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STATISTICAL ANALYSIS OF Li CONCENTRATION AND THE $^{6}Li/^{7}Li$ ISOTOPIC RATIO FROM SPECIFIC PROVENANCE ENVIRONMENTS

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Abstract:

Starting from the necessity of a geospatial footprint existence of mineral waters in Romania, this study followed lithium concentration distribution and the $^{6}Li/^{7}Li$ isotopic ratio using the ICP-MS technique. Stable isotopes are potent tracers of chemical and biological transformations in natural environments. Lithium is commonly found as a dissolved species in groundwater and surface water, making this valuable metal a conservative tracer in hydrogeological studies. This study followed the geographical distribution of lithium concentrations and the $^{6}Li/^{7}Li$ isotopic ratio, considering the comparative characterization of Romanian waters (from different geographical regions) and foreign waters sold on the Romanian market and independent food stores. The determination of the median values was based on the bootstrap method, which allowed the identification of high values of the standard errors in the case of Li concentration in the approved waters and the organic material. In the case of the isotopic ratio, the highest value is found in foreign waters. The waters of Southern Muntenia presented significantly different values compared to all other regions, having the lowest concentration of Li (0.44 µg/L) but having the highest isotopic ratio (0.10). The waters of the S-W Oltenia and Central Transylvania regions have the highest concentrations of Li, respectively 10.45 µg/L and 10.03 µg/L, much lower than the values of the other regions. Also, the organic material shows a degree of Li concentration dispersion but the slightest variation in the isotopic ratio. The involvement in human health of Li exposure is needed for further investigation even if no regulation on the safe limits of Li in drinking water for humans is addressed.

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1. INTRODUCTION

Lithium (from the Greek “lithos”, for stone) is the first metal in the periodic table, included as 1 of 16 essential elements. It is the lightest metal in its elemental form and highly reactive as a pure element, so, as a result of this reactivity, it does not occur naturally but occurs only in stable minerals and salts [Kszos L.A. and Stewart A.J., 2003].

Sustained technological advances in the chemical industry have created several prospects for using lithium in a variety of applications; it is one of the most essential metals in the energy industry, being used for energy storage (batteries) for electronic equipment and instruments and the transition to renewable energy due to its high reactivity [Abdollahzadeh M. et al., 2022; Bakhtiarvand B. et al., 2021; Ding Y. et al., 2019]. Lithium has other uses, for example, in the production of glass and ceramics, in the lubricants industry due to its ability to withstand high temperatures, in the construction of space vehicles and airplanes due to the properties of this metal to be light and resistant to heat [U.S. Geological Survey, 2021].

There is a high demand for lithium, and the market it has increased very much (700 times higher in the last decade), one of the reasons being the development of lithium as a battery for electric power vehicle propulsion [Guo X. et al., 2021; Cardoso-Fernandes J. et al., 2020; Yokoi R. et al., 2021; Ni’mah Y.L. et al., 2022]. The very high demand gave birth to a race to identify new sources of lithium, its exploitation being a solution to combat global warming. Mining companies "hunt" for lithium in the most isolated corners of the world, from Tibet to South America. The leading producer of lithium from brine is Chile, and from pegmatites is Australia, but the lithium potential of Bolivia is also known, and in Europe of Portugal. Exploration for lithium deposits is not as intense as for other metallic resources (Au), so economically viable lithium deposits will likely remain to be discovered. However, its extraction comes with high environmental costs, being a very corrosive and flammable metal (polluted water, contaminated soil, lack of animal life, etc.). It is extracted from brines pumped from arid sedimentary basins and granitic pegmatite ores. Worldwide lithium resources are estimated to be more than 39 million metric tons, enough to meet projected demand by 2100 [Bradley D.C. et al., 2017]. Lithium-ion battery recycling is expected to play a significant role in the medium to long-term lithium supply.

There are more and more concerns related to the distribution of lithium in the environment. However, the existence of this metal in the terrestrial food chain still raises questions, not knowing how it affects the living biota. Environmental lithium can be derived from natural and anthropogenic sources [Bradley D.C. et al., 2017]. Lithium is commonly found in volcanic rocks, mineral sources, clays, geothermal brines, oilfield brines, and zeolites. The concentrations in those resources are varied, so effective and efficient methods to evaluate the lithium deposition in the rock and in the alternative resources are required [Rohiman A. et al., 2023]. Potential anthropogenic lithium sources include mine wastes and a wide range of manufactured products after disposal.

Being a highly soluble element, lithium is commonly found as a dissolved species in both groundwater and surface water, which makes this valuable metal as a conservative tracer in hydrogeological studies [Bencala K.E. et al., 1990]. There are differences between the lithium contents of sediments in hydrologically open (0-150 mg/kg) and closed basins (30-2000 mg/kg), these differences are owing to hydrological flow patterns. In soils, lithium is found in authigenic minerals, and the organic fraction and its profile can be poorer in higher layers than in lower layers, being leached by weathering solutions and being able to be incorporated into underlying clay minerals [Ribas B., 1991; Schrauzer G.N., 2002]. At the global level, lithium concentration in agricultural soil is <10-300 mg/kg. However, the pollution level is unknown, especially since there are no regulatory standards for Li in different environmental compartments. Li in water fluctuates with natural and anthropogenic activities. Thus, Li quantification and risk assessment are essential

for a sustainable society. Seawater contains approximately 0.17 mg/L. Rivers generally contain only 3 µg/L, whereas mineral water contains 0.05-1 mg/L [Lenntech, 2007]. The concentration of Li in waters is highly variable depending on its geographical location, for example, 220 µg/L (the North Atlantic Sea); 1173 µg/L (the Pacific Ocean); 160 µg/L (the Indian Ocean) [Adeel M., et al., 2023]; 0.87 µg/L (Yellow River, China) [Gou L.-F. et al., 2019]; 2.2 µg/L (Amazon River) [Dellinger M., et al., 2015]; 16.5-1790 µg/L (groundwater from China) [Chen L. et al., 2020]; 300 µg/L (groundwater from Pakistan) [Khalid S. et al., 2020]. Plants assimilate lithium, typically in the 0.2 to 30 mg/kg [Aral H. and Vecchio-Sadus A., 2008]. It was demonstrated that native plants grown in arid basins absorb more lithium than those in more humid regions, with a much greater uptake of lithium by plants in acid soils, as acidity increases the solubility of metals [Schrauzer G.N., 2002; Lenntech, 2007].

