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MINING ACTIVITY AND ITS INFLUENCE IN POTATOES AND IRRIGATION WATER FROM NEARBY FARMS

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Abstract

Lithium's importance for electric vehicles and its Critical Raw Material status increased interest in exploring lithium deposits, particularly in Portugal. This study evaluated the C-57 mine's influence on lithium, arsenic, cadmium, thallium and lead levels in irrigation water and potato crops cultivated by the nearby population from farms near (L1) and away from the mine (L2). The results revealed significant differences between L1 and L2 for lithium and arsenic content. L1 presented higher levels of both chemical elements compared to L2. This study highlights the potential impact of active mines rich in lithiniferous resources on the composition of water and potatoes, emphasizing the need for further research.

Keywords: Lithium, mines, potatoes, irrigation water, inorganic contaminants

1. INTRODUCTION

Currently, batteries used in electric vehicles and renewable energy storage play a crucial role in mitigating climate change. With the advancement of the European Green Deal and the United Nations Sustainable Development Goals, global demand for batteries is expected to increase 14 times by 2030. Lithium (Li) is an essential component of these batteries. It is estimated that the European Union (EU) will require up to 18 times more of this element by 2030 and almost 60 times more by 2050 compared to the current supply of the entire EU economy [1], [2].

Li is an alkali metal found in the Earth's crust, discovered in 1817 by Swedish chemist and mineralogist Johan August Arfwedson. It is the 33rd most abundant element in nature and is widely distributed in trace amounts in rocks, soils, and surface and underground waters. Currently, even though it is not considered an essential element for human health, Li stands out in the health sector as it is crucial in the treatment of mental illnesses and, more recently, demonstrated to be highly effective in treating patients with Alzheimer's disease and mild cognitive impairment. On the other hand, excess Li in the body can lead to kidney problems, diabetes, and cardiorespiratory arrest [3].

Li mining is vital to the EU Green Deal and the green transition. Due to the high risk of shortages and its importance for electromobility, Li was included in the list of 30 critical raw materials recognized by the EU in 2020 [2]. In 2019, Chile, Australia, China, the United States, Canada, Brazil, and Portugal were the countries with the largest Li reserves. Li extraction can generally be carried out through brines or open-pit mining. Portugal has the largest Li reserves in Europe [3]. Currently, in Portugal, Li is extracted in mines associated with quartz and feldspar and is used in the ceramics sector [1].

Mining activity is considered necessary to transition to a low-carbon economy, but it has generated controversy due to its impact on the environment and human health. The impacts vary significantly depending on the location, the type of mining activity, the geology, and the ore to be extracted. In Portugal, Li mining occurs mainly through open pit mines, and impacts can include deforestation, reduction of natural water sources, noise pollution and contamination of soil and water.

Mining is recognized as one of the primary sources of environmental heavy metal contamination. Mining operation is an anthropogenic activity that can contaminate soil and water, potentially affecting food cultivated in the surrounding areas [4]. Arsenic (As), cadmium (Cd), thallium (Tl) and lead (Pb) stand out among the heavy metals that can result from mining activities, primarily due to their significant impact on human health. These metals (Cd, Pb) and metalloids (As) are classified by the International Agency for Research on Cancer (IARC) as human carcinogen and integrate the list of the top ten public health major chemicals of concern defined by the Agency for Toxic Substances and Disease Registry of Substances (ATSDR). Due to a lack of evidence, IARC did not classify Tl according to its carcinogenicity. However, Tl is identified as a priority pollutant, which can have serious health effects, including damage to the nervous system, skin problems, and cardiovascular complications [4].

Nevertheless, despite lithium's economic, technological, and energetic relevance, it is important to consider the potential environmental impacts of its extraction and production. As there are no studies on the impact on human health from open-pit Li mining in Portugal, this pioneering study aims to first evaluate the impact of the C-57 Li pegmatite (Guarda district, Portugal) mine on the content of Li, As, Cd, Tl, and Pb in potatoes and irrigation water from surrounding populations.

2. MATERIALS AND METHODS

2.1 Study area

The C-57 mine is located in the district and municipality of Guarda, in the Gonçalo village. This village is situated on one of the northeast slopes of Serra da Estrela, approximately 20 km south of Guarda [1]. This region is part of the Hercynian Massif geotectonic unit, located in the Central Iberian Zone (ZCI), and stands out for the presence of an extensive aplitopegmatite vein field that is rich in rare metal mineralizations, including Li, Sn, Nb, Ta and Be. Within this geological context, the C-57 mining concession, with an area of 0.91 km^2, is part of the aplitopegmatite field known as the Gonçalo-Seixo Amarelo region. The C-57 mining is an open pit with an annual production of approximately 12,000 tons of lithiniferous feldspar [1] [5].

