Lithium concentration and distribution in Portuguese soils

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Abstract

Due to its growing importance in the energetic transition, it is expected that new projects for lithium (Li) exploitation will emerge in Portugal. In that sense, it is crucial to know the background levels of lithium in the soil, to evaluate and monitor any problems caused by anthropogenic activities. The main objective of this study was to present a geochemical map for the background of Li in Portuguese soils.

The available and "total" Li concentration was analyzed in 152 samples and in a subgroup of 55 samples (after aqua regia and triacid digestion, respectively), with the objective of determining relations between them and its environmental importance.

The statistical analysis of the data showed a median concentration of 14 mg/kg for available Li (range between 0.4 and 158 mg Li/kg), and 60 mg/kg for "total" Li (range between 6 and 193 mg Li/kg). From the spatial analysis, it was possible to conclude that the soils with more Li concentration were located in northern Portugal, where areas with known lithium mineralization occurs. Those soils were mostly Cambisols, developed from granitic rocks. The ratio of available *vs* "total" Li concentration revealed that in at least 63 % of the samples, the average concentration of the available Li that can be mobilized and or dispersed into the environment is high (> 43 %).

Keywords: Lithium, Soils, Geochemical Background, Availability, Geochemical mapping

1. Introduction

Geochemical mapping began with the objective of supporting prospection and research of positive anomalies with economical value for mining exploitation (Inácio et al., 2008). However, over time other uses were discovered and its importance in environmental geochemistry is still expanding, mainly because geochemical maps are prepared to provide the distribution of geochemical background data in soils, water, and plants (Gałuszka et al., 2011). By evaluating contamination using the geochemical background of the elements as a baseline, the researchers can better understand the real impact of the anthropogenic influences in the environment. On the other hand, by evaluating contamination through established reference values, parameters such as the local geological context are not taken into consideration which can lead to errors, like recommending soil remediation without it being strictly necessary (Manuel, 2020).

For many years, soils have been studied and mapped worldwide, and so, numerous Geochemical Atlases have been published regarding soil variety around the world. However, portuguese soils were only mapped in projects regarding the whole European continent. To promote a more detailed work, Aveiro's University did, between 1994 and 2000, a low-density sampling project with one sample per 135 km^2 (Inácio et al., 2008). Those samples were studied and analyzed for various soil parameters and elements concentration and but not for lithium.

Due to lithium's increasingly large importance in the energetic transition, the lithium market has had a positive evolution in the latest years, being now considered a CRM (critical raw material) by EU standards (European Comission, 2020). Portugal has some history in the exploitation of lithium, mainly for ceramic and glass industries (Dinis and Horgan, 2017/18), but with the element's rising importance, it is expected that new projects for lithium exploitation emerge with the objective of using it in the form of lithium carbonate to produce the Lithium-ion batteries (LIBs).

Nowadays, there is no reference value for lithium concentration in soils, as the element is not considered a contaminant, but in the expectancy of new mining projects it is crucial to evaluate the background of the element in the soils, to better evaluate possible contaminations. For that reason, the present study was developed with the main objective of determining the available lithium concentrations in Portuguese soils, and to present a geochemical map that provides the distribution of the soil's lithium background.

This study is a continuation of the work developed by Inácio *et al.* (2008), who provided the soil samples.

2. Materials and Methods

2.1. Sample treatment and chemical analysis

For the geochemical map of the available concentrations of lithium in the portuguese soils, 152 samples were provided from a subset chosen to represent the major soil and rock type of the sampling local. Those samples were collected in the A horizon (0-20 cm) of natural soils, located away from sources of pollution as road and factories (Inácio et al., 2008).

Each sample was prepared and extracted in an open system with a mixture of HNO_3 – HCl (1:3), for a total of 8 ml acid used. This method (ISO 11466) is known as aqua regia digestion.

To know the element's interaction with the environment, the "total" concentration of lithium was also analyzed in a group of samples, selected from country zones with known lithium resources. This group of 55 samples was submitted to a mixture of HF – HNO_3–HCl (1:2:3), a method known as triacid or "total" digestion (EPA 3052). For this method, a total of 6 ml of acid was used per sample.

The preparation for both extraction processes is presented in Figure 1. The only difference between the processes is the digestion type and the rehydration in the "total digestion" that was made with a solution of diluted nitric acid (4N).

To complement the research about the lithium behavior in the environment, two samples collected from agricultural soils located in the surroundings of an active pegmatite mine, designed C-57 "Castanho", located in Guarda region, were also analyzed.