Precise techniques for identifying lithium are critical to fulfill the worldwide demand for lithium. Progress has been made in this regard by many researchers using different methods for lithium detection in geological exploration, environmental, and medical domains: a) classic lithium analysis technique (gravimetry [Jeffery G.H., et al., 1989]; titrimetric [Zhai J. et al., 2017]; flame test [Svehla G., 1997]; colorimetric [Komatsu T. et al., 2020]; b) modern analysis techniques: (spectrochemical approaches: stationary instrumentation (XRD [Pollmann H. and Uwe K. 2021; Mubarok M.Z. et al., 2021], ICP-OES [Lurenbaum C., et all. 2020], ICP-MS [Voica C. et all., 2021]; thermal ionization ion mobility spectrometry [Parchami R. et al., 2020]), spectrophotochemical-based sensors [Cardoso-Fernandes J. et al. 2019; Villemin E. and Raccurt O., 2021]; analysis by electrochemical approaches [Wang Q. et al., 2021; Kushwaha A.K., et al., 2017; Suherman A.L., et al., 2019; Criscuolo F., et al., 2018; Lindino C.A., et al., 2012].

The lithium research has much expanded there are growing numbers of lithium-related scholarly papers, the greatest increase being in 2020, with 252 publications, representing an increase over the previous years (2021 - 239 publications, 2022 - 236 publications). The United States ranks first as a country that intensively researches lithium, followed by Germany, France (Center National de la Recherche Scientifique was the first research institution to research lithium), and China [Rohiman A. et al., 2023].

Stable isotopes are powerful tracers of chemical and biological transformations in natural environments. Stable isotope measurements are used extensively in geoscientific, ecological, chemical, and archaeological research for studies of the biosphere, atmosphere and oceans, food web, dietary and metabolic studies, studies of molecular and biomolecular reactions, environmental chemistry and monitoring, human nutritional studies [Davies P.S.W., 2020]. Applying stable isotope analyses in these ways can lead to solutions that will help mitigate future ecosystem damage, environmental degradation, and the so-called ‘‘ecological forensics'' [Dawson T.E. and Siegwolf R.T.W., 2007]. More recently, isotopes from trace, non-nutrient elements, and toxic are considered essential to discriminate sources, bioaccumulation, and trophic transfers [McCormack J. et al., 2022; Queipo-Abad S. et al., 2022]. Stable isotopes of trace metals are emergently used for studying pollution effects, physiological investigations, species ecology, and biogeochemical cycles [Araújo D. et al., 2022; Blum J.D. et al., 2013; Bonsignore M. et al., 2020; Manceau A. et al., 2021; Renedo M. et al., 2021].

Non-conventional stable isotopes have received increasing attention in the past decade, in this regard, there is a growing interest in lithium isotope studies [Thibon F. et al., 2023]. Lithium has two naturally occurring isotopes, one heavy (^{7}Li, 92.41% abundance) and one light (^{6}Li, 7.59% abundance). The two stable isotopes of lithium have a large mass difference (~16%), resulting in a sizeable mass-dependent fractionation factor, which provides a potential for applying these isotopes as geochemical tracers [Misra S. and Froelich P.N., 2009]. Geochemistry of these isotopes has the potential to reveal important information concerning a wide range of processes, for example, riverine geochemistry, hydrothermal activity and alteration of the oceanic crust, and riverine variability [Maffre P. et al., 2019; James R.H. and Palmer M.R., 2000; Chan, L.H. et al., 2002].

The development of micro-analytical tools for analyzing stable isotopes began in the late 1980s and continues today, with the precision of the analyses improving. It has used two different techniques to extract and analyze samples: laser ablation followed by gas-source isotope ratio mass spectrometry or inductively-coupled-plasma mass spectrometry (ICP-MS, including triple quadrupole ICP-MS—ICP-Q-MS), and secondary ion mass spectrometry (SIMS) utilizing a focused ion beam of oxygen or cesium [Huston D.L. et al., 2023]. Accurate determination of lithium isotope ratios remains an analytical challenge because fractionation based on laboratory processing results in a significant and unreproducible offset from the true value. Determination of the $^{6}Li/^{7}Li$ ratio by inductively coupled plasma mass spectrometry (ICP-MS) suffers from high mass bias and is highly sensitive to possible matrix contamination [Juzer S. et al., 2022].

Starting from the necessity of a geospatial footprint of mineral waters in Romania, this study followed the distribution of lithium and the $^{6}Li/^{7}Li$ isotopic ratio, using alternative methods of analysis that are not frequently used.

2. MATERIALS AND METHODS

2.1. Sampling

Water is one of the most essential components of life, a natural resource vital for the survival of humanity and all species on earth [Quattrini S. et al., 2016]. The importance of water in our diet is apparent; it is involved in many body functions, carries nutrients and substances in the circulatory system, and helps the body perform specific metabolic tasks. 78 sources of mineral water are recognized in Romania, according to Order no 116/2023 [Government of Romania and Ministry of Regional Development and Public Administration. Order no 116/2023], which are marketed under 51 brands.

This study, 96 water samples were characterized, including 53 bottled samples corresponding to 44 brands, 35 spring water samples, and eight river samples. Besides these, organic material (moss, spruce needles) from the specific areas of the river waters was also analyzed. All the bottled waters commercially available in the Romania market were purchased from local supermarkets and independent food stores. These water samples were divided into two groups: approved mineral waters (which fall into the category of recognized waters, according to Order 116/2023) and mineral waters that are not highlighted in the mentioned legislation but are on the market (named non-approved). As a result, mineral water sources from 16 counties out of the 42 existing in the country and 29 brands were taken into account as approved waters, and 12 samples of marketed waters from three counties (Cluj, Ilfov, and Sibiu) as non-approved waters (Table 1).