2.2 Sampling plan and sample collection

The sampling plan was established in the surroundings of the C-57 mine and encompassed seventeen subsistence farms (Fig. 1). Nine farms were located at a maximum distance of 1.5 km from the mine (L1 - site near) and eight ranging between 2 to 8.5 km (L2 - site far away from the mine, acting as control). Samples were collected between April and May 2022. Potatoes were collected from three locations in each farm and analyzed as laboratory pools. Irrigation water was also collected on each farm.

2.3 Reagents, chemical standards and equipment

For all analyses, reagents were of high analytical grade, ensuring the highest purity level for the experiments, and samples were analyzed in clean room facilities. 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 multielement IX (As, Be, Cd,Cr(VI), Hg, Ni, Pb, Se, Tl), for ICP-MS in HNO_3, 100 mg/L, SRM/NIST traceable (Merck, Darmstadt, Germany) and a lithium standard TraceCERT for ICP 1000mg/L in HNO_3 (SPC Science, Montreal, Canada) were used to prepared calibration standards for inductively coupled plasma mass spectrometry (ICP-MS) analysis. In addition, internal standard correction for ICP-MS was made by Germanium (Ge), Yttrium (Y), and Indium (In) at a concentration of 1000 mg/L in HNO_3, SRM/NIST traceable (Merck, Darmstadt, Germany).

All analyses were performed using an ICP-MS Thermo X series II (Thermo Fisher Scientific, Germany) with the software Plasmalab database version 3.51.

2.4 Sample preparation

Before analysis, the potato samples were peeled, washed with tap water, dried at 40 °C in an oven until constant mass, and ground. 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 samples underwent a 4-step digestion program using a 48-well heating block (DigiPREP, SCP Science, Courtaboeuf, France). After digestion, the samples were completed up to 25 mL with MilliQ water and kept at 5 ± 3 °C until analysis. Water samples were filtered (0.45 µm) and acidified to 2% (v/v) ultrapure HNO_3 before being analyzed.

2.5 Quality assurance and quality control

Analytical determinations followed the quality assurance program described in the NP EN ISO/IEC 17025 (NP EN ISO/IEC 17025, 2018) standard. Samples were analyzed in triplicate. Each digestion cycle contained at least one blank to control potential contaminations and one spiked sample to check accuracy. The laboratory also regularly participated in proficiency testing schemes launched by an accredited provider with satisfactory results (Table1).

Table 1. Figures of merit

		Li	As	Cd	Tl	Pb
LOD (µg/L)		0.33	0.05	0.02	0.07	0.06
LOQ (µg/L)		1.0	0.17	0.07	0.15	0.20
Working range (µg/L)		1.0 - 10	0.25 - 10	0.25 - 2.50	0.25 - 5.00	0.50 - 5.00
Repeatability (RSD%)		< 10	< 9.0	< 5.0	< 4.0	< 10
Recovery (%)		80 - 114	86 - 106	86 - 107	82 - 117	81 - 117
Uncertainty(1) (%)	**Potato**	26	23	20	22	22
	Water	18	16	16	16	15

(1) Expanded uncertainty (coverage factor of 2)

