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Study around the Barroso mine (Portugal): Baseline levels of lithium for assessing future exposure and risks from Li mining activity

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ABSTRACT

The energetic green transition is increasing the demand for lithium (Li) exploitation. However, the Li supply faces challenges like limited reserves and environmental concerns. This pioneer study aims to characterize the Li concentrations in the region around the Barroso mine, in Portugal, by collecting and analyzing samples of cabbage, potato, drinking and irrigation water and soil from two nearby sites, and performing a preliminary exposure and risk assessment of local populations. Li levels ranged between 20 and 589 μg/kg in cabbages (n = 23), 2.3–21 μg/kg in potatoes (n = 21), 1.1–5.9 μg/L in drinking water (n = 10), 1.1–15 μg/L in irrigation water (n = 23) and 35–121 mg/kg in soils (n = 23). Significant differences in Li content between sampling sites were observed only for cabbage samples. The risk assessment revealed that none of the participants exceeded the provisional reference dose (p-RfD) (2 μg/kg bw/day), with a hazard quotient (HQ) < 1, suggesting no health concerns for the population. It is expected that the studied area will be affected by the future expansion of the mine concession, thus this pioneer study is crucial for future research as it establishes a initial database for evaluating the potential impact of mining activity on the environment and the population's exposure to Li.

1. Introduction

Lithium (Li) is an alkaline metal with distinctive properties (high electrical conductivity, remarkable electronegativity, and thermal shock resistance) fundamental for energy storage technologies, such as Li batteries, which contribute to reducing carbon emissions in alignment with the Sustainable Development Goals (SDGs) (Opazo, 2023; Sadik-Zada et al., 2023). Considering Li's economic importance as a strategic resource for the future and its high risk of scarcity, the European Union (EU) has classified this metal as a critical raw material (European Commission, 2020; Petavratzi et al., 2022).

Li is not considered an essential element for human health; however, it is widely used in the treatment of psychiatric diseases, particularly bipolar disorder and depression (600–1200 mg/day) (World Health Organization, 2009). Nonetheless, excessive doses of Li can induce adverse and toxic effects, which has influenced scientific research on Li toxicity (Schrauzer, 2002; Tanveer et al., 2019). The Environmental Protection Agency (EPA) reported, in 2008, a provisional subchronic and chronic reference dose (p-RFD) of 2 μg/kg bw/day of Li derived from the LOAEL (lowest-observed-adverse-effect level) (Environmental Protection Agency, 2008).

Li is naturally present in small quantities in soil (7–200 mg/kg) and rocks, and can reach concentrations of up to 500 μg/L in groundwater through weathering processes (Enderle et al., 2020). Its concentration in plants depends on various factors such as soil pH, plant species, and environmental conditions (Shakoor et al., 2023a). The essential nature

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Abbreviations: BW, Body Weight; CD, Consumption Data; EDI, Estimated Daily Intake; EPA, Environmental Protection Agency; EU, European Union; Ge, Germanium; HCA, Hierarchical Cluster Analysis; HQ, Risk quotient; ICP-MS, Quadrupole Inductively Coupled Plasma Mass Spectrometry; IW, Individual's weight; In, Indium; Li, Lithium; LOD, Limit of Detection; LOQ, Limit of Quantification; p-RFD, Chronic reference dose.

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and toxic effects of Li on plants are still unclear. If, on the one hand, this alkaline element stimulates plant growth in low concentrations, on the other hand, it can affect their growth, absorption, and translocation of other biologically important elements (Kabata-Pendias and Mukherjee, 2007; Shahzad et al., 2016). Main Li reserves worldwide are located in brine deposits of South America. Nevertheless, other countries, including Australia and China, have noteworthy Li reserves (Chaves et al., 2021; Kaunda, 2020). Regarding Europe, Portugal stands out for its substantial Li hard-rock deposits (granitic aplitopegmatites), mainly in the north and central regions, with an estimated 270,000 tons of Li resources (Oliveira et al., 2018). In Portugal, Li-bearing minerals are predominantly mined in open pits, with quartz and feldspar extraction for the ceramic industry. However, this situation will change soon with the implementation of the Barroso Lithium project, which will expand the current concession area and progress to the extraction and processing of lithiniferous pegmatite (VISA, 2021). This expansion has raised societal and environmental concerns regarding contamination and its effects on human health, due to the potential spread of Li in air, soil and water, and consequently the food chain, along with the depletion of essential water resources (Aral and Vecchio-Sadus, 2011; Kaunda, 2020; Shakoor et al., 2023b).

Edible crops of cereal and vegetables and drinking water are the main routes of Li entrance into the food chain, and both sources depend on Li dynamics with other chemical elements in soils (Tanveer et al., 2019). Therefore, understanding the behavior and distribution of Li in the environment and its introduction into the food chain is extremely important to evaluate the food safety of populations, especially those residing near lithiniferous resources (Shakoor et al., 2023b).

This exploratory study in Portugal, integrated into the ILiFOOD project (Lithium in food: The impact of lithium mining), will, for the first time, characterize samples from the region surrounding the Barroso mine and establish baselines for evaluating the future influence of the mining activity on the environment and population's exposure to Li. The main goals of the present study are (i) to characterize Li levels on food crops (cabbage and potato), water (drinking and irrigation), and soils from villages located near the mine (ii) to estimate the dietary intake of nearby populations and perform a risk assessment regarding Li exposure (iii) to establish a baseline for monitoring and evaluating potential influence resulting from the future expansion of the mining activity in the Barroso mine.

2. Materials and methods

2.1. Study area

The study area was identified based on the population's proximity to the mining area. This area comprehended the villages closest to the Barroso Mine, located in northern Portugal in the region of Trás-os-Montes, notable for its distinct geomorphological characteristics, evidenced by mountainous topography. The mining concession comprises the parishes of Dornelas and Covas do Barroso. The villages closest to the mine are Dornelas, Antigo, Espertina, Covas do Barroso, Romaínho, and Muro (Fig. 1) (VISA, 2021).