Table 1. Sampling location by geographic distribution

Samples	Center[1]	NE[2]	NW[3]	W[4]	S[5] (Muntenia)	SW[6] (Oltenia)	Foreign countries[7]	Total
Approved waters	13	10	1	2	3	-	-	29
Non-approved waters	2	1	2	1	6	-	-	12
River waters	-	3	5	-	-	-	-	8
Spring waters	7	-	18	2	-	8	-	35
Foreign waters	-	-	-	-	-	-	12	12
Organic material	-	6	2	-	-	-	-	8
Total	22	20	28	5	9	8	12	104

[1] Center (Transylvania) Ardeal: Alba, Braşov, Covasna, Harghita, Mureş, Sibiu; [2] NE Moldova: Bacău, Botoşani, Iaşi, Neamț, Suceava, Vaslui;
[3] NW Transylvania: Bihor, Bistrița-Năsăud, Cluj, Maramureş, Satu Mare, Sălaj; [4] W Transilvaniat: Arad, Caraş-Severin, Hunedoara, Timiş;
[5] S (Muntenia: Argeş, Călăraşi, Dâmbovița, Giurgiu, Ialomița, Prahova, Teleorman, Ilfov; [6] SW (Oltenia): Dolj, Gorj, Mehedinți, Olt, Vâlcea
[7] Foreign countries: Austria, Bulgaria, Fiji, Franța, Germania, Italia, Ungaria.

The samples' distribution according to their origin source is shown in Figure 1. Over 50% of the samples come from the waters from the Romanian market (28% approved waters, 12% each from non-approved waters and foreign waters), and over a third comes from spring waters. Equally, about 16% comes from organic material and river water.

The distribution of the samples according to the geographical criterion is shown in Figure 2. The main regions that have a high share are the North West Transylvania region (27%), the Central Transylvania region (21%), and the North East Moldova region (19%).

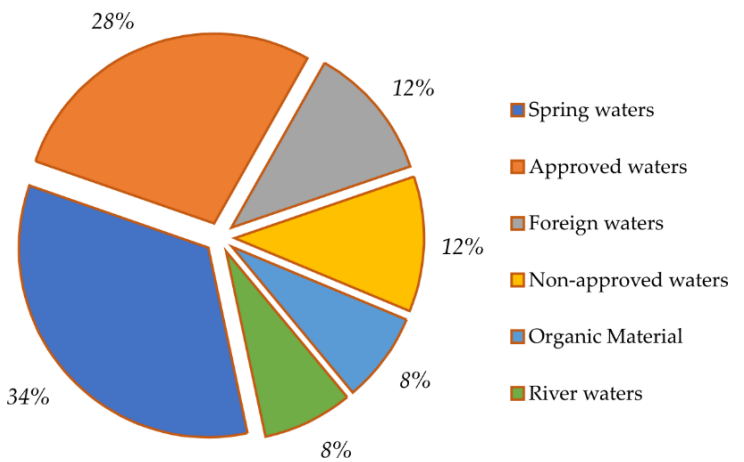


Figure 1. Sample distribution by sample source

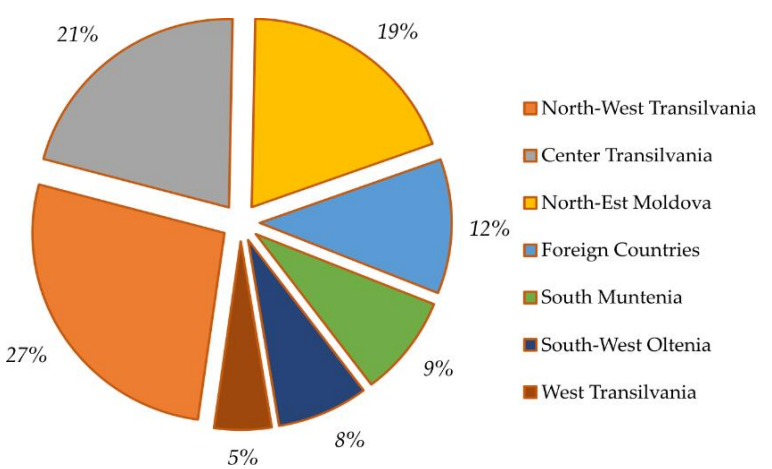


Figure 2. Distribution of samples by geographic criterion

2.2. Sample preparation

Drinking water was mineralized with 1% HNO_3 solution. The other studied samples were subjected to microwave-assisted nitric acid digestion using a closed iPrep vessel speed system MARS6 CEM One Touch. The digestion vessels were cleaned with 10mL HNO_3 using the microwave cleaning program and rinsed with deionized water.

The water samples (river and spring) (45 mL + 5 mL HNO_3 69%) were digested according to the digestion program from US EPA method 3015 A. Organic material samples (~0.5 g of dry

sample + 10 mL of HNO_3 69%) were digested according to the digestion program in the Animal Tissue/Dry/Plant Tissue CEM Mars 6 Method Compendium Note 2019). After the complete digestion and cooling, the samples were filtered, transferred to 50 mL graduated polypropylene tubes, and diluted to volume with deionized water.

2.3. Analytical measurements

2.3.1. ICP-MS for lithium concentration

Inductively coupled plasma mass spectrometry was used to determine lithium concentrations. A Perkin Elmer ELAN DRC (e) instrument was used for lithium in studied samples. The analysis was performed in standard mode using argon gas (purity 4.8) for the plasma following the manufacturer's recommendations. Ultra-pure deionized water (resistivity of 18 $\Omega \cdot cm^{-1}$) from a Milli-Q analytical reagent grade water purification system (Millipore) was used.

The operational conditions were optimized using a tuning solution (Elan 6100 Setup/Stab/ MassCal Solution 10 µg/L Ba, Cd, Ce, Cu, In, Mg, Pb, Rh, U, from Perkin Elmer). The optimal conditions were as follows: nebulizer argon flow rate 15 L/min.; Lens voltage 7.25V; Radiofrequency power 1100 W; sample uptake flow rate 1 L/min; CeO/Ce ratio 0.028; and Ba^{++}/Ba ratio 0.030.

A multielement calibration standard from Perkin Elmer (10.0 µg/mL of 29 elements, including Li, in 5% nitric acid) was employed to prepare the calibration curve for the quantitative analysis. The analytical method for assessing elements in studied samples was validated by measuring several quality parameters, such as sensitivity, linearity, precision, accuracy, and recovery. Linearity was established using calibration solution calibration curves, and the instrument's sensitivity was estimated by determining detection limits for all elements studied. The limit of detection (LOD) and limits of quantification (LOQ) were calculated by three and ten times the standard deviation of the blank sample divided by the slope of the analytical curve, respectively. The performance parameters were: correlation coefficient (R) -0.9999; LOD- 0.001 µg/L; LOQ - 0.01 µg/L; relative standard deviation <0.5%.