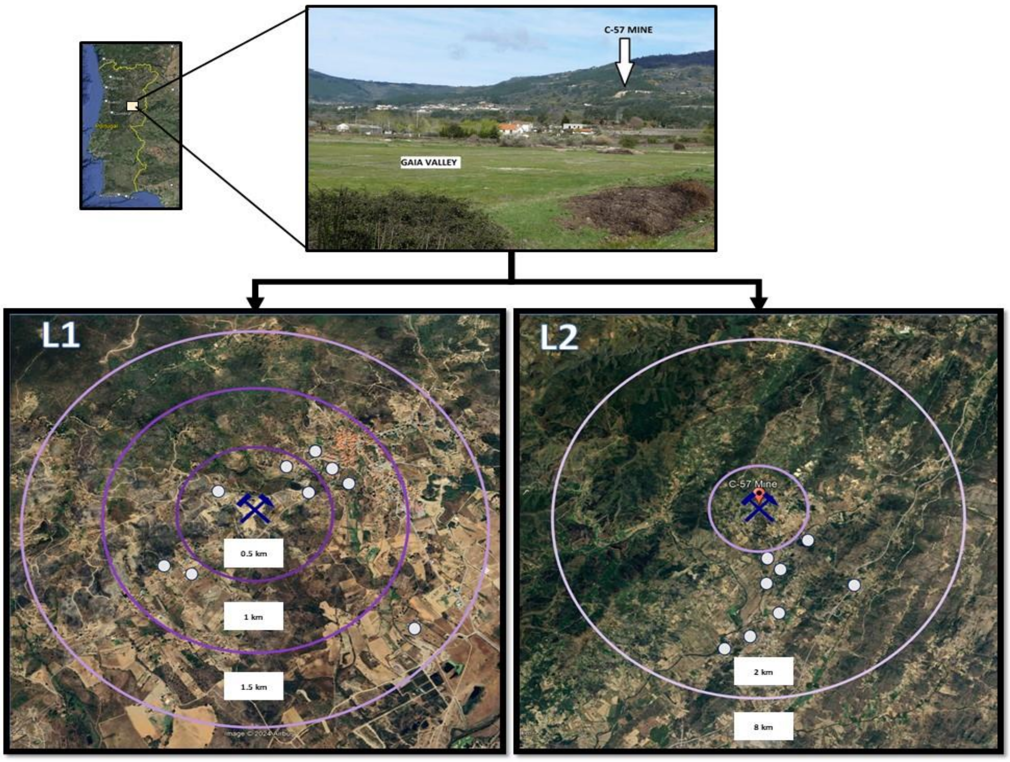

Figure 1. Location of sampling points

2.6 Statistical analysis

Tests were performed using IBM SPSS Statistics version 27. Statistical significance was established at a p-value<0.05 for all analyses.

3. RESULTS AND DISCUSSION

The current study aimed to evaluate the potential impact of Li mining activity by collecting and analyzing potatoes and irrigation water samples collected in farms near (L1) and far (L2) from the C-57 mine (Figure 1).

Irrigation water

The irrigation water collected for this study included wells, holes and springs waters. In all water samples, the Cd, Tl and Pb levels were below the limit of quantification (LOQ), 0.3 µg/L, 0.3 µg/L and 0.5 µg/L, respectively. From the data in Figure 2, significant differences were observed for Li levels between L1 and L2. Li concentrations in the irrigation waters at L1 ranged from 6.1 to 24 µg/L, with an average of 14 ± 5.5 µg/L, whereas at L2, results were lower, ranging from 2.4 to 17 µg/L, with an average of 7.6 ± 4.9 µg/L.

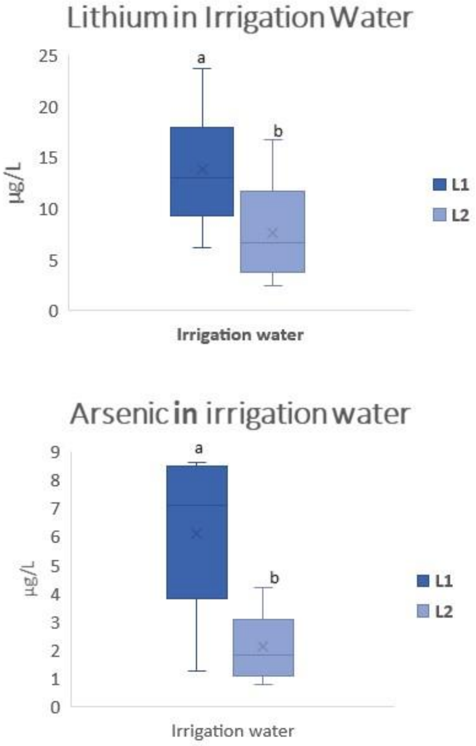

Figure 2. Li and As levels in irrigation water. Significant differences ($p < 0.05$) between sites 1 and 2 are denoted by different lowercase letters.

All samples in this study were below the Li concentrations previously reported for natural waters collected around the C-57 mine (mean = 30.2 µg/L) [1]. Based on the results, all irrigation waters comply with the legal limits for Li levels [6]. The differences in Li levels in irrigation waters between L1 and L2 can be attributed to water/rock interactions, which promotes the weathering of lithiniferous minerals from the bedrock or exposed mine stockpiles, and the release of this trace element into waters.

Differences in As levels between L1 and L2 were also significant. Arsenic concentrations in the waters at L1 ranged from 1.3 to 8.6 µg/L, with an average of 6.1 ± 2.7 µg/L, whereas at L2, levels of this trace element were lower, ranging from 0.8 to 4.2 µg/L, with an average of 2.1 ± 1.2 µg/L. Andrade et al. (2013) reported higher levels of arsenic in waters justifying that those results could be associated with mining areas, either abandoned or active [7]. Furthermore, all water samples exhibited arsenic levels below the legislated threshold for irrigation waters (Maximum Permissible Value: 10 mg/L) [6]. Given that rocks/mineral deposits in the region under study do not present arsenic bearing minerals, it is unlike that the levels of this element have a geogenic origin. Nevertheless, the origin of this element can stem not only from ore processing or waste leaching but also from the application of fertilizers or organic waste. Hence, further research is essential to understand the sources of this element in these regions and to discern the underlying reasons for the disparities observed in the current study.