Concessioned in 2006 (C-100 mine), the activity was focused on

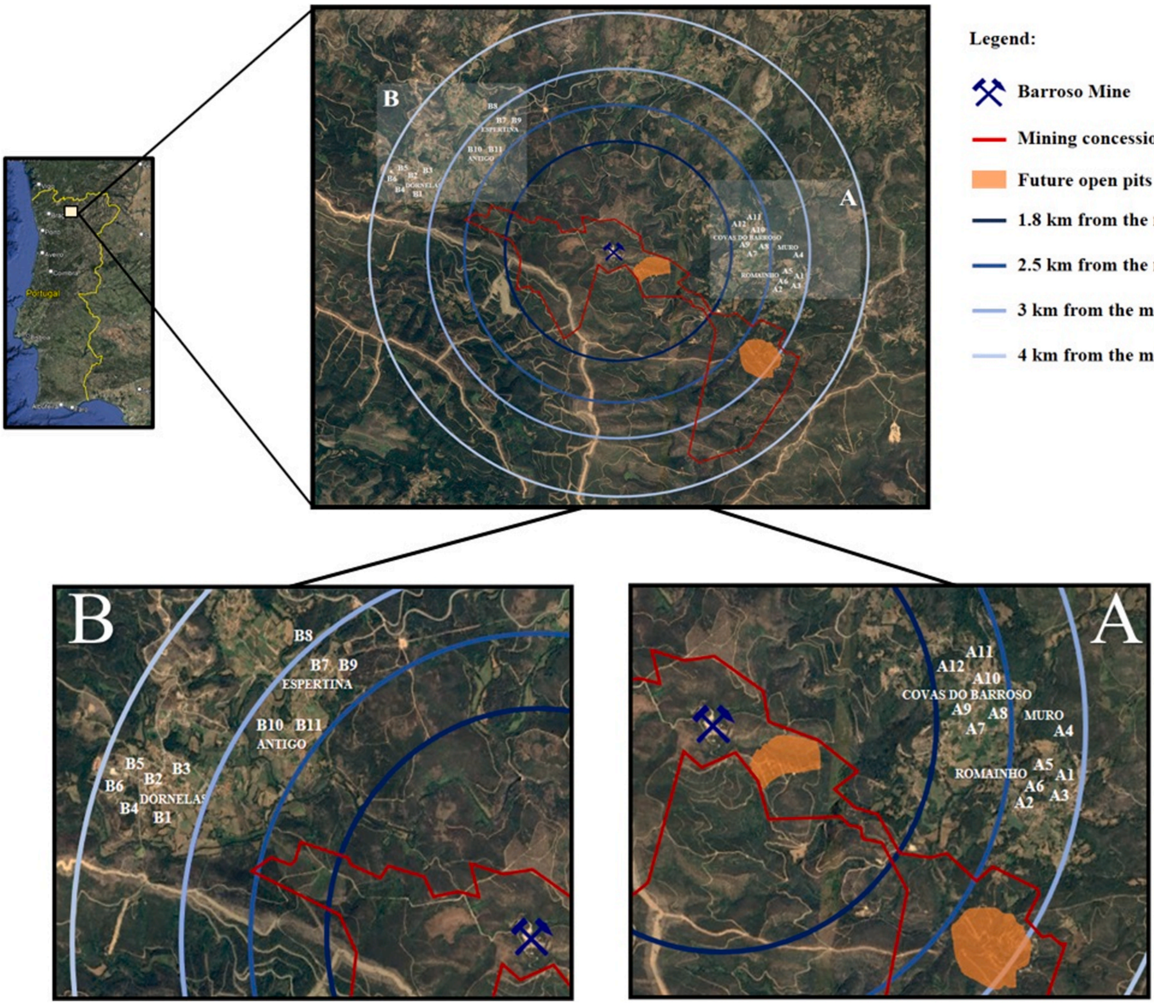

Fig. 1. Map of sampling sites. Letters A1 to A12 identify farms at site A. Letters B1 to B11 identify farms at site B.

small open pits only for mining aplitopegmatites with quartz and feldspar and Li minerals (mainly spodumene) (VISA, 2021). After 2006, following a scoping study that outlined a conventional mine and a concentrator operation, Savannah Lithium Company has been progressing with the development and licensing of the Barroso Li Project. This project will increase the mining concession area, foreseeing two new future open pits near Covas do Barroso, Romaínho, and Muro, for the extraction and processing of Li minerals from pegmatites (Fig. 1).

2.2. Sampling plan and sample collection

The sampling strategy considered the populations closest to the Barroso mine concession and anticipated its future expansion. Due to the forest area, relief and population distribution, samples were collected from 23 subsistence farms located in northwest and east villages of the mine. Site A gathers the villages on the east (Covas do Barroso, Romaínho, Muro), which will presumably be subjected to a higher influence from the expected future open pits. Site B integrates northwest villages (Dornelas, Antigo, Espertina) located further away from the future open pits (Fig. 1). These sites are the closest inhabited areas to the existing mine, thus providing the basis for assessing not only the current situation, but also any of the future impacts.

The food sampling methodology followed the approach of Total Diet Studies (TDS), which involves collecting foods items representative of the target population's diet. Applying the TDS methodology ensures that the collected samples are representative of sites A and B (Pité et al., 2018). The selection of the food items was based on four premises: i) cabbages and potatoes are widely cultivated and consumed by rural populations (Batista et al., 2011; Lopes et al., 2017; System of Agriculture, 2018); ii) vegetables can contribute significantly to Li's daily intake (Aral and Vecchio-Sadus, 2011); iii) cabbages are considered good indicators of the levels of chemical elements present in soils and in air (Edelstein and Ben-Hur, 2018; Gupta et al., 2019); iv) Li data for both food crops are scarce. Also, drinking water was collected since it can be sometimes a good contributor of Li to the diet (Aral and Vecchio-Sadus, 2011; Voica et al., 2021). Furthermore, samples were collected to characterize the Li baselines in the studied areas and establish possible correlations between the different studied matrices and fill the existing knowledge gap for this area. A total of 69 cabbages, 63 potatoes, 44 soils, 23 irrigation water, and 10 drinking water samples from private (wells and springs) and public supplies were collected between May and August of 2022 in the selected villages around the Barroso mine (Fig. 2). The reduced number of drinking water samples (n = 10) is because drinking water from public supplies was the same in several subsistence farms. Corresponding soil samples were collected simultaneously with all cabbage and potato samples, in each farm. Given the preliminary nature of this study, not all collected soils were analyzed for Li content. Therefore, five soils for each crop were selected based on the Li concentration levels (low, intermediate, and high) present in cabbage and potato samples.

In each farm, three samples of each crop, cabbage and potato, were selected, harvested and analyzed as a pooled sample. The corresponding soil samples (1–1.5 kg/site crop) were collected with a shovel, up to 20 cm deep. The samples, sealed in plastic bags, were transported to the laboratory and stored at 5 ± 3 °C. Irrigation and drinking water samples were also collected at each sampling site and parameters such as temperature, pH (WTW, 325/SET) and electric conductivity (WTW, LF325) were measured *in situ* with portable probes. The water samples were transported to the laboratory and stored under refrigeration.

2.3. Socio demographic and food consumption survey

A survey was developed and validated, aiming to collect socio demographic data and characterize the consumption patterns of the population. The survey is divided into four sections: the first covers demographic data such as gender, age and education; the second focuses on working conditions; the third investigates agricultural practices, including the use of chemicals; and the last section explores eating habits, including the type of water consumed and the consumption pattern of foods such as cabbage and potatoes (supported by a photographic manual). The survey was answered by 28 participants, 16 residents from site A and 12 from site B. All participants consumed their homegrown cabbages and potatoes. The questionnaire was applied by trained interviewers in a face-to-face interview, during sample collection. Consumption data (i.e., number of meals per day and size to estimate the amount in each portion) referred to the collected food items (cabbage, potato and drinking water).