2.3.2. ICP-MS for lithium isotope ratio

A Plasma Quant Elite instrument (Analytik Jena, Germany) was used for lithium isotope ratio determination. The plasma analysis was performed using argon gas (purity 6.0) following the manufacturer's recommendations. Ultra-pure deionized water (conductivity of 0.055 ⌾S/cm) from a Purelab Flex 3 ELGA purification system (ELGA, Veolia Water, UK Ltd) was used.

The optimal instrumental parameters were nebulizer argon flow rate - 1.01 L/min and plasma gas flow - 9.0 L/min.; auxiliary gas flow - 1.50 L/min.; Radiofrequency power - 1.28 kW; Lens voltage: 53 V (left mirror lens), 44 V (right mirror lens), 33 V (mirror lens down). Data acquisition parameters for quantitative mode were: measurement mode - peak hopping; scan/replicas - 500; integration time - 152.26 s.

A certified reference material, LSVEC (Li-carbonate) Reference Material for Li-isotope ratio, IAEA, Vienna, with the following value for the isotopic ratio of lithium, was used for calibration: $^{6}Li/^{7}Li = 0.08215 \pm 0.00023$ (the reported uncertainty is calculated using an expansion factor of k=2, which corresponds to a confidence level of approximately 95%). Performance parameters were: standard deviation-0.0040; accuracy (%) 0.545; precision (%) 0.450.

2.4. Statistical analysis

After processing and validating the resulting data, the statistical description of the resulting distributions was carried out. In this sense, the indicators that express the central tendency (mean, median, and quartiles), as well as the indicators that express the degree of dispersion expressed by the standard deviation, were used for the statistical description, the inter-quartile deviation and the coefficient of variation and the relative amplitude of the variation. Also, the statistical description of the distributions was completed with graphic representations, which highlighted what was found through the previously mentioned statistical indicators listed. Shapiro-Wilk, Anderson-Darling, Lilliefors, and Jarque-Bera statistical tests were used to test normality. Tests were interpreted in comparative p-values with a significance threshold of 0.05. After the application of the normality tests, it was found that the analyzed distributions were different from the normal distribution, and as a result of this fact, in the subsequent comparisons, the median was used as an indicator of the central tendency and to test the statistical differences, the non-parametric Kruskal-Wallis and the Mann-Whiteny test. In the case of the Mann-Whitney test, the p-values were corrected with the Bonferroni correction. Moreover, all highlighted aspects are detailed in the body of the article.

3. RESULTS AND DISCUSSIONS

The distribution of the lithium concentration is relatively more homogeneous from the point of view of the source of provenance of the samples than from the geographical point of view (Figure 3).

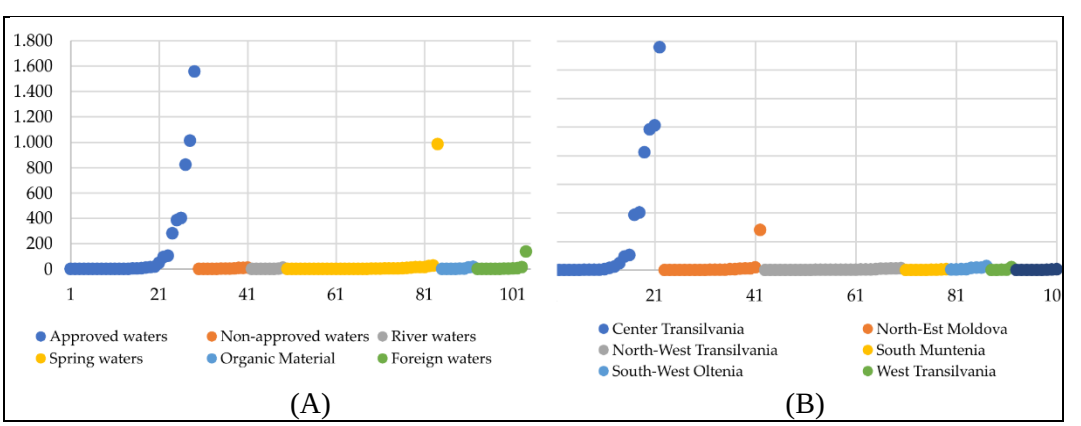


Figure 3. Distribution of lithium concentrations by geographic criterion (A) and sample provenance (B)

The distribution of the $^{6}Li/^{7}Li$ ratio according to the provenance of the samples suggests a relatively homogeneous dynamic compared to the geographic distribution, which is rather inhomogeneous (Figure 4).

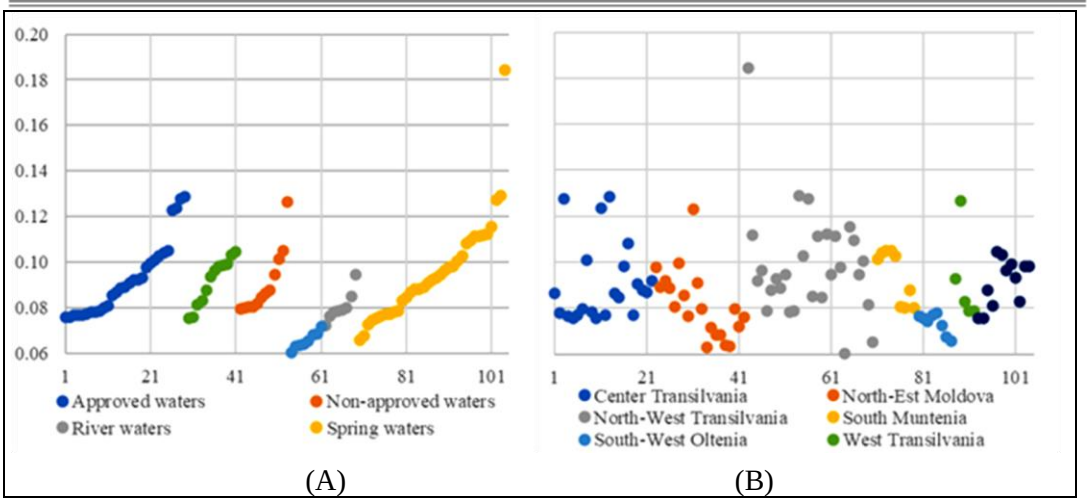


Figure 4. Distribution of $^{6}Li/^{7}Li$ ratio by geographic criterion (A) and sample provenance (B)