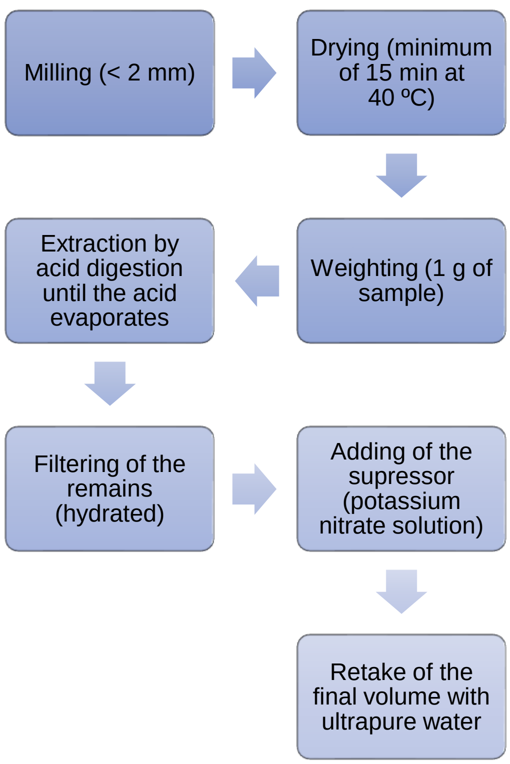

Figure 1 - Schematic representation of soil samples preparation.

The lithium concentration in the soil samples was analyzed by Flame Atomic Absorption Spectroscopy (FAAS) using an AAnalyst 200, PerkinElmer spectrometer, with a wavelength of 670.8 nm.

2.2. Quality control

To provide more precise results, several measures of error control were implemented during the laboratory work, such as:

- analysis of two soils samples with known lithium concentration (previous analyzed at a certificated laboratory) to validate the laboratorial method;
- 10 % of the original samples were analyzed, for both digestions, in duplicate to verify the reproducibility of the method;
- FAAS readings were done from a calibration line with four standard solutions (0, 1, 2 and 4 Li ppm); a blank solution (without soil sample) was made for each extraction method; calibration lines with correlation < 0.995 were always discharged, and
- all the readings that deviated more than 0.1 from the average readings were discarded.

2.3 Statistical analysis and mapping

For both “total” and available lithium concentrations, basic statistical parameters were calculated using the Statistica 13.6.0 software and Microsoft Excel.

To present the maps of lithium concentrations distribution, the Geostatistical Analyst application from ArcGIS 10.4.1 was used. For each digestion method two maps were provided, one with the individual lithium concentration and the other with the spatial distribution, estimated by the ordinary kriging algorithm of the program.

3. Results and Discussion

3.1. Statistical analysis

From the data regarding the lithium concentrations, it was possible to obtain the following statistical results (Table 1, Figure 2, and Figure 3).

In Figure 2, it can be noted that the distribution for the available lithium is asymmetrical. As such, and in conjunction with the differences between the median and the average values, it was considered that the concentrations may follow a log normal distribution. By transforming the data to the logarithmic form, an average of 20 mg Li/kg and a median of 14 mg Li/kg was obtained, which indicates that the assumption made was correct and the available lithium concentration follows a log normal distribution. On the other hand, in Figure 3 the distribution for the “total” lithium follows almost a normal distribution, with little asymmetry.

Table 1 – Statistical parameters (mg/kg) obtained for aqua regia (AR) and "total" (T) digestion.

	Average (mg/kg)	**St. Dev. (mg/kg)**	**Median (mg/kg)**	**Range (mg/kg)**	**P25 (mg/kg)**	**P75 (mg/kg)**
AR	20.13	23.22	13.99	0.4 – 157.82	3.35	28.45
T	66.40	37.32	59.62	6.34 – 193.23	41.13	80.50

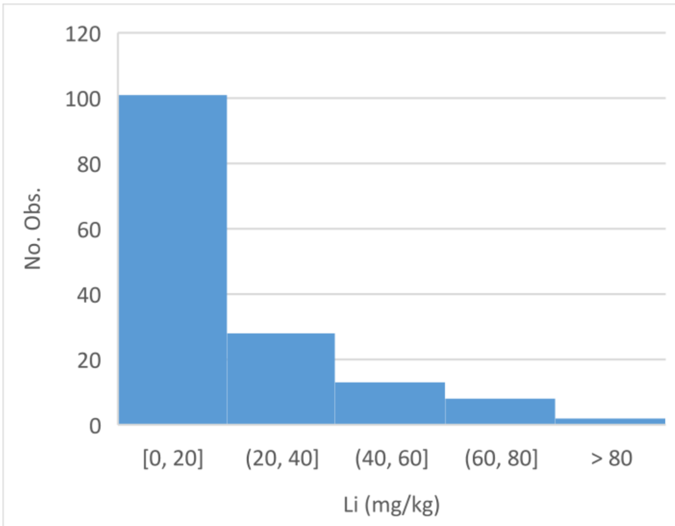

Figure 2 – Histogram for the available lithium concentration distribution.