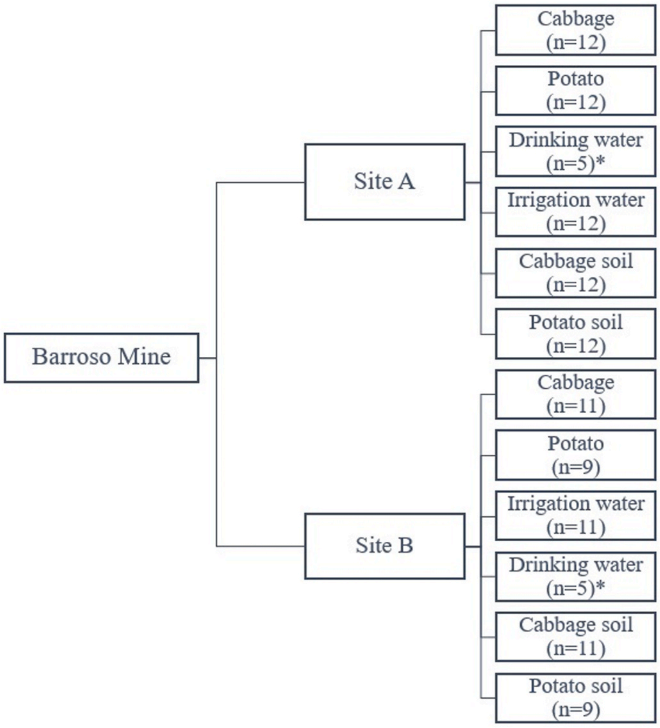

Fig. 2. Sampling plan. * The drinking water consumed in several subsistence farms was the same, so 5 samples were collected for each site.

2.4. Reagents, chemical standards and equipment

All reagents used in the present study were of high analytical grade, ensuring the highest purity level for the experiments, and samples were analyzed in clean room facilities. All containers and laboratory materials were made of plastic, either perfluoroalkoxy (PFA) or polypropylene (PP) and decontaminated with ultrapure HNO_3 before usage. Ultrapure water was obtained using a Milli-Q Plus Millipore system (Q-POD Millipore, Interface, Portugal). HNO_3 pro analysis (65% v/v) (Merck, VWR, Portugal) was purified in the laboratory, through an acid distillation system (Milestone, Unicam, Portugal). A multi-element standard solution containing 100 mg/L of Li was purchased in highest purity from Merck Multi XVI (VWR, Portugal) and was used to prepare calibration standards for quadrupole inductively coupled plasma mass spectrometry (ICP-MS) analysis. In addition, Germanium (Ge), Yttrium (Y) and Indium (In) were utilized as internal standards at a concentration of 1000 mg/L (Merck, Darmstadt, Germany). The 4.0 and 7.0 standard pH solution (Merck, Germany), quality control 7.0 pH (Fluka, Germany) and ultrapure water were used to determine pH value.

The Li analysis was performed using ICP-MS. Cabbage and potato samples, were analyzed using an ICP-MS Thermo X series II (Thermo Fisher Scientific, Germany) with the software Plasmalab database version 3.51. Soil and water samples were outsourced. The soil pH was determined using a 780 pH meter (Metrohm, Switzerland) associated with a sensitive electrode after the calibration with 4.0 and 7.0 pH standard solutions.

2.5. Sample preparation

Soil: Soil samples were air-dried at room temperature and stirred until complete dryness (minimum moisture content). The samples were sieved at a 2 mm sieve and stored at room temperature until their physical-chemical analysis. The pH analysis of the soil samples followed the method described in the literature (Póvoas and Barral, 1992). A soil: water suspension (1:2.5 ratio) was prepared for each duplicate sample and then shaken at regular intervals of 10 min over an hour. Samples chemical analysis were performed by ICP-MS, after aqua regia digestion.

Irrigation and drinking water: Water samples were filtered (0.45 μm) and acidified to 2% (v/v) ultrapure HNO_3 before being analyzed by ICP-MS.

Cabbage: The cabbage samples from each farm were analyzed in the laboratory as pools. The edible leaves of 3 cabbages from each farm, were washed thoroughly with tap water and mixed. The samples were oven-dried, in a heating oven, at 40 °C until reaching a constant mass and grounded and homogenized in a knife mill. The analysis of Li in cabbage samples followed the procedure described in the literature with slight modifications (Coelho et al., 2013). Samples weighing 0.5 g were placed in a microwave vessel (Ethos 1, Milestone) and 3 mL of ultrapure water, 4 mL of concentrated HNO_3, and 1 mL of concentrated H_2O_2 were added to each vessel. A separate vessel containing only reagents was included as a blank to monitor potential contamination from the digestion process. The following digestion program was applied: 1) increase temperature to 90 °C, in the first 25 min; 2) maintain temperature at 90 °C for 5 min; 3) increase temperature to 180 °C for 15 min; 4) keep temperature at 180 °C for 5 min 5) increase temperature to 210 °C and maintain for 12 min. After cooling to room temperature, the content of each vessel was transferred to a volumetric flask and diluted up to 25 mL using ultrapure water. Subsequently, the Li analysis was performed using ICP-MS, and digested samples were kept at 5 ± 3 °C until further analysis.

Potato: The potato samples were peeled, washed with tap water, dried at 40 °C in an oven, until constant mass, and ground. A 48-well heating block (DigiPREP, SCP Science, Courtaboeuf, France) was used for the digestion. For each sample, 0.5 g of potato was weighed into 50 mL PP DigiTUBEs (SCP Science, Quebec, Canada) and left overnight with 7 mL of ultrapure HNO_3. Then, 1 mL of H_2O_2 was added, and digestion was as follows: temperature was increased to 85 °C for 45 min and kept at this temperature for 180 min. After digestion, the samples were completed up to 25 mL with MilliQ water and kept at 5 ± 3 °C until analysis.

2.6. Quality assurance and quality control

Analytical determinations followed the quality assurance programme described in NP EN ISO/IEC 17025 standard (ISO/IEC, 2017). Work range, limit of detection (LOD), limit of quantification (LOQ), repeatability, spiked samples, Certified Reference Materials (Typical Diet 1548a and IPE 898 Cabbage) and uncertainty were used to control the quality of results (Table 1). The laboratory also participated regularly in proficiency testing schemes launched by an accredited provider with satisfactory results. Analytical results are expressed by the average ± standard deviation of three replicates. To control contaminations, one reagent blank was performed in each acid digestion cycle.

2.7. Estimated daily intake and risk characterization

Calculations of estimated daily intake (EDI) and risk characterization were carried out according to the procedure described by Assunção et al. (2015). Briefly, food consumption and body weight (BW) data were obtained through socio-demographic questionnaires during food collections. To handle consumption data, an approach was adopted where, given the reported frequency of consumption within a range of values, an intermediate value from that range was used (refer to Table ST1). The EDI was calculated for each food matrix (cabbage, potatoes and drinking water) by multiplying the Li concentration (C_{Li} in μg/kg) by the consumption data (CD in kg/day), from the corresponding inhabitant's farm, and dividing by the individual's weight (IW in kg), according to equation 1 (Assunção et al., 2015):

$$EDI = \frac{C_{Li} \times CD}{IW}$$

The daily water consumption was based on the reported by IAN-AF 2017 (869.8 g/day), since this information was not collected in the surveys (Lopes et al., 2017).