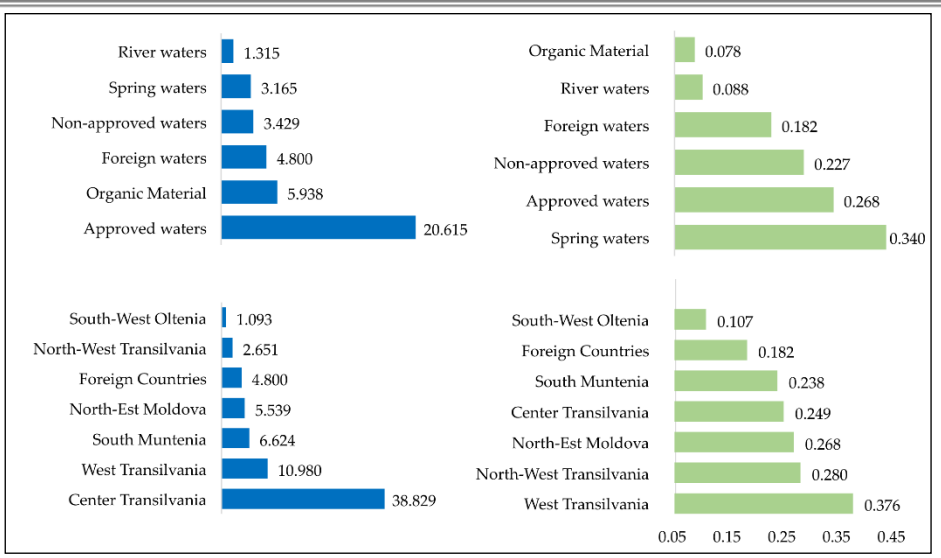
The statistical description of lithium concentration and isotopic ratio of studied samples is presented in Table 2.

Table 2. Statistical description of lithium samples and isotopic ratio

Nr. crt	Statistic	Li concentration	$^{6}Li/^{7}Li$ ratio
1	Nr. of observations	104	104
2	Minimum	0.0168*	0.0604
3	Maximum	1,557.2690*	0.1844
4	1st Quartile	0.5237	0.0777
5	Median	1.8430	0.0872
6	3rd Quartile	8.8244	0.0993
7	Mean	59.73	0.0902
8	Variance (n-1)	50,081.17	0.0003
9	Standard deviation (n-1)	223.78	0.0185
10	*Interquartile range*	4.50	0.2473
11	*The coefficient of variation*	3.74	0.2053
12	*Relative amplitude of variation*	26.06	1.3742

*µg/L

This study followed the geographical distribution of lithium concentrations and the Li^{6}/Li^{7} isotopic ratio, considering the comparative characterization of Romanian waters (from different geographical regions) and foreign waters on the Romanian market. It was noted that the two analyzed variables are different regarding the distribution of the recorded values (Figure 5). Lithium presents a larger interquartile range compared to that recorded by the isotopic ratio, and the coefficient of variation is very high, which indicates a high heterogeneity of the distribution of values related to lithium. If, in the case of lithium, there was a heterogeneous distribution of information, in the case of the isotopic ratio, the data are relatively homogeneous.



(A) (B)

Figure 5. Dynamics of the quartile interval of the lithium concentration (A) and the $^{6}Li/^{7}Li$ isotopic ratio (B) of the samples according to the provenance and geographical dispersion of the samples

The condition of normality is an important aspect of the statistical analysis of the distribution of values both for lithium and for the $^{6}Li/^{7}Li$ ratio, which is why specific statistical normality tests were used. If the p-values show values higher than the threshold of 0.05, then it can be said that the recorded values are normally distributed (normality condition – hypothesis H0) and, thus, parametric tests can be used (t-tests, correlation, ANOVA, regression, etc.). The arithmetic means for the various specific statistical analyses and comparisons. If the condition of normality is not met (hypothesis H1), the P-value presents values lower than the 0.05 threshold and it is recommended to use non-parametric tests (Mann-Whitney test, Kruskall-Wallis test, etc.) and use the median as an indicator which expresses the central tendency of evolution. Table 3 shows the results of these tests.

Table 3. Normality tests for the distribution of values for lithium and $^{6}Li/^{7}Li$ ratio

Variable\Test	Shapiro-Wilk	Anderson-Darling	Lilliefors	Jarque-Bera
Li concentration	<0.0001	<0.0001	<0.0001	<0.0001
$^{6}Li/^{7}Li$ ratio	<0.0001	<0.0001	0.023	<0.0001

The p-values are lower than the 0.05 threshold, which shows us that the values recorded for lithium and the ratio $^{6}Li/^{7}Li$ are not normally distributed, or in other words, the values recorded for the 104 samples differ significantly from the normal distribution. The elimination of outliers did not lead to the normalization of either the series of lithium-specific values or the $^{6}Li/^{7}Li$ ratio values. The median and non-parametric tests will be used in the various analyses and specific statistical comparisons.

To see if there are significant differences depending on the geographical criterion or the provenance of the samples, the Kruskal-Wallis test was used, which is based on the rank analysis, i.e. the ranking of the values of the $^{6}Li/^{7}Li$ ratio regardless of these grouping criteria. As a result, each group-specific mean rank was analyzed.

The null hypothesis (H0) of the test assumes that all groups present average rank values close to the general average rank, and the alternative hypothesis (H1) is that which assumes that the average ranks by groups differ from the general average rank. If the p-value (Sig.) shows values lower than 0.05, the null hypothesis is rejected, and the alternative hypothesis is accepted; that is, there are significant differences between the analyzed groups. In this situation, the Kruskal-Wallis test concretely certifies the groups between which there are significant differences. In this sense, they were compared two by two, applying the Mann-Whitney test, and the significance threshold was adjusted according to the number of comparisons (Bonferroni correction).

After establishing the groups with significant differences, comparable median values were determined. Table 4 presents the results of the Kruskal-Wallis test to determine the significant differences in the waters depending on the source of origin. The average ranks in the case of lithium concentrations may be relatively close; in the case of the lithium isotopic ratio, the distribution of the average rank is more heterogeneous with a greater variation.

