution of lithium in soil from selected states of Brazil: mineral potential and health relationships

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Abstract

Lithium (Li, atomic number 3), the lightest metal on Earth, is in growing demand due to its use in batteries to power various electrical devices and electric vehicles. Li is also used to stabilize mood and prevent suicide in patients with affective disorders. Geochemical mapping provides a means of visualizing spatial variations in the chemical composition of the surface of the Earth. The objective of the study was to determine the concentration and distribution of Li in soils to identify areas with potential for prospecting and look for relationships with human health. The research was carried out between 2003 and 2017 in 13 Brazilian states, covering an area of 3,313,750 km², in which 3688 soil samples were collected in a grid of 25x25km (625km²). The samples (2kg) collected at the top of the B horizon (up to 30 cm) were reduced at the laboratory with aqua regia and analyzed by ICP-MS. The data indicate that in the total of the 13 states, the concentration of Li in the soils (mg/kg) ranges between 0.5 and 167, with a median of 2. Higher levels stand out in the states of Paraíba (0.5-167.15), Ceará (0.7-63.7), Pernambuco (0.5-63.7), Minas Gerais (0.5-83.2), Alagoas (2.0-40.4) and Mato Grosso do Sul (0.5-61.2). In the Pernambuco and Minas Gerais states, the highest values overlap with the Borborema Province and District of Araçuaí, respectively, which already produce Li hosted in pegmatites and have the potential for new deposits. Anomalous Li values above 11.75 mg/kg (estimated as national reference) cover a prospective area of around 25,225 km², distributed for 140 municipalities, or approximately 0.76% of the studied area. On a regional scale, there was no causal correlation between state suicide rates and the levels of Li in the soil.

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1. Introduction

The demand for lithium (Li) in international markets is on the rise and will increase further with the massive use of electric vehicles (Martin et al. 2017). Lithium is today a key element in the manufacture of rechargeable Li-ion batteries (LIB), with different configurations, for energy storage and essential for the decarbonization of transport and the fight against climate change. This technological solution, which is claimed to be the most advantageous and which is expected to prevail until 2050, has led to a rush for lithiniferous raw materials, encouraging prospecting and mineral research (e.g., Deng-hong et al. 2020; Benson et al. 2023). Currently, primary lithiniferous raw materials occur mainly in two types of deposits: brine-type lithium is found in Bolivia, Chile and Argentina, as well as China and the USA. On the other hand, lithium deposits in pegmatites are located in Australia, Austria, Brazil, Canada, China, the Congo, Czech Republic, Finland, Germany, Mali, Namibia, Peru, Portugal, Serbia, Spain, the USA and Zimbabwe (SGB-CPRM 2023). Different mineral phases are explored in pegmatite rocks, including spodumene, petalite, lepidolite and amblygonite, among others. The most commercialized Li compounds are carbonate (Li_2CO_3) and hydroxide (LiOH).

Regardless of its exploration, knowledge of the resources available in each region is essential for local development and must therefore be promoted. The identification of areas of potential interest for each resource must be a priority for each country, as the concept of reserves is not immutable over time and resources discovered today could be solutions to future problems (Pinheiro 2020).

In Brazil there is also a significant increase in interest in this element, such as studies carried out by Paes et al. (2016), which describes six regions in Brazil with Li potential: (1) Pegmatite district of Araçuaí, Minas Gerais, where they carried out excellent research that led to a boom in the discovery of

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new deposits in the following years, with some already being explored; (2) Borborema Pegmatite Province, covering the states of Rio Grande do Norte and Paraíba; (3) Sub Province of Solonópolis Ceará; (4) Eastern Region of Minas Gerais; (5) Pegmatitic Province of São João Del Rei, Minas Gerais; and (6) Northwest of Rio de Janeiro.

Chaves and Dias (2022) reported that Li minerals occur associated with granitic pegmatites, mainly in Minas Gerais in the Eastern Pegmatitic Province of Brazil, in the following districts: (1) Araçuaí; (2) São José da Safira; (3) Conselheiro Pena; (4) São João Del Rei (outside the aforementioned province). Chaves and Dias (2022) highlight that the Li deposits in the Araçuaí region are of the LCT (Lithium-Cesium-Tantalum) type and that there is great favorability for new Li deposits in Brazil.

One of the ways to identify possible places of interest is through soil geochemical mapping. Although initially these were only prepared with the aim of obtaining background or reference levels for mineral prospecting, they are currently also used in the context of environmental impact studies, agricultural practice and geomedicine (Inácio et al. 2008).

It is estimated that it is possible to find Li in trace amounts in any type of soil. Concentrations between 10 and 40 mg/kg are accepted as background concentrations, with an average of 20 mg/kg to 30 mg/kg in the soils derived from granitic rocks (Kavanagh et al. 2018). In general, lower values are found in sandy soils (average levels reported between 6 and 30 mg/kg) and higher values in calcareous soils (average levels reported between 26.5 and 80 mg/kg) from different countries (Kabata-Pendias 2010).

Lithium is a very soluble and mobile element during the initial phases of soil formation, becoming more stable due to its firm bonding with clay minerals, organic matter, and iron and manganese hydroxides (Kabata-Pendias and Mukherjee 2007; Yalamanchali 2012). The abundance of Li in the surface layer of the soil is highly correlated with the clay fraction (Kabata-Pendias and Mukherjee 2007), therefore, there is apparently a correlation between its concentration and soil texture.

The daily intake of Li depends largely on the geographic locations, due to the constitution of rocks and soils, so estimates can vary from a few to several milligrams per day, which is believed to be a reflection of the uneven distribution of Li on the earth surface, resulting in a very variable intake by populations from different regions. Schrauzer (2002) proposed a provisional daily dose of 1 mg Li for a 70 kg adult. However, despite it being estimated that a large part of the population consumes deficient amounts of Li, there is still no dose recommended by the World Health Organization (Sobolev et al. 2019).

The largest sources of Li in the human diet are cereals and vegetables (0.5-3.4 mg/kg), dairy products (0.5 mg/kg), meat (0.012 mg/kg) (Weiner 1991), and in some areas, drinking water (0.1-2.0 µg/L). In a recent study carried out in water supply from 88 municipalities in the northeast region of the State of São Paulo (Brazil), Dovidauskas et al. (2019) reported that 34.8% of the 4,347 samples analyzed present the Li maximum concentration of 28 µg/L. Neves et al. (2015) detected a variation between <1 and 191 µg Li/L in public water supplies from 45 municipalities on the Portuguese mainland (from surface and/or underground origin). In this study, around 75% of the samples presented a concentration below 10 µg/L and a median of 4 µg/L, close to that indicated by Birke et al. (2010) for this type of water in several European countries (average of 2.65 µg/L, in 579 samples) and like that determined in Germany (4.45 µg/L, in 164 samples).

Several bottled mineral waters are naturally enriched with Li; the highest value (9.86 µg/L) was recorded in bottled water from Slovakia (Reimann et al. 2010). In Portuguese bottled waters, Neves et al. (2015) recorded Li levels between < 1 and 2210 µg/L, with 73% of samples showing levels below 45 µg/L and a median of 16 µg/L. Within the scope of the European Groundwater Geochemistry Atlas (Reimann and Birke 2010), which involved 38 European countries and the analysis of 1785 samples of bottled water, a median value of 14.9 µg/L was also detected.

In recent years, several studies have emerged that suggest that taking Li in low doses can also promote mental health benefits, demonstrating positive effects. Schrauzer and Vroey (1994) showed beneficial effects on well-being and mood in a group of recovering drug addicts through the daily intake of a supplement with 400 µg of Li. Its neuroprotective effect was observed in clinical trials in patients with Alzheimer's disease by taking 300 µg per day of Li (Marielza et al. 2013) and in individuals at very high risk for psychosis (Berger et al. 2012). Other studies, carried out in geographic locations with different climates, habits and diets, have indicated an inverse relationship between the Li content in drinking water and the suicide rate (Schrauzer and Shrestha 1990; Ohgami et al. 2009; Kapusta et al. 2011; Giotakos et al. 2013; Liaugaudaite et al. 2017), among others. Although this trend has not always been observed in all studies (e.g., Kabacs et al. 2011; Oliveira et al. 2019), some researchers debate whether the addition of Li to public water supplies would be beneficial for the mental health of the general population. (Kabacs et al. 2011). However, the threshold level of natural Li that could provide protection against suicide is still unknown.

According to data from the WHO (OPAS 2021), more than 700,000 people die each year due to suicide, which represents one in every 100 recorded deaths. The global suicide rate decreased by 36% between 2000 and 2019, but in the Americas, the rates increased by 17% in this period. And, in 2019, suicide rates in the regions of Africa (11.2/100 thousand inhabitants), Europe (10.5/100 thousand inhabitants), and Southeast Asia (10.2 per 100 thousand inhabitants) were higher than the global average (9/100 thousand). The lowest suicide rate (6.4/100 thousand inhabitants) was recorded in the Eastern Mediterranean region (OPAS 2021). In Brazil, the suicide rate in 2019 was 6.68 and the global rate was 9.0 (Ministerio da Saúde 2021). According to the Brazilian Public Security Yearbook from the Brazilian Public Security Forum, released in 2023, there were 16,262 suicide records in Brazil in 2022.

Suicidal behavior is the most extreme self-destructive tendency. Globally, more than 90% of people who commit suicide have psychiatric diagnoses at the time of death, most commonly mood, psychotic, and/or substance use disorders (Bertolote and Fleischmann 2002). Brazil has the third-worst mental health index among the 64 countries studied. In the annual Mental State of the World report, the country scored 52.9 MHQ (Mental Health Quotient), ahead of only the United Kingdom and South Africa and 11 points below the general average. A study on the global burden of disease showed that, worldwide, mental disorders account for 32.4% of years of life lived with disability (Vigo et al. 2016) and, in Brazil, recent estimates (GBD 2016 Brazil Collaborators 2018) showed that depression and anxiety are, respectively, the fifth and sixth causes of years of life lived with disability. As an example, Figure 1 illustrates the distribution of suicide mortality rate in Brazil for the period between 2009 and 2011 (Mota 2014). The author reported, for example, a rate of 10 to 15 suicides per 100,000 inhabitants in the states of Minas Gerais and Mato Grosso do Sul and the highest suicide rate (15 to 26) in the northwest region of Brazil. However, Wroblevski et al. (2020) also analyzed the spatial distribution of suicide among Brazilian micro-regions in the years 2000, 2005, 2010 and 2015. The results showed that the southern region of Brazil had the highest suicide rate over the years, and the lowest rate was observed in the Northeast region. Other study on suicide cases in the Northeast of Brazil, between 2010 and 2014 shows that among the ten municipalities with the highest suicide rates in the Northeast, São José do Seridó stands out, in first place, with 35.63 deaths/100 thousand inhabitants, and Ouro Branco, in third place, with 29.21 deaths/100 thousand inhabitants. An important series of bibliographical references can be found in the work of Cortez et al. (2019) in Cruz et al. (2022).

This research presents the results of Li in the soil, from a low-density geochemical survey, carried out in 13 states by the Geological Services of Brazil-CPRM, between 2003 and 2017 (Viglio et al. 2022), with the aim of a) identifying new areas in municipalities with lithiniferous potential for eventual prospecting of the element and b) recognizing areas that can contribute to environmental health benefits (human and animal), focusing on possible relationships between suicide rates and Li contents in the soils of the regions under study.