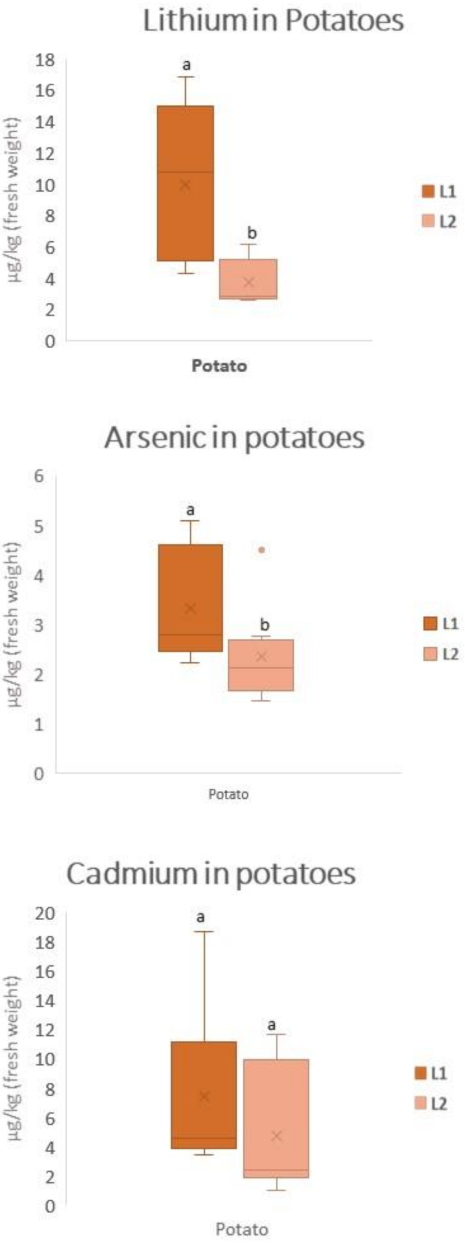

Figure 3. Li, As and Cd levels in potato samples. Significant differences ($p < 0.05$) between sites 1 and 2 are denoted by different lowercase letters.

Potatoes

Thallium and lead contents in potato samples were below the LOQ, 2.3 µg/kg and 4.5 µg/kg, respectively.

Analysis of the results revealed significant differences in Li levels between the two sites (L1 and L2). Results are presented in fresh weight. In L1, Li levels in potato samples varied between 4.3 and 17 µg/kg, with an average of 10 ± 5 µg/kg, while in L2, the values ranged between 2.6 and 6.2 µg/kg, with an average of 3.7 ± 1.4 µg/kg. This difference can indicate a potential influence of local factors on Li absorption and concentration in potatoes. Among these factors, a greater availability of Li in soils close to the mining area is considered, which will have to be confirmed. Comparing the results with the values reported in the French Total Diet Study (TDS), it is observed that these are similar (16 µg/kg of fresh weight) [8]. However, the French TDS reported data for cooked potatoes, whereas the samples in this study were analyzed raw.

Currently, there are no published data on Li retention factors in foods. However, considering other alkali metals from group I of the periodic table, sodium and potassium have retention factors in cooked potatoes of 95 - 100 and 90 - 100, respectively [10]. Assuming similar chemical properties between these elements, a close retention factor could be supposed for Li. However, this hypothesis requires further research.

Significant differences were observed for arsenic between L1 and L2, with average concentrations of 3.3 ± 1.1 µg/kg and 2.4 ± 1.0 µg/kg, respectively. At L2, an outlier stands out which corresponds to the highest arsenic content in the irrigation waters. However, no correlations were identified between the two matrices under study for this element. The As results are in accordance with those reported in the Danish Food database (13 ug/kg of dry matter) [9].

For cadmium, no significant differences were found between the two locations. In L1, concentrations ranged from 3.5 µg/kg to 19 µg/kg, with an average of 7.4 ± 5.5 µg/kg, while in L2, concentrations ranged from 1.0 µg/kg to 11.7 µg/kg, with an average of 4.7 ± 4.4 µg/kg. These results are consistent with those reported by the Danish Food database (21 µg/kg of dry matter) [9]. Additionally, the results from the present study are below the legislation level (0.10 mg/kg fresh weight) [10].

4. CONCLUSIONS

This study aimed to evaluate the potential impact of the C57 mine's proximity on potatoes and irrigation water quality in surrounding areas, shedding light on the relationship between food production and mining activity.

In the present study, all chemical elements remained within permissible limits for irrigation water, with cadmium levels in potatoes found to be below regulatory thresholds.

While the results demonstrate higher levels of lithium and arsenic in irrigation water and potatoes from farms near the C57 mine, it is crucial to understand the intricate interplay between environmental parameters and the bioaccumulation of metals in agricultural products. This underscores the urgent need for further in-depth analysis to advance our understanding of these complex relationships.

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