Table 4. Comparative aspects provide the average determination ranks of the two variables (Li and $^{6}Li/^{7}Li$)

Source provenance	Sample number	Li concentration	$^{6}Li/^{7}Li$ ratio
Approved waters	29	57.31	56.76
Non-approved waters	12	48.17	56.92
River waters	8	45.25	35.06
Spring waters	35	53.09	59.84
Foreign waters	12	53.42	59.50
Organic Material	8	44.88	5.25
Total	104	*	*

The value of the Kruskal Wallis test is greater than the threshold of 0.05 for the concentration of lithium and less than 0.05 for the value of the $^{6}Li/^{7}Li$ isotopic ratio, as a result, it can be said that for lithium there are no significant differences depending on the origin of the sample, but for the isotopic ratio there are significant differences between the samples, depending on their origin (Table 5).

Table 5. Test statistics[1,2]

	Li concentration	$^{6}Li/^{7}Li$ ratio
Chi-Square	1.983	25.855
df	5	5
Asymp. Sig.	,852	,000

1. Kruskal Wallis Test;
2. Grouping Variable: Sample provenance

To determine which are the categories between which there are differences, the Mann-Whiteny test was used to compare the provenances of the samples. In this sense, it was necessary to adjust the significance threshold by applying the Bonferroni correction. This

correction is determined as a ratio between the significance threshold (0.05) and the number of comparisons (15). $p' = 0.05/15 \approx 0.00333$

Just as an example, the result of the Mann-Whiteny test for the comparison of approved waters versus organic material is presented in Table 6. It was observed that the p-value is lower than the Bonferroni correction (0.00333) which means that there are significant differences between the values of lithium concentration and $^{6}Li/^{7}Li$ isotopic ratio recorded for the comparison of Approved waters versus Organic Material.

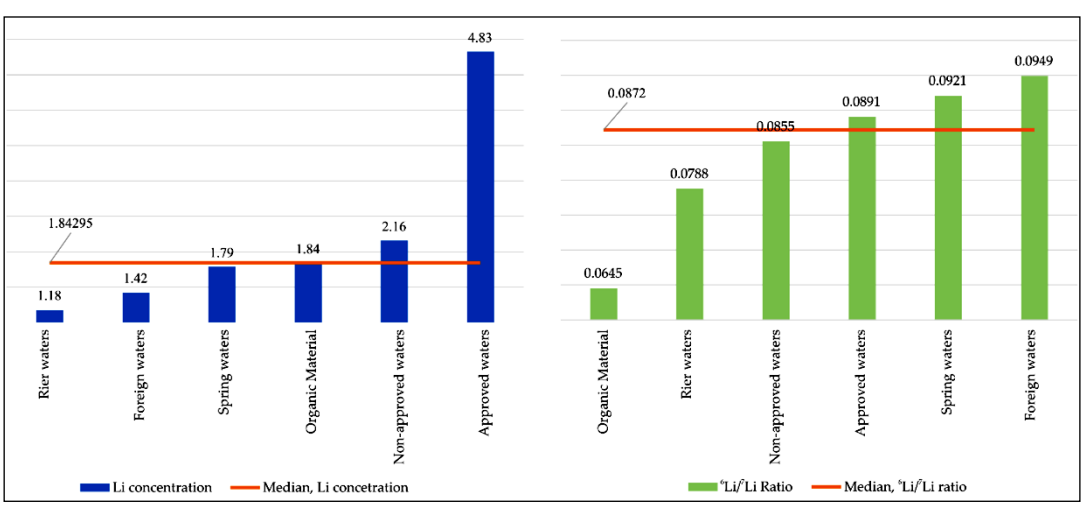
Table 6. Mann-Whitney test results: approved waters versus organic Material

Source code	Source	N	Mean Rank	Sum of Ranks
Li	Approved waters	29	20.21	586.00
	Organic Material	8	14.63	117.00
	Total	37		
$^{6}Li/^{7}Li$ ratio	Approved waters	29	23.00	667.00
	Organic Material	8	4.50	36.00
	Total	37		

Test	Li	$^{6}Li/^{7}Li$ ratio
Mann-Whitney U	81.000	0.000
Wilcoxon W	117.000	36.000
Z	-1.291	-4.280
Asymp. Sig. (2-tailed)	,197	,00002
Exact Sig. [2*(1-tailed Sig.)]	,207[b]	,000[b]

a. Grouping Variable: Source code
b. Not corrected for ties.

The analysis of the 15 comparisons shows statistically significant differences in the isotopic ratio between the organic material and all the other sources of provenance of the samples (Figure 6). There are also slight differences in the isotopic ratio between non-approved waters and river waters, as well as between river and spring waters. As seen in Figure 6, the lowest isotopic ratio is found in organic material, and the highest isotopic ratio is found in commercial waters originating from external sources. The national sources of provenance of the samples have the highest value of the isotopic ratio in the spring waters.



(A) (B)

Figure 6. The median value for lithium concentration (A) and $^{6}Li/^{7}Li$ isotopic ratio (B) depends on the provenance of the samples

Regarding lithium concentrations, even if there are major differences between the approved waters and all other sources of provenance of the samples, they are not statistically significant. This fact is also highlighted by the high standard error of the median of the approved waters determined with the Bootstrap method and the amplitude of variation (Table 7).

Table 7. Median values by sample source

Source	Characteristics	Median	Bias	Std. Error	95% Confidence Interval	
					Lower	Upper
Approved waters	Li concentration	4.8271	0.5519	±6.5157	0.5723	19.6320
	$^{6}Li/^{7}Li$ ratio	0.0891	0.0000	±0.0038	0.0797	0.0976
Foreign waters	Li concentration	1.4225	0.5365	±1.6176	0.6627	6.8236
	$^{6}Li/^{7}Li$ ratio	0.0949	-0.0016	±0.0049	0.0821	0.0988
Non-approved waters	Li concentration	2.1570	0.3209	±1.5866	0.4824	7.0353
	$^{6}Li/^{7}Li$ ratio	0.0855	0.0005	±0.0045	0.0804	0.0980
River waters	Li concentration	1.1778	0.0935	±0.7304	0.6330	2.3739
	$^{6}Li/^{7}Li$ ratio	0.0788	0.0004	±0.0020	0.0763	0.0850
Spring waters	Li concentration	1.7869	0.2944	±1.0162	1.1780	4.4698
	$^{6}Li/^{7}Li$ ratio	0.0921	0.0000	±0.0037	0.0868	0.0980
Organic Material	Li concentration	1.8388	0.8154	±2.8762	0.0495	13.3580
	$^{6}Li/^{7}Li$ ratio	0.0645	0.0006	±0.0017	0.0632	0.0684
Foreign waters	Li concentration	1.4225	0.5365	±1.6176	0.6627	6.8236
	$^{6}Li/^{7}Li$ ratio	0.0949	-0.0016	±0.0049	0.0821	0.0988

a. Unless otherwise noted, bootstrap results are based on 1000 bootstrap samples

To determine the significant differences in the waters depending on the geographical distribution, the Kruskal-Wallis test was performed, the results being presented in Table 8. Both for the lithium concentration and for the isotopic ratio, there are statistically significant differences in the geographical distribution of the samples, a fact highlighted by the p-values lower than 0.05 (Table 9).