2. Methodology

In the period between 2003 and 2017, the Geological Survey of Brazil-CPRM, based on the methodology proposed by IUGS in Project IGCP-259, carried out low-density geochemical surveys (3688 samples), in 13 states, covering an area of 3,313,750 km², equivalent to around 38.9% of the Brazilian territory (Viglio et al. 2022). In this research , the results and interpretation of Li in soil from the states of Alagoas (AL), Bahia (BA), Ceará (CE), Espírito Santo (ES), Goiás (GO), Mato Grosso do Sul (MS), Minas Gerais (MG), Pará (PA), Paraíba (PB), Pernambuco (PE), Rio de Janeiro (RJ), Roraima (RR) and São Paulo (SP) are presented. It is important to highlight that the states of Bahia, Goiás, Pará and Roraima were partially covered, and in Roraima, there was no access to 51.3% of the state because they are Indigenous and environmentally protected lands.

Soil samples were collected generally in road cuts and auger holes (cultivation areas, pastures) in a 25x25 km net, with duplicates every 20 collections and at the top of the B horizon (average depth between 20 and 30 cm). Sample analysis was carried out by inductively coupled plasma emission spectrometry (ICP-OES/MS) in the fine fraction (< 80 # or 0.177 mm), after drying at low temperature (maximum 50°C), grinding at 150 #, and solubilization with aqua regia (AR: 3ml HCl:1 ml HNO_3), in the SGS-Geosol laboratories.

The statistical treatment of the data obtained was carried out using the *Statistic* software. All results below the detection limit (DL=1 mg/kg) were replaced by the value 0.5 mg/kg. The background value presented here refers to a range of variation between quartiles 1 (25%) and 3 (75%), which contains 50% of the results obtained and is represented by the median value. The Li distribution maps were generated by the inverse square distance with a maximum neighborhood number of 8, using the ArcGis 10.8 software, through rendered surfaces that represent bands of continuous content, separated into 5 intervals. These intervals are defined from smallest to largest by values: below quartile 1 (25%), between quartile 1 and the median (50%), between the median and quartile 3 (75%), between quartile 3 and the UW (Upper Whisker) and above.

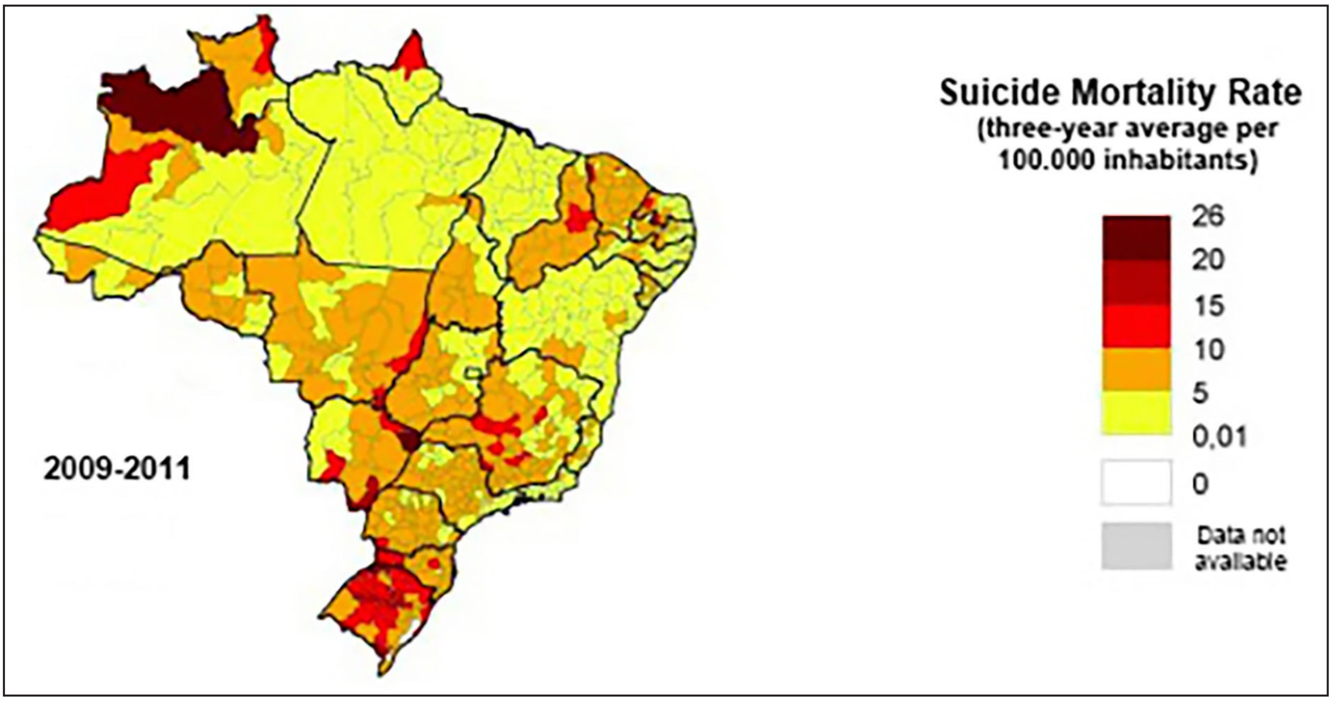

FIGURE 1. Suicide mortality rate in the three-year period 2009-2011 (Mota 2014)

The UW value is calculated by the formula 1.5 x IQR, where IQR is the difference between quartile 3 and quartile 1. Values above the UW are considered anomalous, as they deviate from the natural distribution of the population. For states with many values below the detection limit, which “flatten” the boxplot with values equal to the quartiles 1 and the median (Bahia, Roraima and Pará), the 5 intervals were maintained using the limits of the natural break in the distribution also calculated by the ArcGis 10.8 software.

3. Results and discussion

The results of Li concentration in soils for the 13 Brazilian states studied, the Li potential for prospecting, and the relationship with suicide in each state are discussed. To identify and map areas with Li potential for prospecting, the estimated UW value for each state was used and compared with the UW Brasil (11.75 mg/kg) estimated for the national reference (Table 1).

3.1. Lithium distribution and cartography

Table 1 presents the results of the analyses of available Li (mg/kg) (extraction with AR) in the soils of the 13 Brazilian states, the statistical treatment for each state based on data from Viglio et al. (2022), and for the total data population of all states (3688 samples: 1 sample/625km²) called Brazil. The states are ordered by the lithiniferous potential found.

The median results for the soils of the different states under study and for the national median (2.00 mg/kg) are mostly lower when compared to other published low-density studies. In the GEMAS project carried out at the European level (Reimann et al. 2014), which involved 13 countries and a total of 2218 samples collected from agricultural and pasture soils (but in the fraction < 2 mm), the calculated European median was 11.30 mg/kg for available Li, a value that is close to UW Brasil (11.75 mg/kg) and also the median of 15.00 mg/kg, calculated for agricultural or pasture soils in Southern Europe (Négrel et al. 2019).

Based on Li’s results on the soils, the following presents, in sequence, the states with the greatest potential for prospecting new deposits: Minas Gerais, Paraíba, Ceará, Pernambuco, Bahia, Alagoas, São Paulo, Rio de Janeiro and Espirito Santo. The other states, perhaps due to the lack of information and sample coverage, have a low potential for the occurrence of Li deposits.

3.1.1. Minas Gerais State

The distribution of lithium across the state of Minas Gerais (MG), based on the statistical analysis carried out on the results of analyses of 1,012 soil samples (with 65% > DL) is shown in Figure 2. In this state, the UWMG value for Li (11.75 mg/kg) overlaps with the UWBrasil value, meaning that the areas with the greatest potential for this element are distributed across approximately 47 municipalities (Figure 2): Matias Cardoso, Mamonas, Catuti, Nova Porteirinha (substrate with detrital-lateritic deposits, metalimestone with silt-clay intercalations); Taiobeiras, Salinas, Araçuaí, Itinga, Coronel Murta, Itaobim (with mica-quartz-schist, gneisses, biotite-quartz-schist, alkaline, subalkaline, calciosilicate granite series and peraluminous granites); Governador Valadares, Central de Minas, Galileia, São Geraldo do Baixio, Tumiritinga, Conselheiro Pena (presents mica-schists, alkaline, subalkaline, calciosilicate and peraluminous granite series, metadacite, gneisses with quartzite and carbonate intercalations); Várzea da Palma, Joaquim Felício, Olhos d’Água, Santo Hipólito, Monjolos, Cordisburgo, Jequitibá, Baldim, Paraopeba, Araçaí, Funilândia, São João Del Rei, Lagoas, Matozinhos, Lagoa Santa, Divinópolis (metalimestones with intercalations of clayey siltstone metasediments and sandy, calciosilicate and calciferous shale); Nepomuceno, Miradouro, Caldas, Jacutinga, Bom Repouso, Monte Sião, Bueno Brandão, Cambuí, Munhoz, Liberdade, Carvalhos, Itamonte, Bocaina de Minas and Passa Quatro (which covers quartzites, granulites,

TABLE 1: Statistical parameters for Li (mg/kg) in soils from 13 Brazilian states . Source: Modified from Viglio et al. (2022)

STATES	N° SAMPLES	SAMPLES >DL*	MINIMUM	1° QUARTILE	MEDIAN	3° QUARTILE	UW*	MAXIMUM
Minas Gerais	1012	663	0.50	0.50	2.00	5.00	11.75	83.00
Paraíba	84	81	0.50	7.00	15.00	24.00	49.50	167.00
Ceará	219	185	0.70	3.00	7.00	13.50	29.25	67.00
Pernambuco	152	130	0.50	2.00	7.00	12.00	27.00	63.00
Bahia	437	125	0.50	0.50	0.50	2.00	4.25	28.00
Alagoas	45	42	0.50	2.00	4.00	11.00	24.50	40.00
São Paulo	376	325	0.50	1.75	2.00	6.00	12.38	39.00
Rio de Janeiro	55	55	1.00	1.00	4.00	11.00	26.00	35.00
Espirito Santo	66	38	0.50	0.50	1.00	4.00	9.25	27.00
Mato Grosso do Sul	364	281	0.50	1.00	2.00	5.00	11.00	61.00
Roraima	160	75	0.50	0.50	0.50	2.00	4.25	23.00
Goiás	195	147	0.50	1.00	2.00	5.00	11.00	34.00
Pará	523	173	0.50	0.50	0.50	2.00	4.25	33.80
Brasil	3688	2320	0.50	0.50	2.00	5.00	11.75	167.00