To characterize the risk, the EDI results were compared with reference values, namely the provisional reference dose (p-RfD) daily intake of Li (2 μg/kg per day), to calculate the risk quotients (HQ – the ratio between exposure and a reference dose). An HQ < 1 indicates a tolerable exposure level, and an HQ ratio >1 indicates a non-tolerable exposure level (European Food Safety Authority, 2013).

2.8. Statistical analysis

Descriptive statistical data, including mean, average, maximum, and minimum values, were reported to characterize and describe the distribution of Li in the study area (Supporting Information ST1, ST2, ST3, ST4). The values between the LOD and LOQ were considered as presented in equation 2 (European Food Safety Authority, 2010):

$$X = \frac{LOQ + LOD}{2}$$

Statistical analysis was performed using IBM SPSS Statistics version 27. Significance levels were set at a p-value <0.05 for all analyses. Spearman correlation coefficients were calculated to further explore connections within the dataset.

3. Results and discussion

To evaluate the occurrence of Li levels in areas rich in lithiniferous deposits, food (cabbage and potatoes), drinking water, irrigation water and soil samples were collected from farms east and northwest (sites A and B, respectively) of the Barroso mine. The levels of Li in samples were combined with food consumption data to conduct a risk assessment analysis of surrounding populations.

Table 1
Figures of merit.

Matrix	LOD	LOQ	Working range	Repeatability (RSD%)	Recovery (%)	Uncertainty (%)
Cabbage	0.44 μg/kg	1.8 μg/kg	0.5–10 μg/kg	<7.5	90–112	26
Potato	0.54 μg/kg	2.3 μg/kg	0.5–10 μg/kg	<10	91–104	26
Irrigation/drinking water	0.33 μg/L	1 μg/L	1–2.5 μg/L	<4.0	80–114	18
Soil[a]	n.a.	0.1 mg/kg	n.a.	<4.0	90–119	39

n.a. – not available.

[a] analyzed by an external laboratory.

The results of Li in the agricultural soil, irrigation water, cabbage and potato samples collected from sites A and B are present in Fig. 3 and in Supporting Information (ST1, ST2, ST3, ST4).

3.1. Levels of Li and pH in agricultural soils and irrigation water

3.1.1. Agricultural soils

As observed in Fig. 3, there are no significant differences in the pH value of cabbage and potato soils from the two sites (p-value<0.05). Comparing the pH values between the soils of the two food matrices, it is observed that they have similar values. Cabbage soils presented a median value of 5.6 in site A, and 5.9 in site B. On the other hand, the median pH in potato soils was 5.1 in site A, and 4.9 in site B. Soils A9 and B2 have the highest pH levels in cabbage soils, and are statistically considered outliers. Regarding potato soils, only one outlier (A11) was identified. This difference in pH in soil A11 compared to other soils at site A can be explained by the application of insecticide for potato beetles that was applied to this specific crop. Maneepitak and Cochard (2014) observed, in rice crops, an increase in pH with the application of synthetic insecticides.

The pH values observed in this study are slightly higher than the results available for the Ap horizon reported in 1991 in Covas do Barroso ($pH = 4.7$, $n = 1$) and Dornelas ($pH = 4.8$, $n = 1$) (INIAV, 2020). This minor variation in pH could be attributed to various factors, including natural weathering processes or human activities (Msimbira and Smith, 2020). However, further studies over time are required to understand the behavior of this parameter. According to Moreira (2012), the favorable pH for cabbage cultivation is between 5.5 and 7.5 and for potatoes, it is between 5 and 6.5. Thus, all pH levels in potato soils are favorable for the production of this food crop; however, in the case of cabbage soils, only 52% are favorable for cabbage cultivation. The remaining cabbage soils, which have a more acidic pH, could have a negative effect on the development and health of the plant.

The results shown in Fig. 3 suggest no significant differences in Li content between cabbage and potato soils (p-value<0.05) from sites A and B. Cabbage soils exhibited a median of 59.3 mg/kg and 65.4 mg/kg at sites A and B, respectively. Similar outcomes were observed in potato soils, with a median of 62.4 mg/kg at site A and 66.0 mg/kg at site B. Pinheiro (2020) also reported Li concentrations of 77.45 and 55.77 mg/kg in cabbage and potato agricultural soils in the proximity of the C-57 mine (Gonçalo, Guarda), that exploited aplite-pegmatites with lepidolite.

The Li levels reported in this study are also higher than those mentioned by Pinheiro (2020) (0.4–16 mg/kg) in non-agricultural soils in areas without lithiniferous mining activity, or higher than the ones reported in Project GEMAS, for agricultural European soils, averaging 11.4 mg/kg (Reimann et al., 2018). The higher Li concentration observed in the soils from both sites A and B display the chemical signature of the geological substrate in this region. They are also within the Li levels reported by Pinheiro (2020) for non-agricultural soils of Northern Portugal (25.88–157.82 mg/kg) mainly derived from granitic and metasedimentary rocks, where Li mineralized bodies are mainly located. Within the Barroso concession mine area, the Li in soils (mostly derived from pelitic shales and some Li aplite-pegmatite veins) present great variability, from 16 to 403 mg/kg (digestion with aqua regia) with estimated lower levels towards Dornelas (Site B) and occasionally higher levels towards the Covas do Barroso (Site A) (VISA, 2021). Despite the limited number of soils analyzed, this different trend was not observed in the Li soil levels of sites A and B, and the Li levels seem not to express the influence of past and current open pit mining activity.

The Li content in soils is expected to be higher in acidic soils compared to alkaline ones (Sobolev et al., 2019). However, the data obtained did not show any significant correlation between soil pH values and the Li levels in the soil.