Table 8. Kruskal Wallis test by geographical criterion

Region	N	Li	$^{6}Li/^{7}Li$ ratio
Center Transilvania	22	66.14	52.14
North-Est Moldova	20	46.65	36.85
North-West Transilvania	28	46.46	66.68
South Muntenia	9	32.11	66.56
South-West Oltenia	8	78.88	15.63
West Transilvania	5	42.00	54.20
Foreign Countries	12	53.42	59.50
Total	**104**	*	*

Test	Li	$^{6}Li/^{7}Li$ ratio
Chi-Square	17.212	26.142
df	6	6
Asymp. Sig.	***,0085***	***,0002***

a. Kruskal Wallis Test,
b. Grouping Variable: Region code

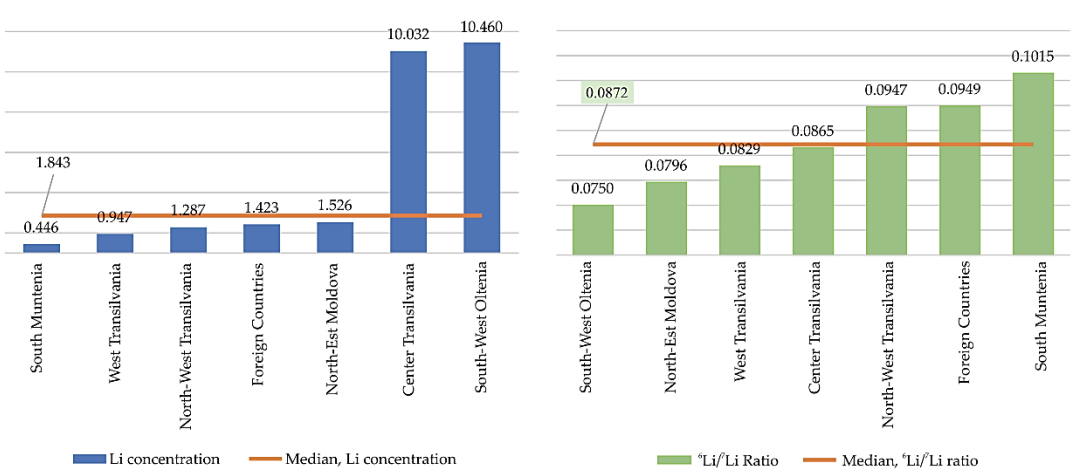
Table 9. Median values by geographic distribution of samples

Region	Characteristics	Median	Bias	Std. Error	95% Confidence Interval	
					Lower	Upper
Center Transilvania	Li concentration	10.0321	13.7810	±41.8007	0.9054	104.7885
	$^{6}Li/^{7}Li$ ratio	0.0865	-0.0008	±0.0035	0.0779	0.0921
North-Est Moldova	Li concentration	1.5256	0.2875	±1.4529	0.4895	5.5520
	$^{6}Li/^{7}Li$ ratio	0.0796	0.0001	±0.0043	0.0718	0.0891
North-West Transilvania	Li concentration	1.2866	0.1242	±0.4641	0.6913	2.8145
	$^{6}Li/^{7}Li$ ratio	0.0947	0.0007	±0.0037	0.0885	0.1059
South Muntenia	Li concentration	0.4460	0.5699	±0.9977	0.0732	2.2740
	$^{6}Li/^{7}Li$ ratio	0.1015	-0.0058	±0.0089	0.0802	0.1050
South-West Oltenia	Li concentration	10.4597	0.1876	±4.3275	4.4710	16.1857
	$^{6}Li/^{7}Li$ ratio	0.0750	-0.0005	±0.0020	0.0701	0.0771
West Transilvania	Li concentration	0.9473	1.0801	±4.4418	0.2138	19.6320
	$^{6}Li/^{7}Li$ ratio	0.0829	0.0041	±0.0115	0.0786	0.1266
Foreign Countries	Li concentration	1.4225	0.5767	±1.8188	0.6627	6.8236
	$^{6}Li/^{7}Li$ ratio	0.0949	-0.0017	±0.0049	0.0821	0.0988

a. Unless otherwise noted, bootstrap results are based on 1000 bootstrap samples

Mann-Whitney tests for each of the 21 comparisons show significant differences regarding the concentration of lithium between the South Muntenia region and the other developing regions (North East Moldova, North West Transylvania, and West Transylvania). There are significant differences in the isotopic ratio between the region of South Muntenia and the area of North West Moldova, West Transylvania, South West Oltenia, and waters of foreign origin. The samples from the South West Oltenia region show the highest lithium concentration but also the lowest lithium isotopic ratio, unlike the South Muntenia region, where they vary inversely.

Figure 7 shows the median value for lithium concentration and isotopic ratio according to geographic distribution. It is observed that there is an inverse-proportional relationship between the lithium concentration and the isotopic ratio. In other words, the high lithium concentration in the development regions of Central and Western Transylvania presents the lowest isotopic ratio values. Also, there are statistically significant differences regarding lithium concentration but no significant differences regarding the isotopic ratio.



(A) (B)

Figure 7. The median value for lithium concentration (A) and $^{6}Li/^{7}Li$ isotopic ratio (B) as a function of geographic distribution

Another aspect of this study's analysis looked at how the sources of evidence are geographically distributed. In the case of approved waters, it was noted that the concentration of lithium is the highest in the Central Transylvania development region, followed by the West Transylvania region (Figure 8). These regions show much higher median values than those recorded in the other development regions: South Muntenia, North West Transylvania, and West Transylvania.