* DL: detection limit, UW: upper whisker

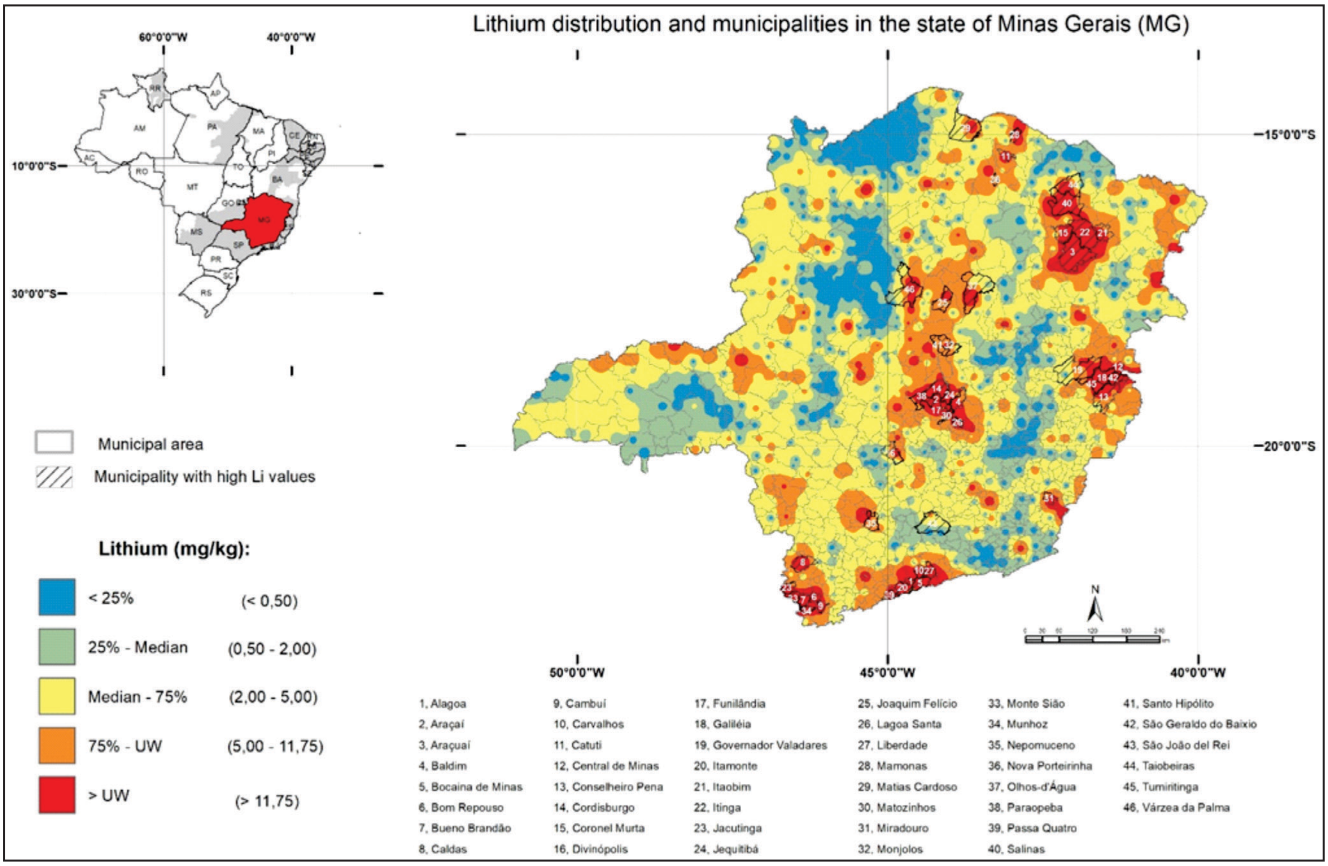

FIGURE 2. Distribution of Li in the soil (mg/kg) in the municipalities of the State of Minas Gerais. Modified from Viglio et al. (2022)

migmatites, charnockites, tuffs and basic volcanics). These higher values are distributed over an area of approximately 5,400 km² of Minas Gerais territory and may be one of the states that has the highest potential for Li prospecting, both in the already known regions (Araçuaí, São Jose da Safira, Conselheiro Pena and São João Del Rei) as well as new targets in the northern, central and southern portions of the state (Figure 2). The municipalities that have soils with a Li content lower than the median for MG (2.00 mg/kg) occur in two vast north-south alignments and in the west of the state.

In the region of Araçuaí, northeast of the state of Minas Gerais, in an area of 600 km² around the CBL Mine (Companhia Brasileira de Lítio), the only one in production in Brazil since 1966 and which explores Li in granitic rocks as pegmatites with spodumene, Silva (2011) analyzed Li in different sample media (Table 2). In stream sediments, the author detected a median of 33.7 mg/kg, while in natural soils (non-agricultural and only dedicated to pasture), the concentration of available Li showed a large variation and median (72.60 mg/kg) with a value much higher than the representative median for the entire state of MG. This result is due to the proximity to the mining area and its relationship with the geological substrate enriched in Li. According to Paes et al. (2016), Li contents are uniformly distributed, with the Teixeirinha-facies 1 Granite presenting most contents above 250 mg/kg and the Murici Granite having around 50% of its contents above this value. The Córrego da Chuva Granite has lower levels, but most of them are in the range between 60 and 249 mg/kg. These levels show that an enrichment occurs in this region in relation to the content of 21 mg/kg indicated by Rudnick and Gao (2003) as the world average value of Li for the continental crust or when compared with the Li value of 41 ± 6 mg/kg, established by Hu and Gao (2008), for the upper continental crust. In surface water (streams), Li values also showed a large variation (Table 2), but with a low median of 0.80 µg/L compared to other countries. Toupal et al. (2022), detected higher Li concentrations (5 to 13.00 µg/L) in the 47 samples of surface water close to four lithiniferous deposits located in Central Europe. In surface waters (140 samples) draining an unexplored spodumene deposit in southeast Ireland, Kavanagh et al. (2018) recorded Li contents between 0 and 91.00 µg/L (average of 20.00 µg/L) and similar concentrations in groundwater (average and maximum, respectively, 23.00 and 97.00 µg/L).

Among the plant foods that included leaves of 3 chives (*Allium schoenoprasum*), 3 cabbages (*Brassica oleracea:* 3), 2 mustards (Brassicales); 1 mango (*Mangifera indica L.*), 1 gherkin (*Cucumis anguria L.*), and bean grain (*Phaseolus vulgaris*), the levels are also variable (Table 2) and depend on the Li available concentration in the soil and the capacity of the plants to absorb and transport them to the edible parts. It has a median of 1.63 mg/kg, with the highest content of 6.68 mg/kg dry weight (Table 2) being detected in mustard samples. There are limited references in the bibliography regarding the concentration of Li in vegetables. Ammari et al. (2011) detected an approximate value of 12.00 mg/kg dry weight for cabbage leaves (*Brassica oleracea var. capitata*) grown in limestone soils in the Jordan Valley. Miranda (2023) detected a similar content in samples of cabbage (*Brassica oleracea*) (11.14 mg/kg dry weight, for a moisture content of 85.4%), in a kitchen garden located 0.5 km downstream from a Portuguese mine (C57, Gonçalo) that explores aplitopegmatites for the ceramic industry and which contains lithiniferous micas (lepidolite).

For healthy individuals, Goullé et al. (2005), indicated as a reference for a median blood plasma a Li concentratio of 3.40 µg/L (range between 5th and 95th percentiles: 1.80 - 18.80 µg/L). In a more recent study with 922 individuals from a community in Northern Germany aged 61 ± 13 years, Enderle et al. (2020) observed significantly lower values for blood plasma: 0.96 and 0.70 - 1.37 µg/ L for the median and interquartiles 1 – 3, respectively.

Silva (2011) also analyzed the Li content in the blood plasma of around 133 people (children, young adults) from 2 communities on the banks of the Piauí River, a tributary of the Jequitinhonha River (the only communities with perennial water in the dry period in the region) that demonstrated great variability and a median of 1.06 µg/L. The concentrations detected are a consequence of the variability in the soil-water-food-plasma route and the characteristics associated with everyone that contribute to the daily exposure dose.

The levels detected by Silva (2011) seem to indicate, according to available literature data, that the majority of Li levels found in the plasma of these communities fall within normal values and these individuals were not medicated with drugs associated with Li-based therapeutic treatments.

3.1.2. Paraíba State

The distribution of Li contents across the state of Paraíba (PB), based on the data of the 84 soil samples collected (with 96.4% > DL), is presented in Figure 3. Among the various

TABLE 2: Distribution of Li in different sampling matrix (Silva 2011).

SAMPLES	Nº SAMPLES	MINIMUM-MAXIMUM
Stream sediments (mg/kg)	39	10.70 – 84.44
Soils (mg/kg)	46	17.20 – 281.40
Surface water (µg/ L)	51	0.70 – 4293.40
Plant foods (mg/kg dry weight)	12	0.26 – 6.68
Human plasma (µg/L)	133	0.06 – 101.97

states, PB was the one with the highest median, 3rd quartile and UWPB values (49.50 mg/kg). The areas with the greatest potential for this element, mapped in Fig. 3 for Li values that are higher than the median (15.00 mg/kg) and higher than WPBrasil, cover many municipalities. A series of alkaline granites appear throughout much of this state, similar types of rocks that hosted Li deposits in other states, which probably explains the high spatial distribution of this element's content. However, 7 municipalities that have soil levels higher than UWPB, and approximately 3 times higher than UWBrasil, are highlighted: Frei Martinho, Pedra Lavrada, São Jose de Piranhas, Picui, Nova Palmeira, Soledade and Pocinhos (substrate with of silt-clay metasediments, with intercalations of metarenites, peraluminous granitoid gneisses, shoshonites, subalkaline, calcalkaline and tholeiitic granitic series, and orthoderivative gneisses with migmatitic portions), That cover a total area of 1,163 km². There is potential for new Li deposits to occur in the municipalities mentioned above, which fall within the probable southern extension of the Borborema Pegmatitic

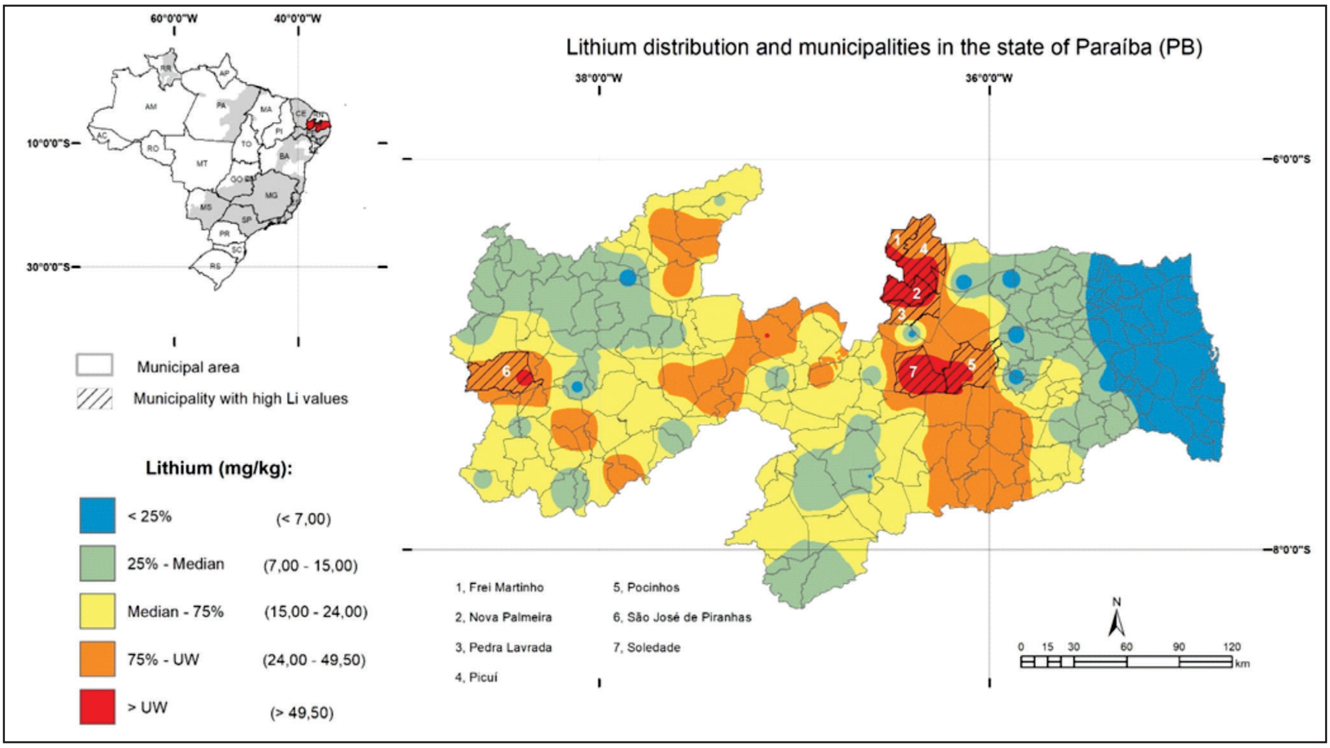

FIGURE 3. Distribution of Li in soil (mg/kg) in the municipalities of the state of Paraíba. Modified from Viglio et al. (2022)

Province. On the other hand, the areas with the lowest Li values in the soil (< 1st quartile: 7.00 mg/kg) are mostly located in the eastern portion, where sandstone, siltstone, claystone and gravel formations occur.