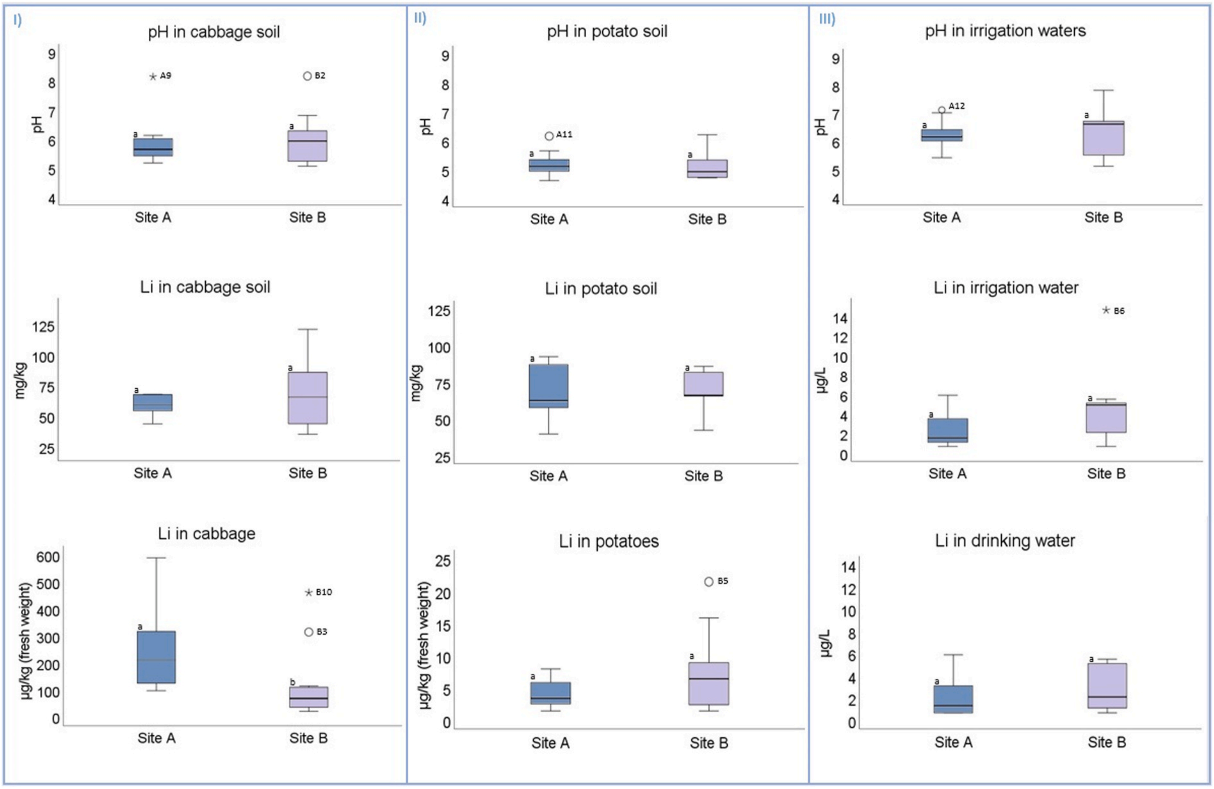

Fig. 3. Box-plots of pH values and Li concentrations in (I) cabbage related samples, (II) potato related samples, (III) drinking and irrigation water. Significant differences ($p < 0.05$) between sites A and B are denoted by different lowercase letters. Outliers are denoted with ° and extreme values with *.

3.1.2. *Irrigation water*

The median pH value of irrigation water for cabbage and potato crops is 6.2 and 6.6 for sites A and B, respectively. Based on Fig. 3, there are no significant differences in the pH of irrigation waters from the two sites (p-value<0.05). Of the irrigation waters analyzed, 83% are acidic, and the remaining samples presented a neutral pH. The average pH value of irrigation water slightly increases in the following order: springs < boreholes < wells. Approximately 61% of waters have pH values below the maximum recommended value (VMR) limit (6.5) but all samples within the maximum admissible value VMA (4.5–9.0) (Diário da República, 2023). Using water with pH outside the VMA range can negatively affect crops, as a very low pH can cause nutritional imbalances in the soil and plants, affecting crop growth.

The Li content in irrigation water from sites A and B did not show significant differences (p-value<0.05). Samples from site A ranged between 1.1 and 5.9 μg/L, while those from site B ranged between 1.1 and 5.5 μg/L. In general, the average Li content of irrigation water increases in the following order: wells < springs < boreholes. At site A, two samples from springs are below the LOQ. At site B, an outlier stands out with a Li content of 14.6 μg/L, and one of the two well waters analyzed is below the LOQ. All results are below the limit established for Li by Portuguese legislation for irrigation water, set at 2.5 mg/L (Diário da República, 1998). This legislative limit ensures that Li concentrations in irrigation water remain acceptable for environmental and human health considerations. Rodrigues et al. (2019) studied Li content in waters near a mine C-57, in Guarda, Portugal. The author reported an average Li concentration of 30 μg/L, higher than observed in the present study. In addition, a study carried out near a spodumene deposit in Ireland observed higher concentrations than those reported in this study (20 μg/L) (Kavanagh et al., 2017). In contrast, Toupal et al. (2022) investigated the influence of three deposits of Li mica and one of spodumene on the Li content in surface waters. The study reported mean Li concentrations (5 μg/L, 6 μg/L, 11 μg/L and 13 μg/L) like those obtained in the present study. The Li levels in the studied water sources are in line with or even lower than concentrations reported in areas with Li mineral deposits, suggesting that the current Barroso mining exploration does not appear to influence Li levels in groundwater.

3.2. *Lithium in food items: drinking water, cabbages and potatoes*

3.2.1. *Drinking water*

Concerning sources of drinking water, it is observed that the population under study (sites A and B) consumes water from tap (61%), springs (21%), boreholes (7%), wells (4%) and bottled water (7%). It is important to note that the Li content in bottled water was not analyzed and is not within the scope of the present study.

The maximum Li concentrations in drinking water were 5.9 μg/L and 5.5 μg/L in sites A and B, respectively. At site A, the tap water is below the LOQ, and the highest Li content corresponds to spring water. On the other hand, at site B, only one of the well irrigation waters is below the LOQ, and the highest content corresponds to the tap water. Oliveira et al. (2019) analyzed tap water from 54 municipalities in Portugal, reporting an average Li concentration of 10.9 μg/L. Furthermore, Helbich et al. (2015) and Izsak et al. (2022) recorded an average of this chemical element of 10.0 μg/L and 11.2 μg/L, respectively. The results observed in the present study are lower than these values.

To date, the World Health Organization has not established specific limits for Li content in drinking water. However, the Eurasian Economic Union has defined a threshold of 30 μg/L for Li in drinking water (EAEU, 2017). Based on this limit, the levels detected in the water consumed by the population under study are within the established limit.

3.2.2. *Cabbage and potato*

Fig. 3 shows a dispersion of cabbage Li concentration in site A, ranging from 96 ± 2 μg/kg to 589 ± 35 μg/kg (fresh weight), with an average of 239 ± 140 μg/kg. In contrast, at site B, Li levels varied between 20 ± 1 μg/kg and 114 ± 3 μg/kg, with an average of 62 ± 35 μg/kg and were significantly lower than site A (Mann-Whitney test; p-value <0.05). In addition, there are two outliers, B10 and B3. Compared to the literature, the results for sites A and B are lower than those observed by Ammari et al. (2011). This author reported an average of 1200 μg/kg (fresh weight) in cabbages harvested in the soils of the Jordan Valley, a lithium-producing region. Furthermore, Figueroa et al. (2013) found higher levels in samples from another lithium-producing region in Northern Chile, ranging between 3200 and 3800 μg/kg (dry weight). Converting the Li concentrations at sites A and B to dry weight, they range between 660 and 4033 μg/kg and 135–3149 μg/kg, respectively. Considering both sites, one sample from site A stands out with a 4033 μg/kg Li content. In another study, Kabata-Pendias & Pendias (2001) reported lower Li levels, with an average of 500 μg/kg dry weight in this vegetable product. All results at site A are higher; however, at site B, only six of the eleven cabbages show concentrations above the value observed by Kabata-Pendias & Pendias (2001).