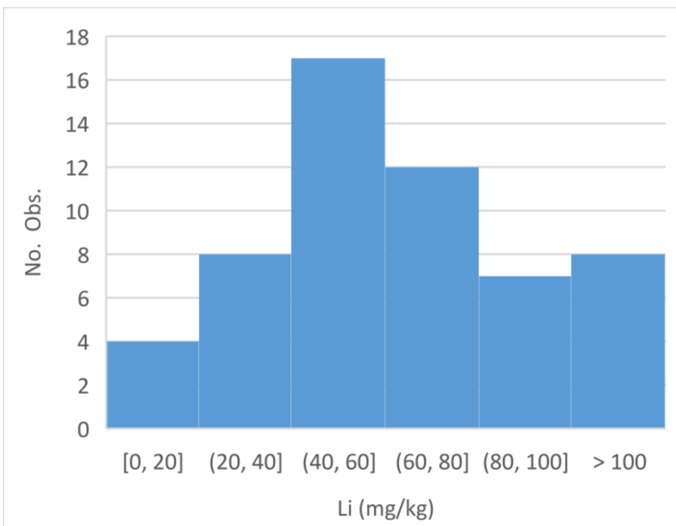

Figure 3 – Histogram for "total" lithium concentration distribution.

3.2 Spatial analysis

As stated previously, to evaluate the spatial distributions of the lithium concentrations determined in the soil samples, two types of geochemical maps were presented.

Figures 4 (a) and (b) show the distribution of the available lithium concentrations using two different approaches. Figure 4 (a) presents the individual spatial distribution of the available lithium concentrations, and figure (b) presents the mapping of the estimated available lithium concentrations. Even though individual concentration distribution maps are more accurate, since these only show the concentration obtained at a determined location, to illustrate the background of an element at a relatively extended area the estimation maps become an attractive option. Doing this, the error of prediction can be minimized by: a) employing a careful sampling procedure that reflects the main geology and soils of the area, and b) choosing geostatistical methods of estimation that allows more input.

In Figure 4 (a), it is possible to verify that the most frequent class (with 45 % of the samples) had the lower concentrations (< 10 mg Li/kg). However, the higher contents (> 76 mg Li/kg) represent only 10 % of the samples, which justify the histogram distribution present in Figure 2. By comparing the maps representing the distribution of available lithium (Figures 4 (a) and (b)) with the national geological environment, the principal pedological units and soil pH distribution maps (not presented), it was observed that the majority of the samples with higher content (> 76 mg Li/kg) were linked to Cambisols, located in areas with acid soils and plutonic parent rocks. On the other hand, most of the samples with lower lithium content (< 10 mg Li/kg) were associated with Podzols and Luvisols, and areas with sedimentary detrital formations.

Figures 5 (a) and (b) show the spatial individual distribution of “total” lithium concentrations. As the area is mostly dominated by Cambisols, the trend is not as marked as in the previous case. However, it is possible to verify that the samples with higher content follow the same trend as the distribution of available lithium concentrations. Analyzing Figure 5 (a), the map is mostly composed by the middle grades (26 – 87 mg Li/kg) that represent at least 69 % of the samples, which is expected since in this map only samples from northern Portugal were analyzed, which is an area with known lithium mineralizations.