3.1.3. Ceará State

The Li results in the 219 samples (with 84.4% > DL) collected in the state of Ceará (CE) indicate that in the center NE-NW and in the South center, in a huge estimated area of 17,866 km² equivalent to 12% of Ceará's territory, the soils present levels higher than the median of 7.00 mg/kg of Li (Figure 4). Values higher than the UWCE of 29.25 mg/kg of Li (2.5 times higher than UWBrasil) occur in scattered points in 9 municipalities (total approximate of 1,836 km²): Massape (substrate with ortho-derived gneiss), Itapagé, Itapiúna, Pacoti, Milha, Quixeramobim, Solonópole, Jucás and Iguatu (which present argillaceous silt metasediment, metalimestones, calciosilicates, alkaline, calc-alkaline granitic series). In this domain, we highlight pegmatite bodies belonging to the Pegmatitic Lithiniferous da Região de Solonópolis-Ceará, which contains some lithiniferous minerals such as amblygonite and spodumene associated with columbite-tantalite and cassiterite (Moreira and Silva 2012). The geochemical data and results obtained also indicate Li potential in the state of Ceará. On the other hand, the lowest Li values (≤ 2.00 mg/kg) were observed in the municipalities that surround the northwest, north and northeast borders of the state, where Mesozoic and Paleozoic sedimentary and volcanic covers are presented, as well as Cenozoic sediments and Mesozoic clasto-carbonate sedimentary sequences.

3.1.4. Pernambuco State

The results of the 152 soil samples (with 85.5% > DL) in the state of Pernambuco (PE) presented median values of 7.00 mg/kg of Li (Figure 5). The estimated value for the 3rd quartile is like that estimated for UWBrasil and the areas mapped for UWPE 27.00 mg/kg, cover 7 municipalities: Itapetim, Quixaba, Iguaraci, Betania, Serra Talhada, Custódia and Jatobá (substrate with silty-clay metasediments, represented by schists with levels of quartzite, alkaline and subalkaline granitic series, peralkaline, calcioalkaline and peraluminous, ortho-derived gneisses with migmatite portions). These values are distributed across areas that cover a total of 1,102 km². The greatest potential for Li occurs in the extension of the Borborema Pegmatitic Province, which crops out in the state of Rio Grande do Norte, passing through Paraíba to Pernambuco, and also draws attention to the fact that a large part of this state features a series of alkaline granites, similar types of rocks that hosted Li deposits in other states. The lowest Li values (< 2.00 mg/kg) were found in the eastern and central portions of the state, where unconsolidated and calcareous Cenozoic sediments, clayey silt sediments and sandy and conglomeratic quartz sediments occur.

3.1.5. Bahia State

The Li results from 437 soil samples (with 28.6% > DL) collected in the state of Bahia (BA), not yet fully sampled as seen in Figure 6, revealed low median values of (0.50 mg/kg) for the target sampling areas. The cartography of the estimated value for UWBA (4.25 mg/kg), which is lower than the UWBrazil, and covers around 4,547 km² of the Bahian territory (Figure 6), is distributed across 18 municipalities: Pojuca and Camaçari (substrate with predominance of quartz-sandy sediments and conglomerates with silt and/or calciferous intercalations); São Sebastião do Passé (metalimestones, calc-silicate rocks); Sebastião Laranjeiras, Urandi, Pindaí, Palmas de Monte Alto, Malhada, Guanambi, Caetité, Igaporã, Matina, Riacho de Santana (alkaline granite series, low, medium, and high K, calc-alkaline granites, peraluminous, charnockitoid, clayey, metalimestone, siltstone metasediments); Jucuruçu, Itanhém and Medeiros Neto (presence of alkaline, calcium-alkaline series); Itambé and Macarani (granite-gneiss complexes, migmatites and granulites, with occurrences of pegmatites. Most municipalities located in the north, center and south of the stat of Bahia presented very low Li values (< 0.50 mg/kg) and were lower than the median calculated for Brazil. In these areas, silt-clay sediments dominate, with subordinate intercalations of sandstones, graywackes, quartzites and metalimestones. Despite the low results obtained in soil and the lack of full coverage of the state, but considering recent news of Li discoveries in clay materials originating from felsic volcanics in the Caetité Polymetallic District (Fe, Cu and Li) and in the alkaline granite series (the Jaguar spodumene Project), in the region of Petrolina (PE) and Juazeiro (BA) (Brasil Mineral 2023), it allows us to point out the reasonable potential of Li in this state.

3.1.6. Alagoas State

In the state of Alagoas (AL), the fieldwork that was carried out throughout 2011 allowed for the collection of 45 soil samples (Franzen 2020), of which 93.3% > DL. Figure 7 shows the distribution of Li in soils, with a median of 4.00 mg/kg for the 3rd quartile (11 mg/kg) that is close to the estimated UWBrazil. The Li values above of UWAL (24.50 mg/kg) cover an area of 427 km² of Alagoas territory, with the 3 municipalities: Mina do Negrão, Cacimbinhas and Craíbas. In this area, substrates with alkaline, subalkaline, peraluminous, calc-alkaline, granites, metamafic, amphibolite, and metavolcanic rocks with iron formations predominate. The lowest Li contents (< 2.00 mg/kg) are concentrated in the eastern and southeastern portions of this state , where layers of sediments of different compositions occur (sandstone, siltstone, mudstone and gravel).

3.1.7. São Paulo

The results of the 376 soil samples collected (with 86.4% > DL) in the state of São Paulo (SP) revealed a median Li content of 2.00 mg/kg (Figure 8a), and a UWSP value (12.38 mg/kg) slightly higher than that estimated for UWBrazil, which was detected in 21 municipalities: Pereiras, Porangaba, Quadra (substrate with sandstones with intercalations of clayey siltstones and shales, limestones), Itapirapuã Paulista, Ribeira, Iguape, Sete Barras (granitic rocks of subalkaline, calc-alkaline, peralkaline series, clayey silt metasediment, quartzites), Igaratá, São Jose dos Campos, Monteiro Lobato, Santo Antônio do Pinhal, Taubaté, Lagoinha, São Luiz do Paraitinga, Ubatuba, Cunha, Piquete, Areias, Arapeí, São José do Barreiro and Bananal (with subalkaline, calcioalkaline, peralkaline and peraluminous granitoid series). The areas with potential for Li in the total of these municipalities are approximately 2,382 km², with those with the greatest potential for prospecting being mainly

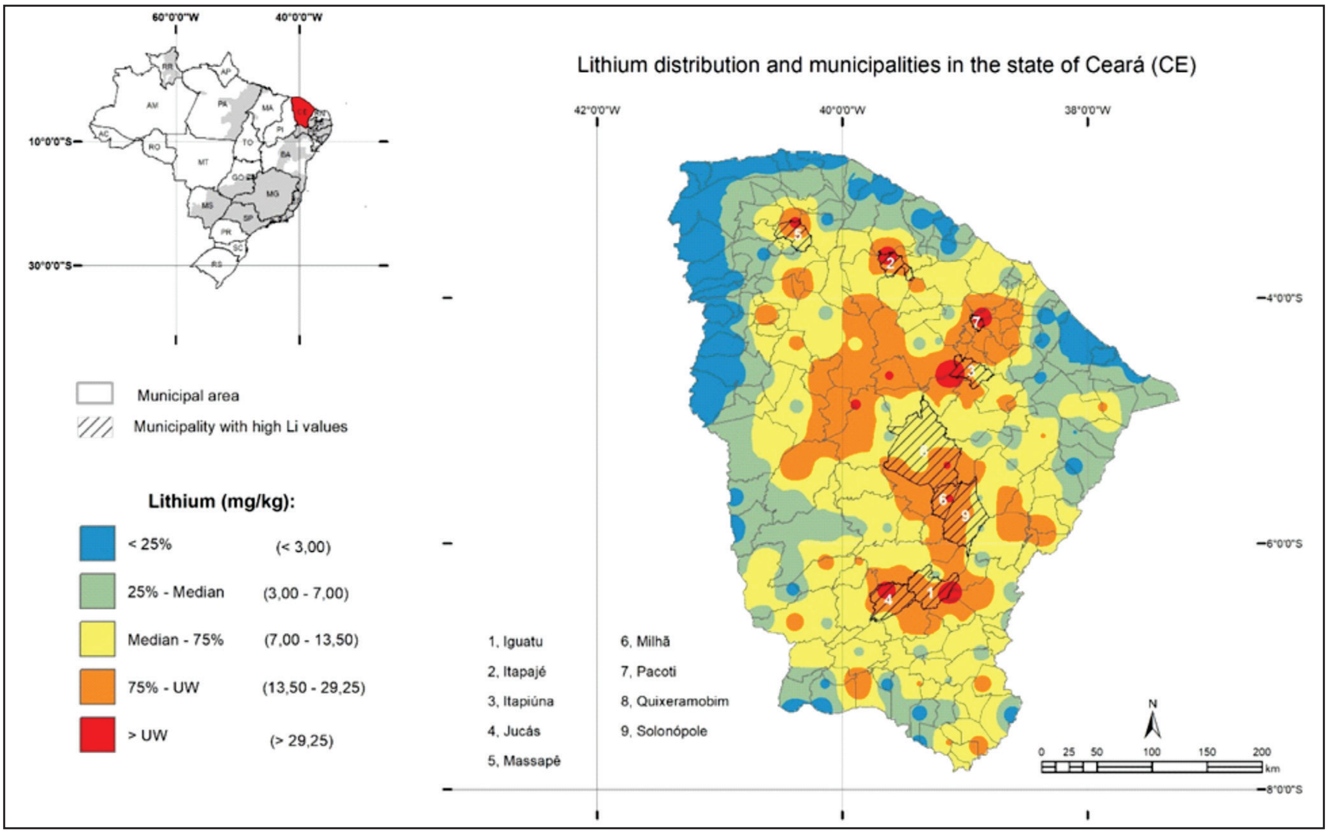

FIGURE 4. Distribution of Li in soil (mg/kg) in municipalities in the state of Ceará. Modified from Viglio et al. (2022)