One possible explanation could be related to the different absorbtion rates of chemical elements through the soil or even due to different contents of other available alkali metals in the soil that can influence the absorption of Li. For example, Ca inhibits Li uptake by plants; therefore, adding lime to high-Li soils may reduce the toxic effects of this element (Duarte Costa, 2015; Environmental Law Alliance Worldwide, 2010; Kabata-Pendias and Pendias, 2001).

A significant negative correlation was also found between the Li concentration in the cabbages and the soil pH of the cabbages (Fig. 4), which means higher Li concentrations in cabbages are related to more acidic soils. This result is aligned with the literature that reported a negative relationship between the Li content in some plants and the corresponding soil pH (Shakoor et al., 2023b).

Based on Fig. 3, the Li concentrations in potato samples do not exhibit significant differences between the two locations (p-value <0.05). At site A, Li concentration in the samples ranged between 2.28 ± 0.02 μg/kg and 7.9 ± 0.1 μg/kg, with an average of 4 ± 2 μg/kg. However, site B showed higher variability of Li content than site A, ranging between 2.4 ± 0.5 and 21 ± 1 μg/kg.

Regarding potatoes, studies are scarce to date, except for the French TDS study, which evaluated the Li content in cooked potatoes (16.3 μg/kg fresh weight) whereas the samples in this study were analyzed raw (ANSES, 2011). As illustrated in Fig. 3, only sample B5, in Dornelas, is above the value reported by the French TDS. In Tenerife (Canary island) in three quality of potatoes the Li ranged between 0.8 ± 0.4 and 1.9 ± 0.4 mg/kg fresh weight (González-Weller et al., 2013).

According to the literature, it is observed that plants have different absorption and translocation capacities for Li, influenced by several factors, such as the properties and chemical composition of the soil, the plant species, the conditions climate conditions and the application of fertilizers or natural fertilizers. When comparing the results obtained

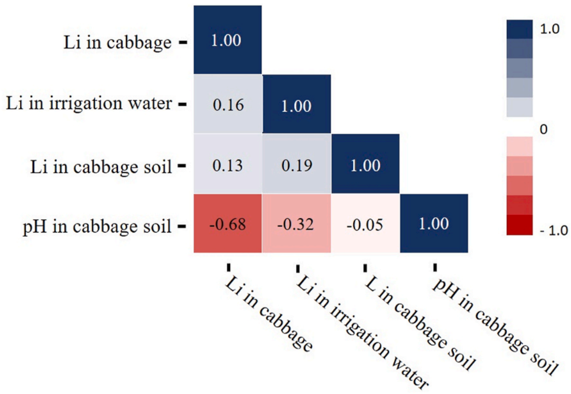

Fig. 4. Heatmap with spearman correlation matrix for cabbage (significative correlation for p-value <0.05).

from cabbage and potatoes, it is clear that cabbage exhibits a significantly higher Li content approximately ten times higher than that found in potatoes. This difference can be explained by the process of Li translocation mechanism in plants (Environmental Law Alliance Worldwide, 2010; Shakoor et al., 2023a; Tanveer et al., 2019). In plants, Li is absorbed by the roots and subsequently transported through the xylem, a primary pathway for water and nutrient transport within the plant. Also, Kabata-Pendias & Pendias (2001) reported that Li content on different edible plants shows that the above-earth parts concentrate a higher proportion of Li than storage roots or bulbs. Consequently, the edible part of the cabbage (the leaves) accumulates a higher Li concentration than the edible part of the potato (the tuber), which reflects the different Li absorption capacities among plant species.

3.3. Risk assessment

The study involved 28 individuals: 15 (54%) females and 13 (46%) males. Regarding the age group, 15 (54%) participants were between 18 and 64, while 13 (46%) were between 65 and 95. When analyzing site A, of the 16 participants, 7 (44%) were female, and 9 (56%) were male. The age group distribution at this site included 11 (69%) participants aged 18–64 years and 5 (31%) participants aged 75–95 years. At site B, with 12 participants, 8 (67%) are female and 4 (33%) are male. The age range at this location showed 4 (33%) participants aged 18–64 and 8 (67%) participants aged 65 to 95.

Upon analyzing the reported consumption data and Li occurrence levels, the intake of Li from the consumption of cabbage and potatoes was estimated (ST5). The maximum estimated Li intake through cabbage and potatoes was found to be 0.909 and 0.015 μg/kg bw/day for site A, and 0.224 and 0.042 μg/kg bw/day for site B. Calculating the total Li intake (cabbage, potato and water), site A demonstrated a higher maximum intake (0.926 μg/kg bw/day) compared to site B (0.432 μg/kg bw/day). In light of the provisional reference dose (p-RfD) established by the (Environmental Protection Agency, 2008) at 2 μg/kg bw/day, our findings indicate that the studied population did not exceed the p-RfD for none of the participants of the study, presenting a hazard quotient (HQ) < 1. This suggests a tolerable exposure level for the population under consideration within the framework of this study.

4. Conclusions

This study aimed to characterize the Li concentration on two diet food crops, soil and water in the closest inhabited villages around the Barroso mine area (sites A and B) to asses' baselines and for evaluate future mining activities impacts from Li minerals exploitation and processing.

No significant differences were observed between the Li levels on irrigation (average: 4.0 mg/L) and drinking water (average: 3.4 mg/L), soils (average: 66 mg/kg) and potatoes (average: 6.2 μg/kg fresh weight) of the selected sites. However, significant differences were observed between cabbage samples in site A (average: 239 μg/kg fresh weight) and site B (average: 62 μg/kg fresh weight). The results observed with this study do not reveal the influence of the past Barroso open pit mining activity.

On the other hand, the estimated Li exposure and the risk assessment from the ingestion of the studied food items did not indicate any health population concern. Nevertheless, additional sources of exposure or other foods may contribute to increasing the exposure level.

Knowledge about other possible contaminants is crucial to assess the potential risks for the quality of irrigation water, soil, and food items and complement this current study. ILiFOOD research project will provide such information by covering Li and other trace elements in additional relevant mining areas in Portugal, besides the Barroso mine.

Since information about this topic is still scarce, such initiatives are essential to evaluate current or future Li mining activities and ensure food safety and public health in these regions. The evaluated sites are both equidistant from the current mine. However, the new open pit Li mines, predicted for the near future, will be located closer to site A than to site B. This study provides crucial information on the area's current status and establishes reference values for future evaluations.

CRediT authorship contribution statement

Susana Jesus: Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **Marta Ventura:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Ricardo Assunção:** Writing – review & editing, Methodology, Formal analysis, Conceptualization. **Sandra Gueifão:** Validation, Resources, Methodology, Investigation. **Inês Delgado:** Validation, Resources, Methodology, Investigation. **Andreia Rego:** Validation, Resources, Methodology, Investigation, Formal analysis. **Mariana Ribeiro:** Validation, Resources, Methodology, Investigation. **Marta Martins:** Writing – review & editing, Conceptualization. **Orquídia Neves:** Writing – review & editing, Resources, Methodology, Investigation, Conceptualization. **Inês Coelho:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fct.2024.114825.