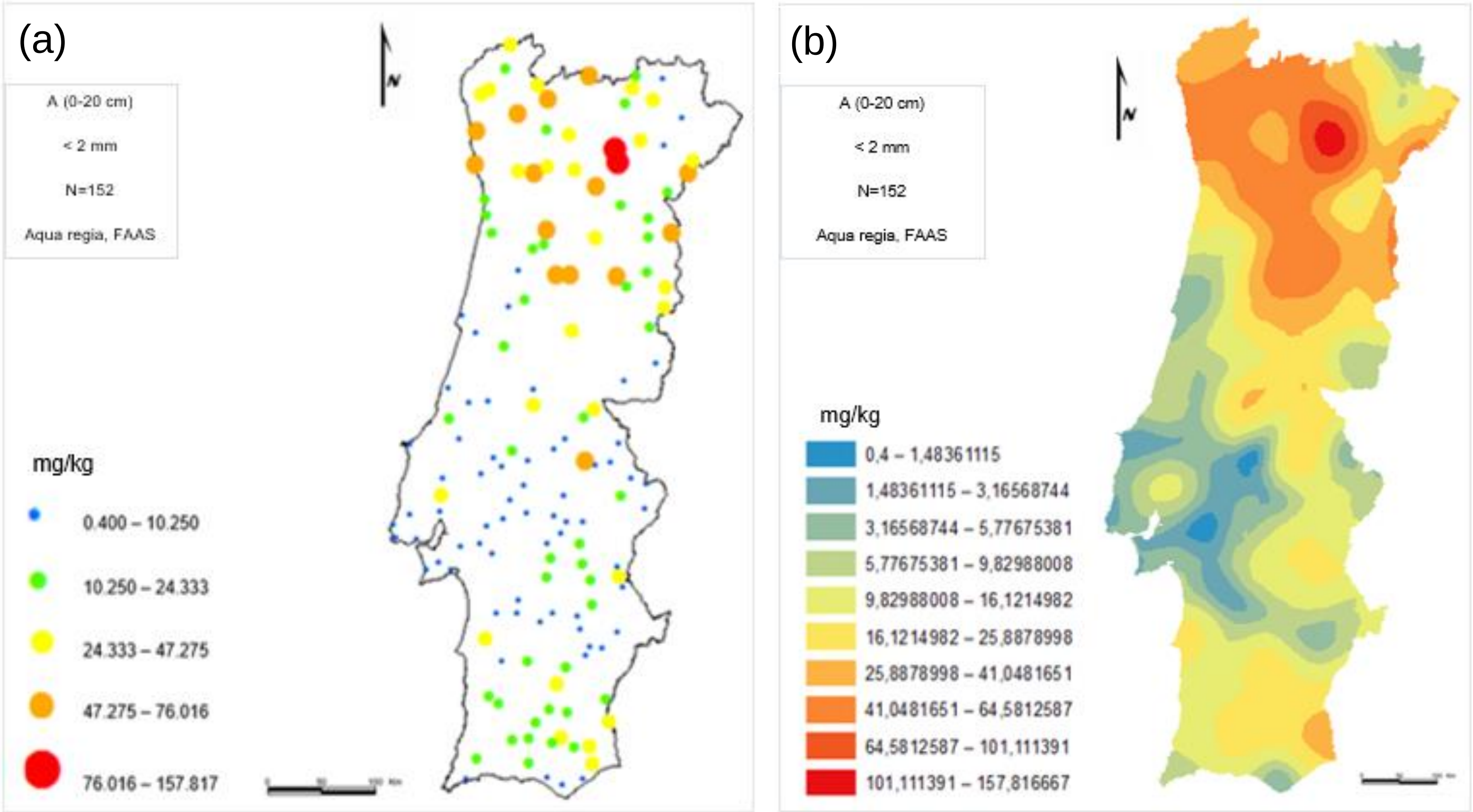

Figure 4 (a) – Available lithium individual distribution and (b) lithium available estimated distribution maps.

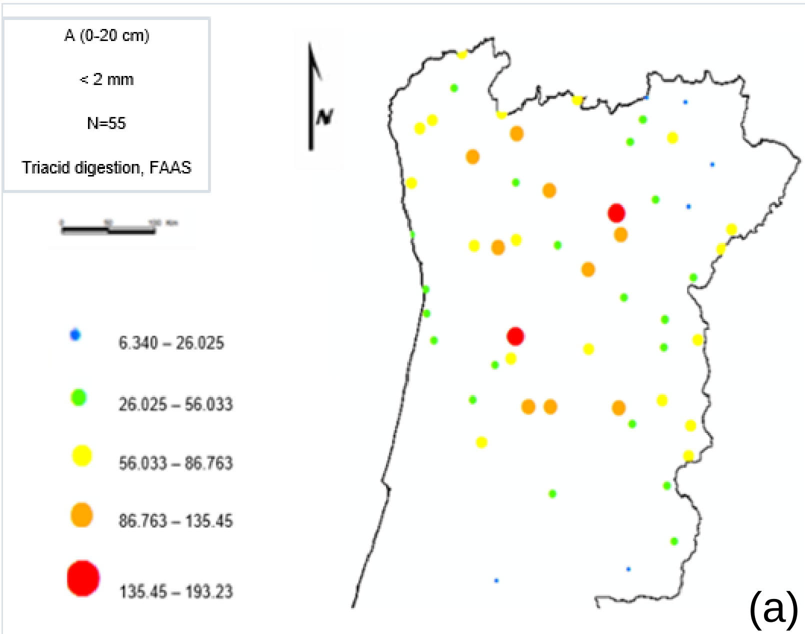

Figure 5 (a) – “Total” lithium distribution map.