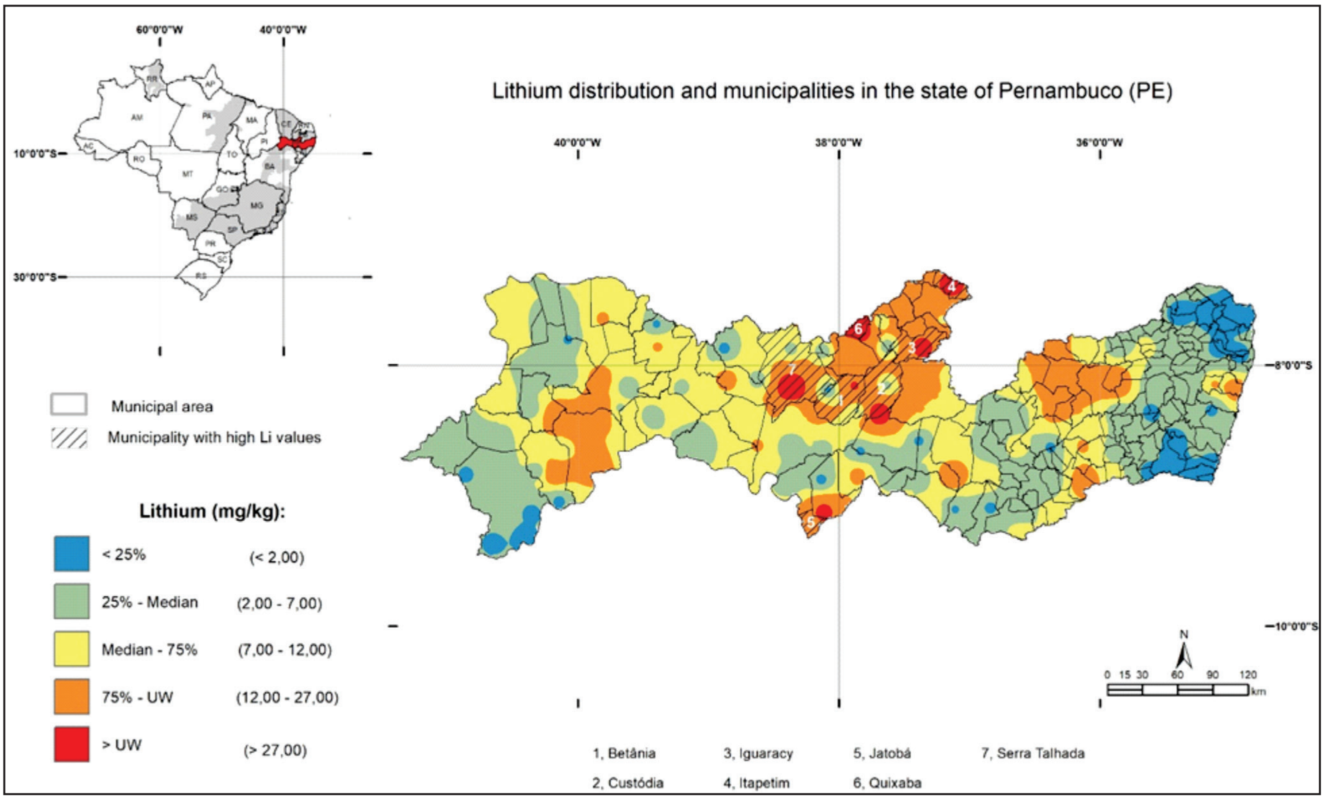

FIGURE 5. Distribution of Li in the soil (mg/kg) in the municipalities of the state of Pernambuco. Modified from Viglio et al. (2022)

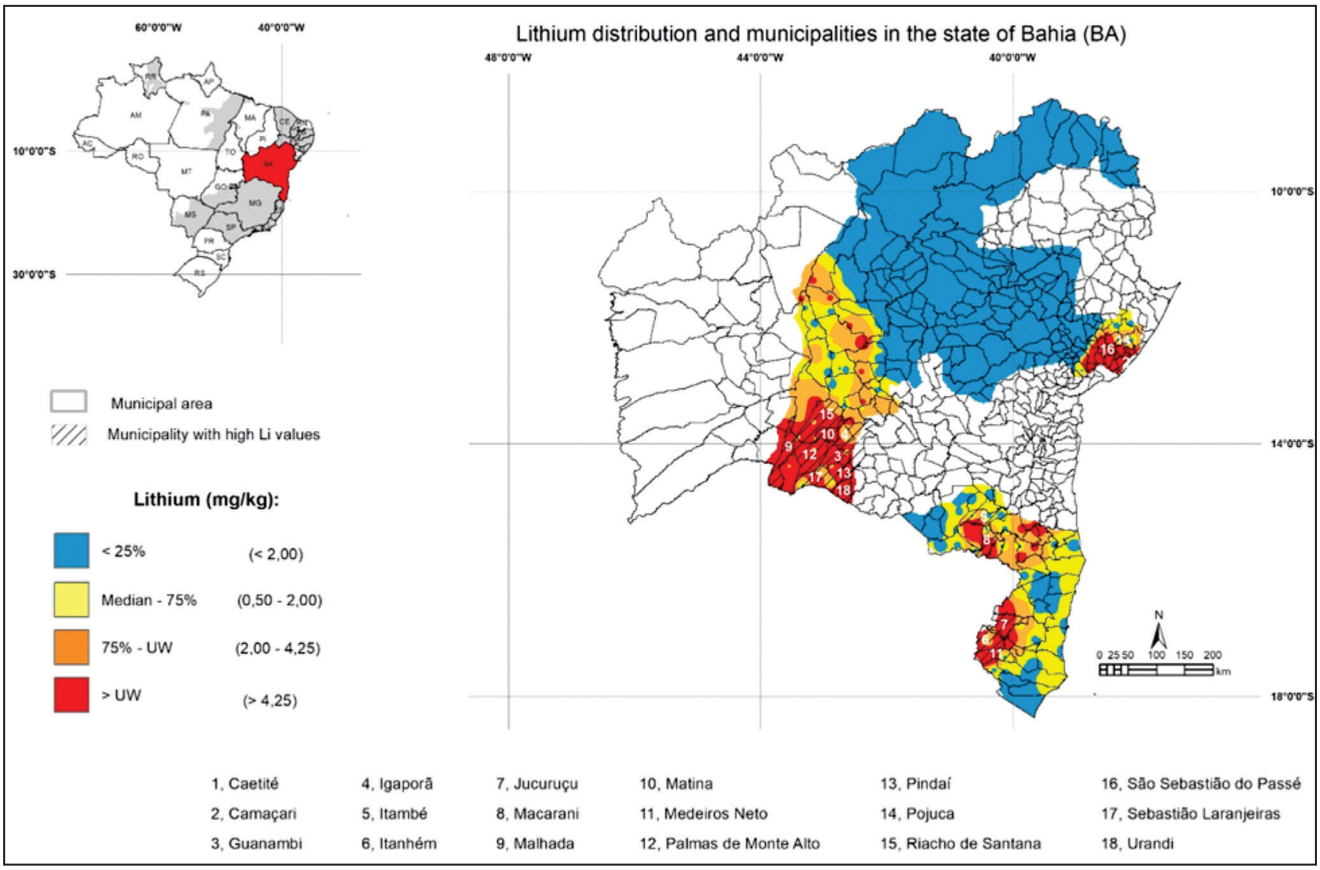

FIGURE 6. Distribution of Li in the soil (mg/kg) in the municipalities of the state of Bahia. Modified from Viglio et al. (2022)

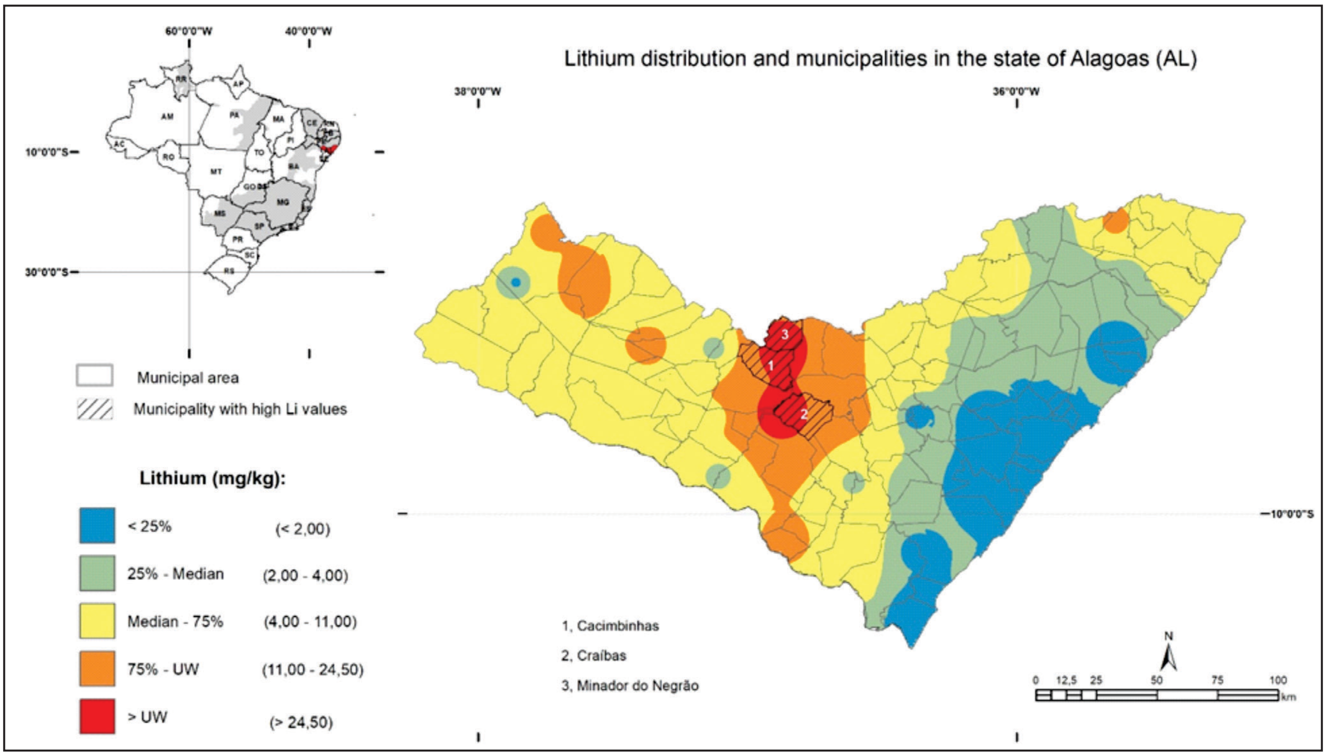

FIGURE 7. Distribution of results from lithium analyzes in soil (mg/kg) in municipalities in the state of Alagoas. Modified from Viglio et al. (2022)

concentrated in the SE quadrant of the state of SP. The lowest Li contents occur in the north, east and west centers of the state of SP, in the sandy portion of the Paraná Basin.

In São Paulo, Silva et al. (2022) determined the geoavailability of Li in water, soil and plants in several regions, to evaluate the contribution of the soil-water-plant route to Li exposure through the human or animal diet. In the Ubatuba/ Santa Isabel region, 27 samples of vegetation were collected, which presented the following concentration of Li dry weight: grass (*Poaceae)* with a variation of 5.70 to 37.60 µg/kg and an average of 17.70 µg/ kg; Aloe vera (*Aloe vera*) with 37.60 µg/kg and chives (*Allium schoenoprasum*) with 30.30 µg/kg. In the Paranapanema/Cajamar region, were collected 11 samples, with grass showing a concentration of 9.10 µg/kg and sugar cane (*Liliopsida*) having a concentration of 5.80 µg/kg.

The concentration of Li found in soils (fraction < 0.177 mm) use mainly for agricultural purposes or sampled in the same places where the vegetables were collected in the two regions, together with those sampled in the region of Santa Cruz do Rio Pardo/Cruzália (7 samples, AR solubilization) showed Li values between 8.00 and 15.00 mg/kg with a median of 11.00 mg/kg, a concentration that is close to that estimated for UWSP. In the Ubatuba/Santa Izabel region, the nine soil samples collected also presented Li concentrations in the range 8.00 to 15.00 mg/ kg with a median of 11.00 mg/kg and in the Paranapanema/ Cajamar region the 13 soil samples presented values of 8.00 to 26.00 mg/kg with a median of 11.00 mg/kg. In 29 surface water samples from the 3 regions, Silva et al. (2022) detected a variation between 5.00 and 12.00 µg/L, with a median of 5.00 µg/L, concentrations that match the levels detected by other authors reported in this research.

3.1.8. Rio de Janeiro State

The Li results in the 55 soil samples collected (with 100% > DL) in the state of Rio de Janeiro (RJ) revealed a median of 4.00 mg/kg of Li (Figure 8b), and a UWRJ value (26.00 mg/kg) above UWBrazil, which were detected in the municipalities of: Barra Mansa and Barra do Piraí (substrate with gneisses with intercalation of marbles, biotite granodiorites, subalkaline, peralkaline and calciosilicate alkaline granites, orthogranites, charnockites), and Bom Jardim and Cantagalo, where pegmatites bodies with rubellite and lepidolite outcrops. These municipalities promising occurrences can be found in approximately an area covering 880 km^2. The north, northeast and east regions have low Li values (< 4.00 mg/kg) and correspond to areas where gneissic-migmatite and granulite complexes, unconsolidated or poorly consolidated Cenozoic sediments, and sandy, clayey and pebbles emerge.