References

Ammari, T.G., Al-Zu'bi, Y., Abu-Baker, S., Dababneh, B., Gnemat, W., Tahboub, A., 2011. The occurrence of lithium in the environment of the Jordan Valley and its transfer into the food chain. Environ. Geochem. Health 33 (5), 427–437. https://doi.org/10.1007/s10653-010-9343-5.

ANSES, 2011. Second French Total Diet Study (TDS 2) Report 1: Inorganic Contaminants, Minerals, Persistent Organic Pollutants, Mycotoxins and Phytoestrogens ANSES Opinion.

Aral, H., Vecchio-Sadus, A., 2011. Lithium: environmental pollution and health effects. In: Encyclopedia of Environmental Health. Elsevier, pp. 499–508. https://doi.org/10.1016/B978-0-444-52272-6.00531-6.

Assunção, R., Vasco, E., Nunes, B., Loureiro, S., Martins, C., Alvito, P., 2015. Single-compound and cumulative risk assessment of mycotoxins present in breakfast cereals consumed by children from Lisbon region, Portugal. Food Chem. Toxicol. 86, 274–281. https://doi.org/10.1016/j.fct.2015.10.017.

Batista, C., Barros, L., Carvalho, A.M., Ferreira, I.C.F.R., 2011. Nutritional and nutraceutical potential of rape (Brassica napus L. var. napus) and ' tronchuda' cabbage (Brassica oleraceae L. var. costata) inflorescences. Food Chem. Toxicol. 49 (6), 1208–1214. https://doi.org/10.1016/j.fct.2011.02.023.

Chaves, C., Pereira, E., Ferreira, P., Guerner Dias, A., 2021. Concerns about lithium extraction: a review and application for Portugal☆. Extr. Ind. Soc. 8 (3), 100928 https://doi.org/10.1016/j.exis.2021.100928.

Coelho, I., Gueifão, S., Matos, A.S., Roe, M., Castanheira, I., 2013. Experimental approaches for the estimation of uncertainty in analysis of trace inorganic contaminants in foodstuffs by ICP-MS. Food Chem. 141 (1), 604–611. https://doi.org/10.1016/j.foodchem.2013.03.040.

Diário da República, 1998. Decreto-Lei *n.*236/298.

Diário da República, 2023. Decreto-Lei n.º *11/2023*.

Duarte Costa, H.T., 2015. Concentração de metais pesados nos solos utilizados para agricultura urbana na cidade de Lisboa. Instituto Superior de Agronomia.

EAEU, 2017. EAEU Technical Regulation on Packaged Water.

Edelstein, M., Ben-Hur, M., 2018. Heavy metals and metalloids: sources, risks and strategies to reduce their accumulation in horticultural crops. Sci. Hortic. 234, 431–444. https://doi.org/10.1016/j.scienta.2017.12.039. Elsevier B.V.

Enderle, J., Klink, U., Di Giuseppe, R., Koch, M., Seidel, U., Weber, K., Birringer, M., Ratjen, I., Rimbach, G., Lieb, W., 2020. Plasma lithium levels in a general population: a cross-sectional analysis of metabolic and dietary correlates. Nutrients 12 (8), 1–15. https://doi.org/10.3390/nu12082489.

Environmental Law Alliance Worldwide, 2010. Overview of mining and its impacts. In: Guidebook for Evaluating Mining Project EIAs.

Environmental Protection Agency, 2008. Provisional Peer Reviewed Toxicity Values for Lithium. *CASRN 7439-93-2)*.

European Commission, 2020. Critical raw materials resilience: charting a path towards greater security and sustainability. http://info.worldbank.org/governance/wgi/.

European Food Safety Authority, 2010. Management of left-censored data in dietary exposure assessment of chemical substances. EFSA J. 8 (3) https://doi.org/10.2903/j.efsa.2010.1557.

European Food Safety Authority, 2013. International frameworks dealing with human risk assessment of combined exposure to multiple chemicals. EFSA J. 11 (7) https://doi.org/10.2903/j.efsa.2013.3313.

Figueroa, L.T., Razmillic, B., Zumeata, O., Aranda, G.N., Barton, S.A., Schull, W.J., Young, A.H., Kamiya, Y.M., Hoskins, J.A., Ilgren, E.B., 2013. Environmental lithium exposure in the north of Chile—ii. Natural food sources. Biol. Trace Elem. Res. 151 (1), 122–131. https://doi.org/10.1007/s12011-012-9543-1.

González-Weller, D., Rubio, C., Gutiérrez, Á.J., González, G.L., Mesa, J.M.C., Gironés, C. R., Ojeda, A.B., Hardisson, A., 2013. Dietary intake of barium, bismuth, chromium, lithium, and strontium in a Spanish population (Canary Islands, Spain). Food Chem. Toxicol. 62, 856–868. https://doi.org/10.1016/j.fct.2013.10.026.

Gupta, N., Yadav, K.K., Kumar, V., Kumar, S., Chadd, R.P., Kumar, A., 2019. Trace elements in soil-vegetables interface: translocation, bioaccumulation, toxicity and amelioration - a review. Sci. Total Environ. 651, 2927–2942. https://doi.org/10.1016/j.scitotenv.2018.10.047. Elsevier B.V.

Helbich, M., Leitner, M., Kapusta, N.D., 2015. Lithium in drinking water and suicide mortality: interplay with lithium prescriptions. Br. J. Psychiatry 207 (1), 64–71. https://doi.org/10.1192/bjp.bp.114.152991.

Iniav, I.P., 2020. Base de Dados INFOSOLO. https://portalgeo.iniav.pt/portal/apps/webappviewer/index.html?id=17574ca60800415dace9a6369ac53208.

Izsak, B., Hidvegi, A., Balint, L., Malnasi, T., Vargha, M., Pandics, T., Rihmer, Z., Dome, P., 2022. Investigation of the association between lithium levels in drinking water and suicide mortality in Hungary. J. Affect. Disord. 298, 540–547. https://doi.org/10.1016/j.jad.2021.11.041.

Kabata-Pendias, A., Mukherjee, A.B., 2007. Alina Kabata-Pendias Trace Elements from Soil to Human.

Kabata-Pendias, Alina, Pendias, Henryk, 2001. Trace Elements in Soils and Plants. CRC Press.

Kaunda, R.B., 2020. Potential environmental impacts of lithium mining. J. Energy Nat. Resour. Law 38 (3), 237–244. https://doi.org/10.1080/02646811.2020.1754596.

Kavanagh, L., Keohane, J., Cleary, J., Cabellos, G.G., Lloyd, A., 2017. Lithium in the natural waters of the south east of Ireland. Int. J. Environ. Res. Publ. Health 14 (6). https://doi.org/10.3390/ijerph14060561.