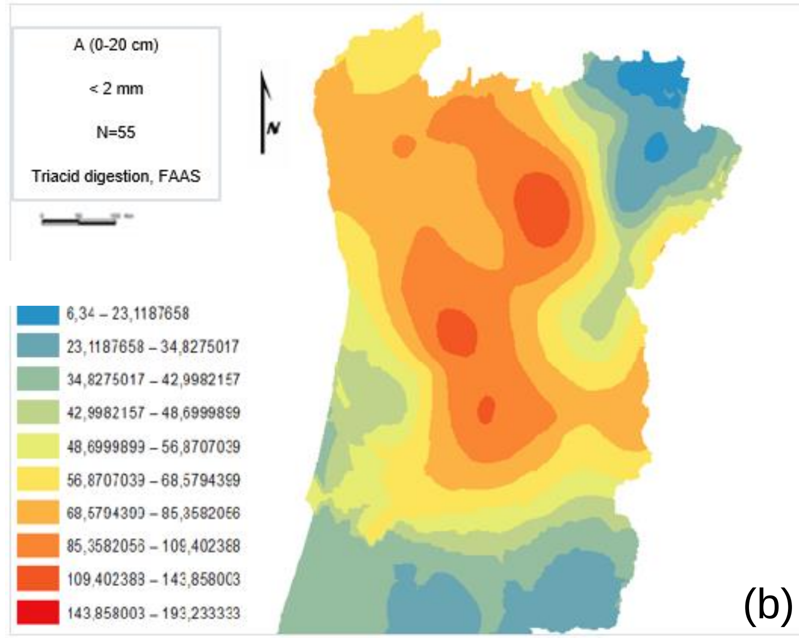

Figure 5 (b) – “Total” lithium estimated distribution map.

The relation between “total” and available lithium concentrations, shown that there is some trend for the samples with higher “total” concentrations also having a higher percentage of lithium available. In fact, at least 63 % of the samples have an available lithium percentage higher than 43 %, which may indicate that a high element fraction can be mobilized by the circulating waters or be adsorbed by the soil colloidal complex.

The environmental importance of this data comes from the fact that aqua regia digestion extracts concentrations like those that can be more easily released into the environment (Gaudino et al., 2007). For this reason, the concentrations obtained by this method should be the ones used to evaluate future local soil lithium enrichments from anthropogenic activities.

In order to analyze the impact of lithium mining exploitation in soils, two samples collected from agricultural soils in the surroundings of C-57 “Castanho” mine (Guarda region) were analyzed for its lithium concentration and compared with the levels obtained from the present study, regarding the samples collected in Guarda’s area of interest for lithium exploitation. The differences between the “total” levels in both types of samples indicated that mining area leads to an enrichment of “total” lithium content. The agricultural soils presented concentrations of 450 and 630 Li mg/kg and in the non-disturbed Guarda´ soils, it was observed an average concentration of 91 Li mg/kg. However, it was not possible to make considerations about the mining area influence in the available lithium content due to the presence of horticultural crops at the time of soil sampling.

4. Conclusions

The analysis in soil samples of the available and “total” lithium concentration, allowed to present the geochemical background maps for the element’s distribution on mainland Portugal’s soils, and to observe the trends with the geological environment, soil unit types and pH as well as evaluate correlations between lithium and other elements.

A median background of 14 mg/kg was obtained for the available lithium concentrations, with the concentrations following a log normal distribution. For the “total” concentrations, a median background of 60 mg Li/kg was calculated. It was possible to verify that, as expected, the higher levels (> 76 mg Li/kg) were found in the northern part of the country, associated to Cambisols in areas of acid soils related to plutonic rocks. The lower concentrations (< 10 mg Li/kg) were associated with Podzols and Luvisols, in areas of sedimentary detrital formations.

In at least 63 % of the soil samples, there was a positive trend between the soil samples with the higher “total” and available lithium concentrations, showing that the average concentration of the available lithium that can be mobilized and or dispersed into the environment is high (> 43 %). From the study of agricultural soil samples collected in the surroundings of an active lithium mine (C-57), it was possible to verify that mining area influenced greatly the “total” lithium concentration at the local soils.

For future studies, it is suggested that the soil samples should be analyzed for pH, texture, cation exchange capacity and humified organic matter to understand if there is any correlation between these parameters and the soil lithium´s concentration.

Some further studies are also suggested, an increasing of the sampling that should include more soils from each of the areas of interest for lithium exploitation, providing a more complete set of data for the lithium background concentrations at these areas.

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