3.1.9. Espirito Santo State

The Li results from the 66 soil samples collected (with 57.5% > DL), revealed for the state of Espírito Santo (ES) the lowest median value (1 mg/kg of Li) and a UWES value (9.25 mg/kg) lower than estimated UWBrazil, which occurs in the NW and South (Figure 8c). Covering an area of approximately 1,688 km², they are distributed across six municipalities: Ecoporanga, Pancas, Afonso Cláudio, Jerônimo Monteiro, São José do Calçado and Cachoeiro de Itapemirim. The outcropping rocks are from the subalkaline, calc-alkaline, tholeiitic, peraluminous granitoids and paraderived gneiss series with migmatitic portions. In the northeastern region of the state the lowest Li levels (< 1.00 mg/kg), were detected in sediments of different compositions (sandstone, siltston thee, mudstone and gravel). The northwest, west, southwest and south regions present some values and lithologies that may have exploration potential for Li.

3.1.10. Mato Grosso do Sul State

The results of the 364 soil samples collected (with 77% > DL) in the state of Mato Grosso do Sul (MS), outside the Pantanal zone located to the northwest, showed a median value of 2.00 mg/kg of Li (Fig. 9a). The sites with a value above the UWMS (11.00 mg/kg) and close to that estimated for UWBrazil, are located in the south-southeast part, covering 13 municipalities: Bonito, Jardim, Guia Lopes da Laguna, Rio Brilhante, Douradina, Dourados, Itaporã, Ponta Porã, Caarapó, Laguna Carapã, Aral Moreira, Tacuru and Sete Quedas (substrate manly with basalts and andesitic basalts with intercalations of sandstone). They occupy an area of approximately 3,400 km² of the MS territory. These levels in soil from basalt rocks require more research aimed at the origin of lithium, which may have potential for prospecting the element. Kabata-Pendias (2000), Taylor (1964) and Turekian and Wedepohl (1961) indicated Li contents in basalt between 6.00 and 20.00 mg/kg.

The lowest Li values (< 2.00 mg/kg) were observed in the northeast and central portions of the state (Figure 9a) associated with sandy and silt clayey sedimentary formations. In the Maracaju/ Nova Alvorada region, Silva et al. (2022), found in 14 samples of agricultural soil (fraction < 0.177 mm, with AR) Li contents that ranged between 1.00 and 26.00 mg/kg, with a median of 11.00 mg/kg. This concentration is similar to that detected for UWMS, in the present study. Also, in 14 samples of surface water, Li levels were detected between 5.00 and 8.00 µg/L (median of 6.00 µg/L), which are like other regions. In vegetation, the same authors detected on 2 samples of chives (*Allium schoenoprasum*) 121.80 and 189.20 µg/kg of Li, on saffron (*Crocus sativus*) 53.60 µg/L, and similar Li concentrations in grass (*Poaceae*) and oranges (*Citrus*), with 5.50 µg/kg and 5.20 µg/kg, respectively. The levels detected in these plants are lower than those reported in plants sampled in the Araçuaí-MG mining area, where Li ranged between 260.00 and 6680.00 µg/kg (Table 2).

3.1.11. Roraima State

Around 46% of the surface area of the state of Roraima (RR) is occupied by indigenous lands, 5.3% by fully protected federal conservation units (three ecological stations and three national parks), and 2.6% by federal units of sustainable use (three national forests). In a large part of the areas occupied by indigenous lands, access for geochemical sampling was not allowed. The results for Li in the 160 soil samples collected (with 46.8% > DL) is presented in figure 9b, which revealed very low values for the median (0.50 mg/kg of Li), over a wide range northeast-southeast, substrate with rocks from the alkaline, subalkaline, peralkaline granite series and charnockite associations outcrop. The UWRR value (11.00 mg/kg) is similar to that estimated for UWBrazil, being detected only in a sample in Pacaraima where the granitic series mentioned above outcrop, in addition to volcanosedimentary sequences.

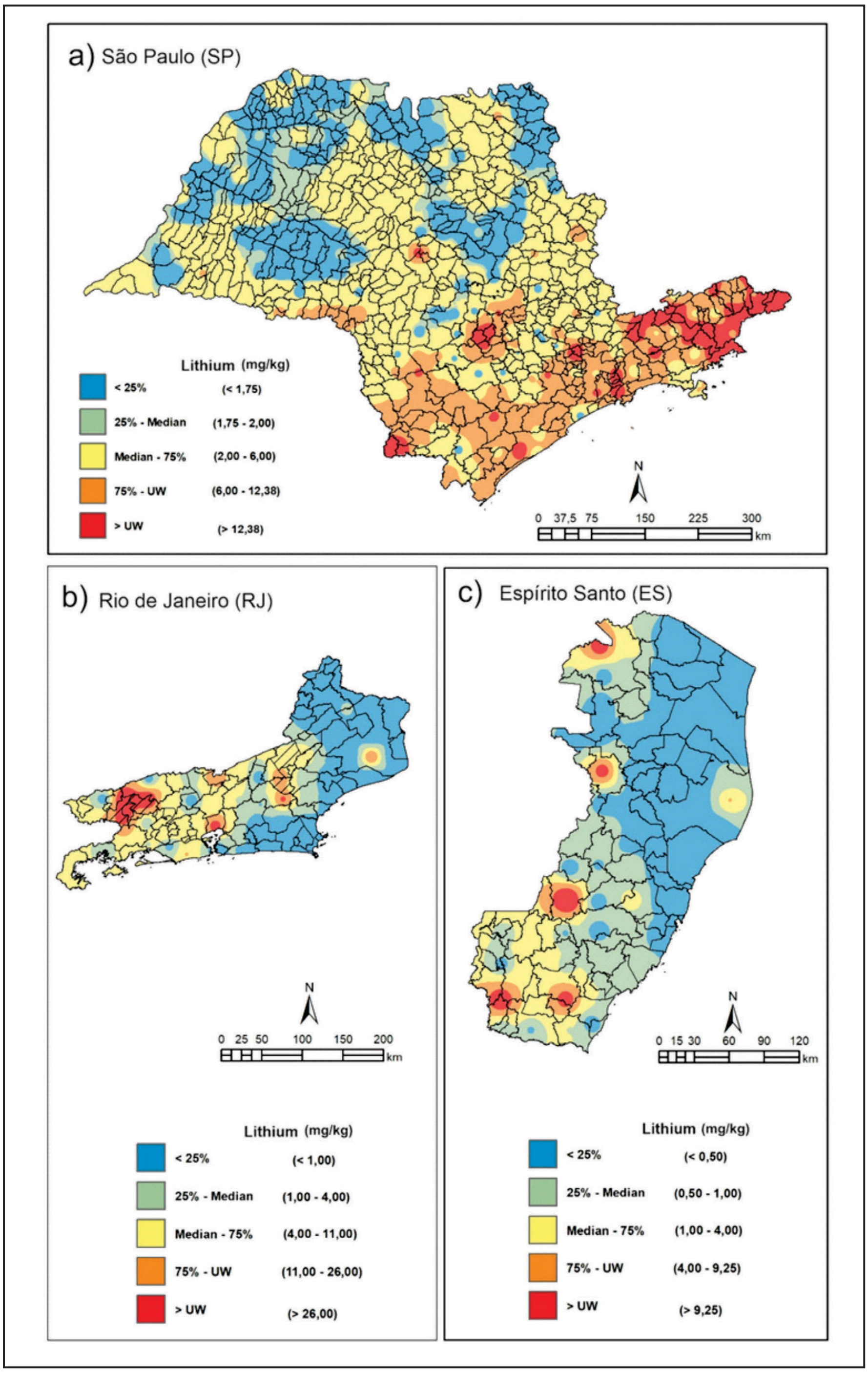

FIGURE 8. Distribution of Li in the soil (mg/kg) in the municipalities of the states of a) São Paulo, b) Rio de Janeiro and c) Espirito Santo. Modified from Viglio et al. (2022)

3.1.12. Goiás State

The state of Goiás (GO) was sampled in only 50% of its spatial coverage (Figure 9c), with the Paranaíba river basin, being entirely covered. The results of the 195 soil samples collected (with 75.4% > DL), revealed low Li median values (2.00 mg/kg of Li), in the southern region, where sandy, conglomeratic and limestone sediments crop out. The values above UWGO (>11.00 mg/kg), like those estimated for UWBrazil, are concentrated in the southeastern part of the state and occur in 4 municipalities: Corumbá de Goiás, Leopoldo de Bulhões, Cristalina and Corumbaíba, in a total of 1,700km². The rocks (substrate) of these municipalities are silt-clay metasediments with intercalations of greywacke with iron and manganese formations and paraderived granulite-gneiss with migmatite portions. The data from this state does not allow significant conclusions to be drawn regarding its Li potential.

3.1.13. Pará State

The results of the 523 soil samples collected (with 33.1% > DL) in the eastern part of the state of Pará (PA) present very low median values (0.50 mg/kg of Li), which are concentrated in the northeast and center of the state (Figure 9d) where sandy sediments, conglomerates, metarenites and metagraywackes

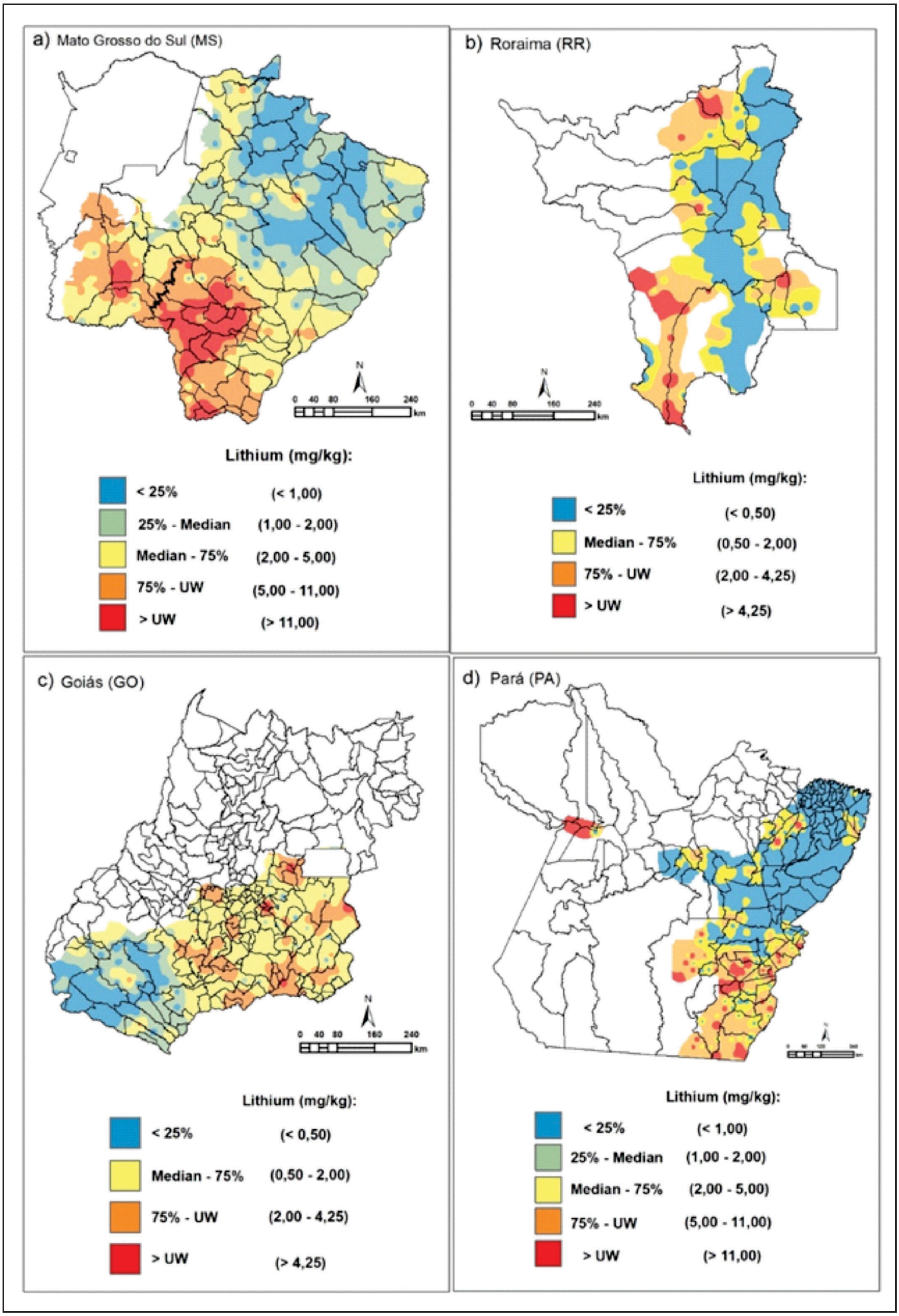

FIGURE 9. Distribution of Li in the soil (mg/kg) in the municipalities of the states of a) Mato Grosso do Sul, b) Roraima, c) Goiás and d) Pará. Modified from Viglio et al. (2022).

predominate. The UWPA Li concentration of 4.25 mg/kg, also low, was detected only in the municipality of Juriti, which presents intercalations of clayey silt and sandy quartz sediments and lateritic detritus covers (substrate). As in the case of the RR and GO states, the data from this state does not allow significant conclusions to be drawn regarding its Li potential.