Lopes, C., Torres, D., Oliveira, A., Severo, M., Alarcão, V., Guiomar, S., Mota, J., Teixeira, P., Rodrigues, S., Lobato, L., Magalhães, V., Correia, D., Carvalho, C., Pizarro, A., Marques, A., Vilela, S., Oliveira, L., Nicola, P., Soares, S., Ramos, E., 2017. Inquérito Alimentar Nacional e de Atividade Física, IAN-AF 2015-2016: Relatório de resultados. www.ian-af.up.pt.

Maneepitak, S., Cochard, R., 2014. Uses, toxicity levels, and environmental impacts of synthetic and natural pesticides in rice fields-A survey in Central Thailand. International Journal of Biodiversity Science, Ecosystem Services and Management 10 (2), 144–156. https://doi.org/10.1080/21513732.2014.905493.

Moreira, U., 2012. Práticas de solos.

Msimbira, L.A., Smith, D.L., 2020. The roles of plant growth promoting microbes in enhancing plant tolerance to acidity and alkalinity stresses. Front. Sustain. Food Syst. 4 https://doi.org/10.3389/fsufs.2020.00106.

Oliveira, D., Vitor, J., Lisboa, V., Manuel, J., Carvalho, F., 2018. Lítio em Portugal: Enquadramento, Geologia e Mineralogia. https://www.statista.com/.

Oliveira, P., Zagalo, J., Madeira, N., Neves, O., 2019. Lithium in public drinking water and suicide mortality in Portugal: initial approach. Acta Med. Port. 32 (1), 47–52. https://doi.org/10.20344/amp.10744.

Opazo, M.A., 2023. Climate crisis: energy storage challenges in the transition to renewable energies. RSC Sustainability 1 (7), 1602–1603. https://doi.org/10.1039/d3su90038j. Royal Society of Chemistry.

Petavratzi, E., Sanchez-Lopez, D., Hughes, A., Stacey, J., Ford, J., Butcher, A., 2022. The impacts of environmental, social and governance (ESG) issues in achieving sustainable lithium supply in the Lithium Triangle. Mineral Economics 35 (3–4), 673–699. https://doi.org/10.1007/s13563-022-00332-4.

Pinheiro, D., 2020. Lithium Concentration and Distribution in Portuguese Soils. Instituto Superior Técnico.

Pité, M., Pinchen, H., Castanheira, I., Oliveira, L., Roe, M., Ruprich, J., Rehurkova, I., Sirot, V., Papadopoulos, A., Gunnlaugsdóttir, H., Reykdal, Ó., Lindtner, O., Ritvanen, T., Finglas, P., 2018. Quality management framework for total diet study centres in Europe. Food Chem. 240, 405–414. https://doi.org/10.1016/j.foodchem.2017.07.101.

Póvoas, I., Barral, M.F., 1992. Métodos de análise de solos. https://opac.ua.pt/cgi-bin/koha/opac-detail.pl?biblionumber=51001&she.

Reimann, C., Fabian, K., Birke, M., Filzmoser, P., Demetriades, A., Négrel, P., Oorts, K., Matschullat, J., de Caritat, P., Albanese, S., Anderson, M., Baritz, R., Batista, M.J., Bel-Ian, A., Cicchella, D., De Vivo, B., De Vos, W., Dinelli, E., Ďuriš, M., et al., 2018. GEMAS: establishing geochemical background and threshold for 53 chemical elements in European agricultural soil. Appl. Geochem. 88, 302–318. https://doi.org/10.1016/j.apgeochem.2017.01.021.

Rodrigues, P.M.S.M., Antão, A.M.M.C., Rodrigues, R., 2019. Evaluation of the impact of lithium exploitation at the C57 mine (Gonçalo, Portugal) on water, soil and air quality. Environ. Earth Sci. 78 (17), 533. https://doi.org/10.1007/s12665-019-8541-4.

Sadik-Zada, E.R., Gatto, A., Scharfenstein, M., 2023. Sustainable management of lithium and green hydrogen and long-run perspectives of electromobility. Technol. Forecast. Soc. Change 186, 121992. https://doi.org/10.1016/j.techfore.2022.121992.

Schrauzer, G.N., 2002. Lithium: occurrence, dietary intakes, nutritional essentiality. J. Am. Coll. Nutr. 21 (1), 14–21. https://doi.org/10.1080/07315724.2002.10719188.

Shahzad, B., Tanveer, M., Hassan, W., Shah, A.N., Anjum, S.A., Cheema, S.A., Ali, I., 2016. Lithium toxicity in plants: reasons, mechanisms and remediation possibilities – a review. Plant Physiol. Biochem. 107, 104–115. https://doi.org/10.1016/j.plaphy.2016.05.034.

Shakoor, N., Adeel, M., Ahmad, M.A., Zain, M., Waheed, U., Javaid, R.A., Haider, F.U., Azeem, I., Zhou, P., Li, Y., Jilani, G., Xu, M., Rinklebe, J., Rui, Y., 2023a. Reimagining safe lithium applications in the living environment and its impacts on human, animal, and plant system. Environmental Science and Ecotechnology 15, 100252. https://doi.org/10.1016/j.ese.2023.100252.

Shakoor, N., Adeel, M., Azeem, I., Ahmad, M.A., Zain, M., Abbas, A., Hussain, M., Jiang, Y., Zhou, P., Li, Y., Xu, M., Rui, Y., 2023b. Interplay of higher plants with lithium pollution: global trends, meta-analysis, and perspectives. Chemosphere 310, 136663. https://doi.org/10.1016/j.chemosphere.2022.136663.

Sobolev, O.I., Gutyj, B.V., Darmohray, L.M., Sobolieva, S.V., Ivanina, V.V., Kuzmenko, O. A., Karkach, P.M., Fesenko, V.F., Bilkevych, V.V., Mashkin, Y.O., Trofymchuk, A.M., Stavetska, R.V., Tkachenko, S.V., Babenko, O.I., Klopenko, N.I., Chernyuk, S.V., 2019. Lithium in the natural environment and its migration in the trophic chain. Ukrainian Journal of Ecology 9 (2), 195–203.

System of Agriculture, 2018. Forestry and Grazing in Barroso-Potential GIAHS/FAO Site.

Tanveer, M., Hasanuzzaman, M., Wang, L., 2019. Lithium in environment and potential targets to reduce lithium toxicity in plants. J. Plant Growth Regul. 38 (4), 1574–1586. https://doi.org/10.1007/s00344-019-09957-2.

Toupal, J., Vann, D.R., Zhu, C., Gieré, R., 2022. Geochemistry of surface waters around four hard-rock lithium deposits in Central Europe. J. Geochem. Explor. 234 https://doi.org/10.1016/j.gexplo.2021.106937.

VISA, 2021. Estudo de impacte ambiental - Ampliação da Mina do Barroso.

Voica, C., Roba, C., Iordache, A.M., 2021. Lithium levels in food from the Romanian market by inductively coupled plasma – mass spectrometry (ICP-MS): a Pilot study. Anal. Lett. 54 (1–2), 242–254. https://doi.org/10.1080/00032719.2020.1748642.

World Health Organization, 2009. Pharmacological Treatment of Mental Disorders in Primary Health Care. World Health Organization.