The Figure 10 (Modified from Silva et al. 2023) shows for the Brazilian territory, extensive occurrences of pegmatites mainly bordering the Atlantic coast from the state of Santa Catarina in the south to the state of Rio Grande do Norte and in the Center West in the states of Tocantins and Goiás, passing through Parana, São Paulo, Rio de Janeiro, Espirito Santo, Bahia, Alagoas, Pernambuco, Paraiba, Rio Grande do Norte and Ceará, where 8 deposits and 7 regions ("provinces") are defined with high potential for Li.

There is a correlation between Li's results in soils from this research with the distribution of the main pegmatitic and deposits already known in 2023 (Figure 10), giving credibility to the suggestions expressed in the descriptions of Figures 2 to 9 of the 13 states, that highlight the probability for new occurrences in the reported municipalities.

The data presented in the geochemical soil survey of approximately 40% of the national territory revealed potential for Li prospecting in 140 municipalities, covering a total area around 25,225 km². These results, associated with data provided by work carried out by several Brazilian institutions, suggest that Brazil may have relevant potential to substantially increase the discovery of new Li deposits. According to Heider and Siqueira (2023), the production in the period from 2018 to 2022 increased by 825%, from 17.35 to 143.72 thousand tons, and could increase if demand for Li and investments in prospecting increase in the next 10 years. It is estimated that the current 1.1% will increase to 5 to 8% of the world production (Paes et al. 2016).

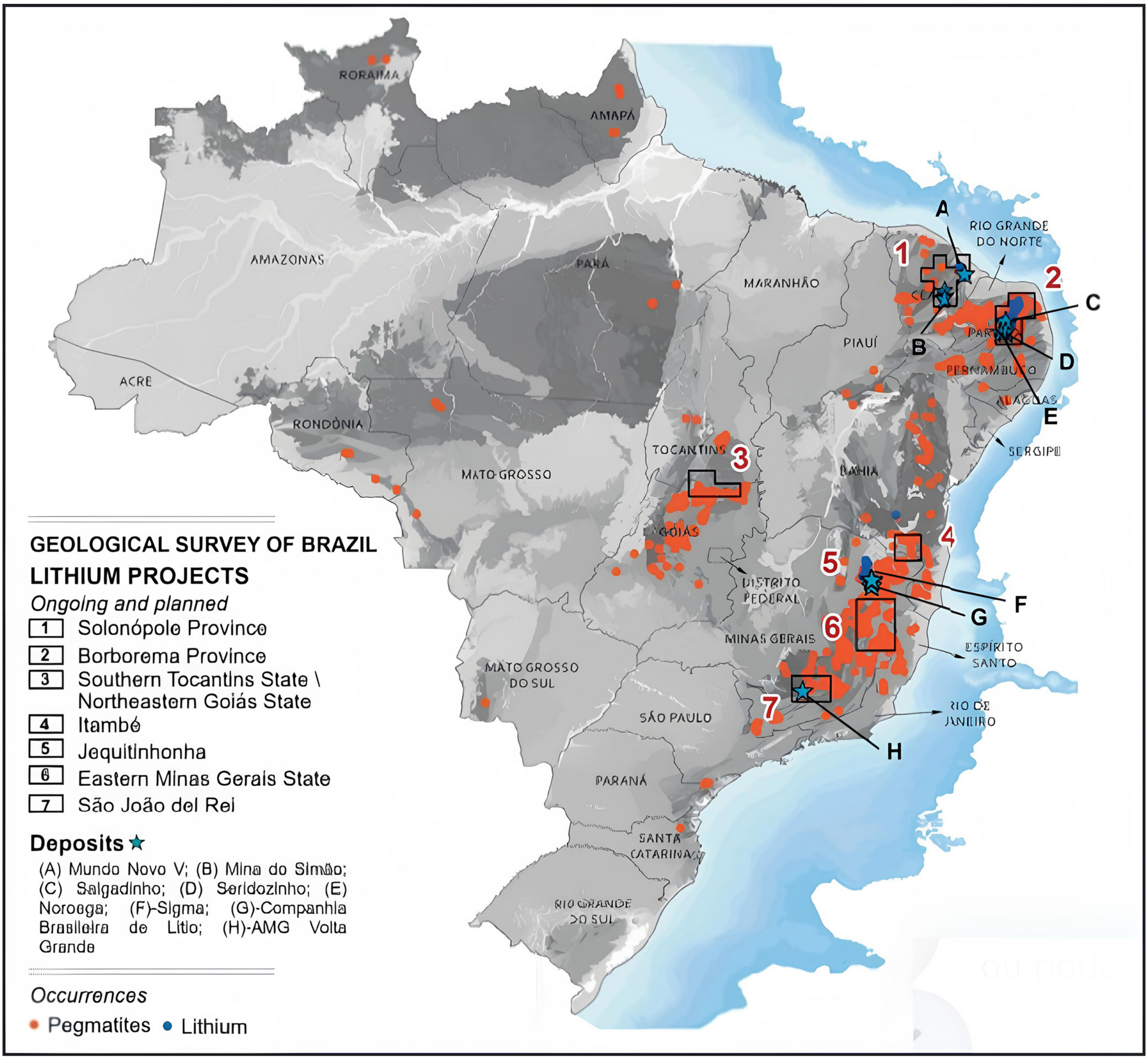

FIGURE 10. Distribution of lithium Projects and deposits in Brazil (Silva et al. 2023)

The results in the soils from this study highlight the states of Minas Gerais, Paraíba, Ceará, Pernambuco, Bahia, Alagoas, São Paulo, and Rio de Janeiro as the ones with higher grades and lithologies with potential for Li prospecting. From this research, it was found that soils with underlying rocks from the alkaline granitic series presented higher Li concentration, suggesting that these types of rocks could be a metallotec for Li prospecting.

3.2. Suicide versus Lithium in the Soils

Suicide is the act of intentionally causing one's own death, which may be the result of social, cultural, religious, and/or socioeconomic factors, among others. According to the WHO, Brazil ranks 8th among the countries with the highest suicide rates (HSM 2023). As suicide is a public health problem, it is essential to investigate and analyze the causes and risk factors to promote actions that can reduce citizens' exposure to premature mortality. Some studies have investigated environmental factors, such as altitude, as a cause of geographic variation that may influence suicide rates (Haws et al. 2009; Helbich et al. 2013; Brenner et al. 2011).

In the present study, like those carried out with the suicide rate and the natural Li content in drinking water, it was assessed in a first approach whether the Li content in the soils of Brazilian states would have any relationship with the respective suicide rate. For this analysis, data available in the bibliography for the period 2011-2020 (DATASUS 2022) and information reported by Mota (2014) were considered. This approach assumes that soils with a higher content of available Li will have, in the soil-plant transfer route, a greater possibility of influencing the dose of exposure of an individual to Li, through the ingestion of vegetables grown in the soil.

Table 3 presents the estimated suicide rate (1/100,00 inhabitants) in the 13 states under study, for the period 2011- 2020.

From the analysis of Table 3, it is observed that the two states with the highest number of suicides per 100,000 inhabitants are RR and MS, and the states with the lowest rate are PA and BA. Comparing with the suicide rate in Brazil of 6.6 (for 2019) and the world rate of 9.0 (Ministério da Saúde 2021), only RR and MS presented a higher suicide rate than Brazil for the considered period, and all the states had suicide rates lower than the world rate.

Figure 11 shows the distribution of the median Li available in soils detected in this study and the respective average suicide rate, for 9 states. At this macroscale there is no correlation between these parameters, as can also be observed by the Spearman correlation value (0.048), for a confidence level of 95%. In this analysis, the states RR, GO, PA and BA were excluded as they had a spatial soil sampling coverage of less than 50%. Considering that suicidal behavior is closely associated with mental health (ABP 2014), this relationship should be tested with data on deaths due to mental disorders for each state or on a more local scale.

Mota (2014) concluded that although the processes of spatial and quantitative expansion of deaths in the country due to suicide and mental disorders are similar, suicide rates do not behave proportionally or inversely proportional to the rates of deaths due to mental disorders. In the absence of this type of data, it was not possible to evaluate the relationship between Li in the soil and the death rate due to mental disorders in each state or municipality.

TABLE 3: Suicide rate calculated per 100,000 inhabitants, referring to the 13 Brazilian states relative to the total average for the period from 2011 to 2020 (DATASUS 2022).

ORDER	STATES	SUICIDE RATE*
1	Roraima (RR)	7.8
2	Mato Grosso do Sul (MS)	7.2
3	Minas Gerais (MG)	6.0
4	Goiás (GO)	5.6
5	Ceará (CE)	5.8
6	Alagoas (Al)	4.8
7	Paraíba (PB)	4.8
8	Espirito Santo (ES)	4.6
9	São Paulo (SP)	4.3
10	Pernambuco (PE)	3.5
11	Rio de Janeiro (RJ)	3.1
12	Pará (PA)	2.7
13	Bahia (BA)	2.3

Suicide and mental disorders in the country are a real concern, which requires more localized spatial analysis to understand how the problem is distributed and to geographically analyze the behavior of risk factors. In a recent study, Maia (2022) presented the spatial distribution pattern of Brazilians diagnosed with a mental disorder in 2019, for the different states (Figure 12). It is also important to know the data on mortality due to mental disorders and the various aspects related to them, but at the microscale of the municipality, as presented by Mota (2014) for deaths due to mental disorders in 2009-2011 (Figure 13).

The results obtained by Silva et al. (2022) in plants collected from the soils in some of the municipalities sampled for the present study, reveal that these are a transfer link for Li into the human body. Estimating the dose of exposure of populations to Li through ingested water and the soil-plant route are variables that must be known to evaluate relationships between natural Li exposure and possible benefits or health problems, that may be related or not.

This very preliminary research with Li on soil versus suicide aims to be an open door for new data research to be developed with a multidisciplinary and interdisciplinary approach within the scope of Geochemistry and health, from researchers in these areas, for the psychosocial well-being of the individual.

4. Conclusions

The results achieved in the 13 Brasilian states, covering an area of 3,313,750 km² (40% of the Brazilian territory), through the low-density geochemical survey, are expressive and indicate the potential for prospecting Li in 140 identified municipalities, in a total area of around 25,225 km².

The states that show the greatest favorability are:

Minas Gerais, as it already has a Province and lithiniferous occurrences and mines in production, such as in the regions of Araçuaí, Conselheiro Pena, Divino das Laranjeiras; Santa Maria do Suaçuí and São João del Rei, also recognized. This study

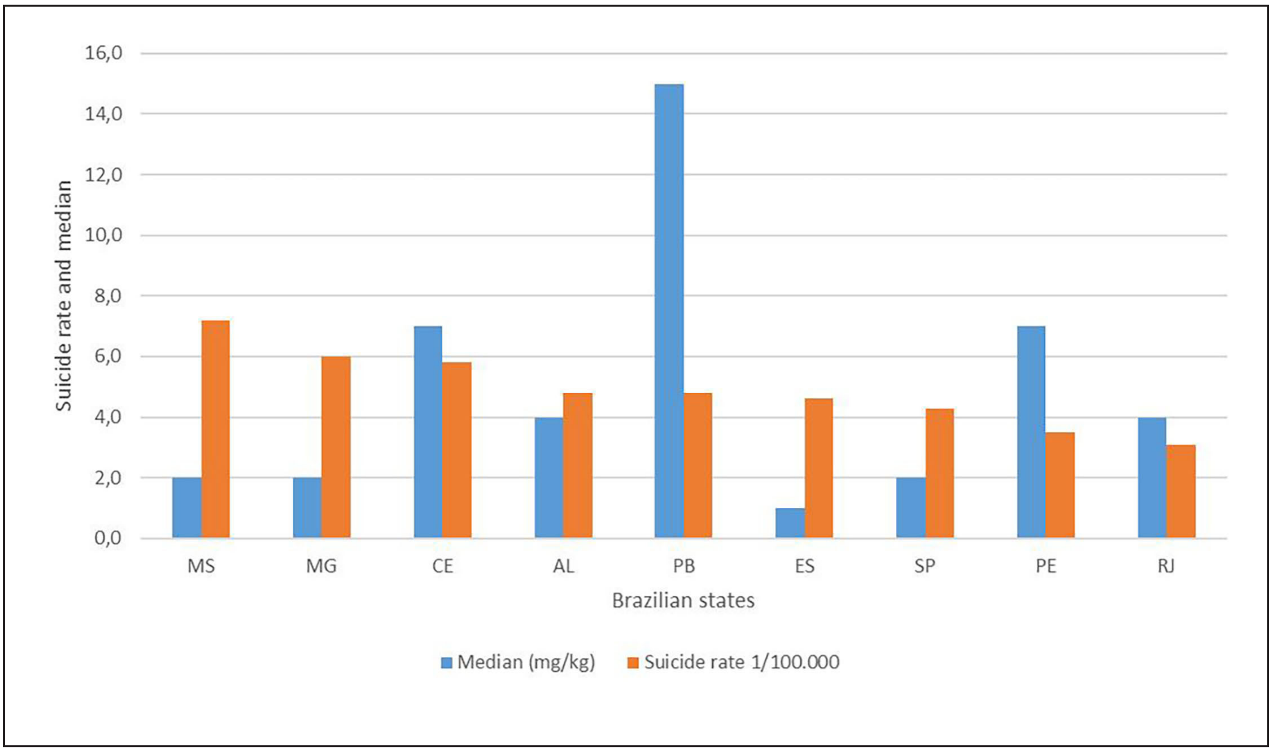

FIGURE 11. Average suicide rate per 100,000 inhabitants in the period from 2011 to 2020 (DATASUS 2022) and median Li concentrations in soil, observed in the states under analysis

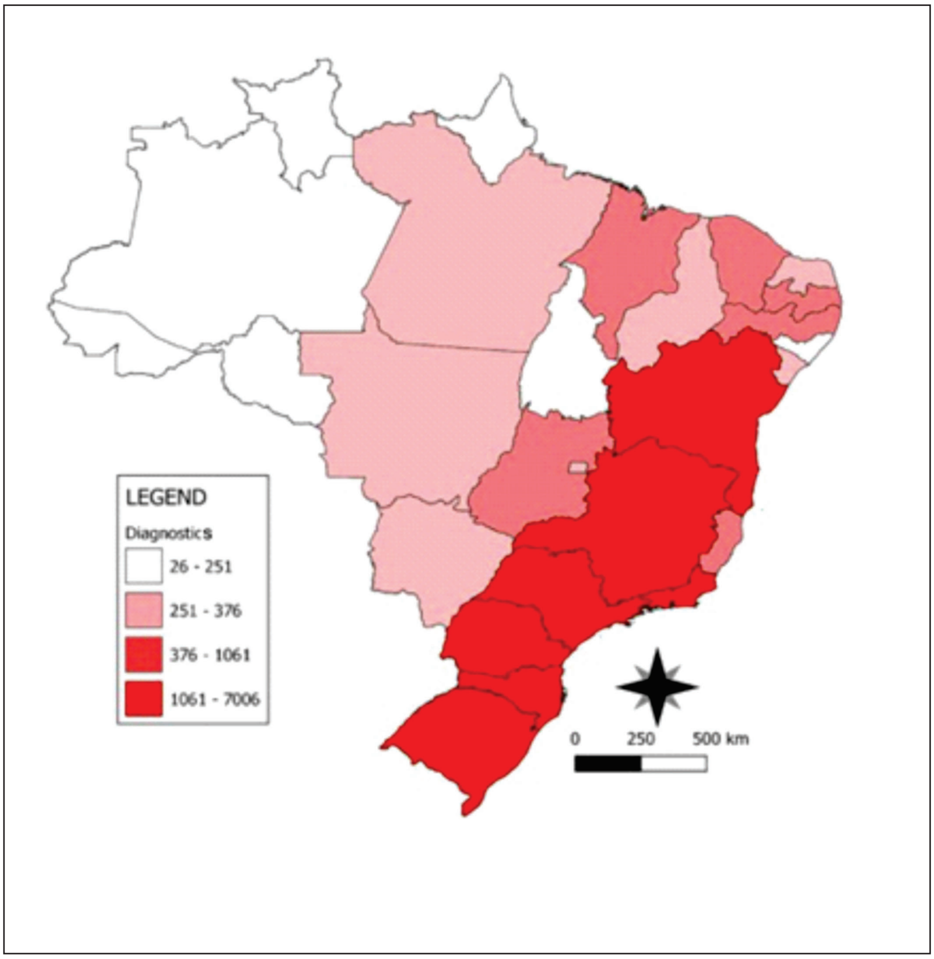

FIGURE 12. Distribution of Brazilians diagnosed with mental disorders (2019) (Maia 2022)

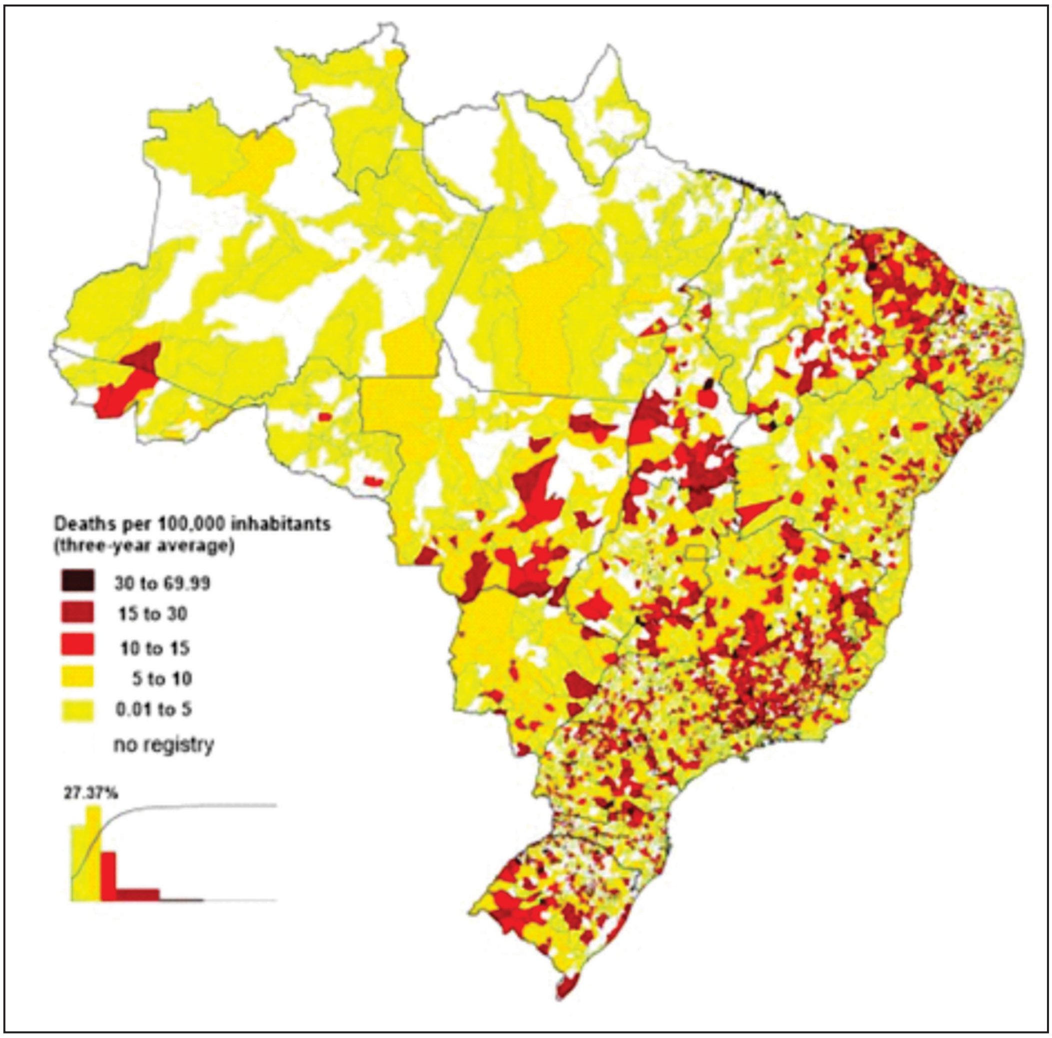

FIGURE 13 Distribution of mortality due to mental disorders in Brazil 2009-2011 (Mota 2014)

also highlights other promising targets.

Paraíba, in the southern part of the Borborema Lithiniferous Province, which may continue to Pernambuco, where there are several samples with values above the 3rd quartile. The highest value of 167.00 mg/kg was found in Paraíba, in the trend of that province.

Ceará has Li potential in the regions that cover the municipalities of Massapé, Itapage, Milha, Solonópolis, Cristais, Itapiuna, Pacoti and Iguatu.

Pernambuco also presents favorable areas that should be researched in greater detail, which could be the southern continuity of the Borborema Province.

Bahia, despite the low results obtained and the lack of full coverage of the state, could reveal potential for new Li deposits in line with the recent discoveries.

Alagoas has high Li values and granite rocks from the alkaline series, which may be southern continuity of the Borborema Province.

São Paulo presents good possibilities of having lithium deposits in rocks with pegmatites, in the eastern part of the state.

Higher Li values were detected in soils from rocks of the subalkaline, calcioalkaline, peralkaline and peraluminous granitoid series and when pegmatites occur, the Li content increases.

For the states of Mato Grosso do Sul, Minas Gerais, Ceará, Alagoas, Paraíba, Espírito Santo, São Paulo, Pernambuco, and Rio de Janeiro, the results of Li available in soil versus average suicide rate show that there is no causal link with the incidence of suicides. For future studies and at the municipal level, it will be important to know the Li content in ingested water and different foods to estimate exposure doses and data on mortality due to mental disorders.

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A - Study design/ Conceptualization **B** - Investigation/ Data acquisition
C - Data Interpretation/ Validation **D** - Writing
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