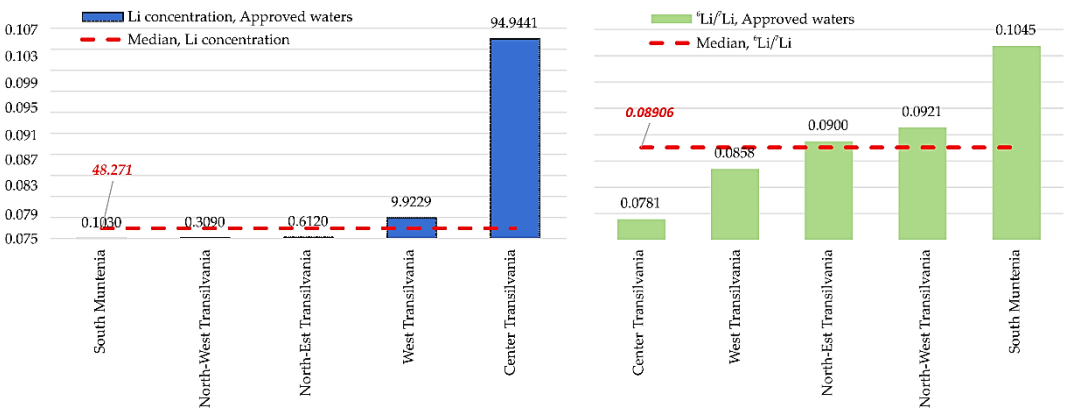


Figure 8. Distribution of median values of lithium concentration (A) and $^{6}Li/^{7}Li$ isotopic ratio (B) depending on the geographical distribution of the approved waters

The geographical distribution of the lithium concentration of unapproved waters is relatively more homogeneous than in the case of approved waters (Figure 9). The relationship of inverse proportionality noticed previously is preserved. Still, between the median level of non-approved waters and that of approved waters, there are no significant differences from a statistical point of view. The West Transylvania region has the lowest lithium concentration but has the highest isotopic ratio.

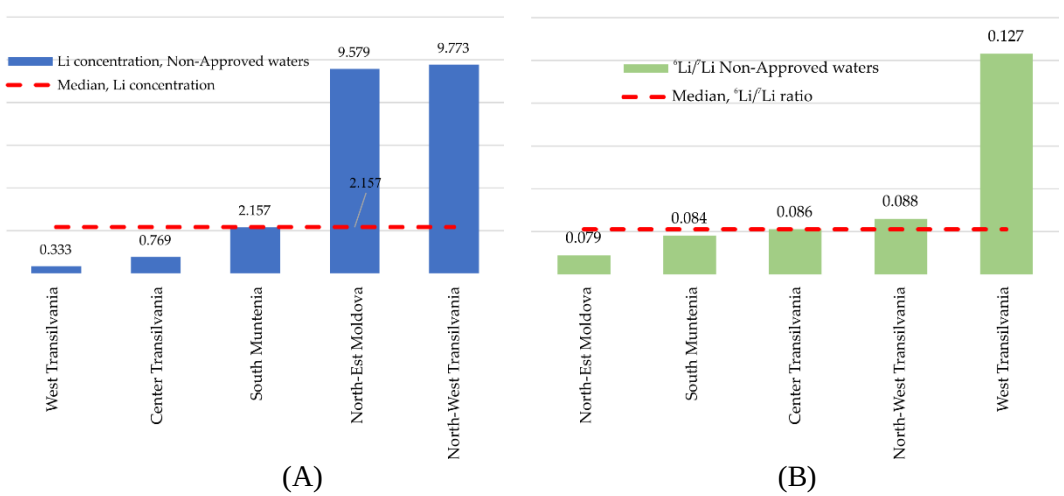
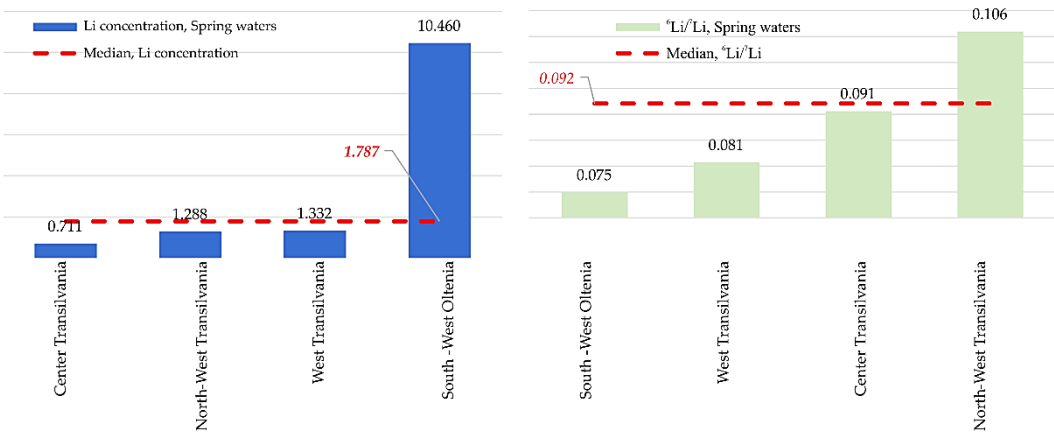


Figure 9. Distribution of median values of lithium concentration (A) and $^{6}Li/^{7}Li$ isotopic ratio (B) according to the geographical distribution of non-approved waters

The lithium concentration of the spring waters is higher in Oltenia's southwest area than the other areas of Transylvania (Figure 10). Regarding the isotopic ratio, the lowest value can be found in the southwest area of Oltenia, and in the other areas of Transylvania, the distribution of the isotopic ratio is more heterogeneous.



(A) (B)

Figure 10. Distribution of median values of lithium concentration and isotopic ratio depending on the geographical distribution of spring waters

4. CONCLUSIONS

In Romania, 78 water sources are currently approved and marketed under the names of 51 brands.

Starting from the need to have a geospatial footprint of the mineral waters on the surface of Romania, this study followed the distribution of lithium and the isotopic ratio in these approved waters but also included 12 waters that are not highlighted in the current legislation to see if there are essential differences from a statistical point of view.

Using alternative analysis methods that are not frequently used, it was found that there is an inversely proportional relationship between lithium concentrations, which are relatively inhomogeneous, and the $^{6}Li/^{7}Li$ isotopic ratio, whose values are relatively homogeneous.

The approved waters present an inhomogeneous distribution of lithium content, with higher values in contrast to non-approved and foreign waters. The waters from the Central Transylvania region show higher concentrations of lithium in an inhomogeneous distribution compared to the waters studied from the other geographical regions. The evidence of the 2 previously mentioned aspects is given by the high values of the quartile interval. Also, the isotopic ratio has a homogeneous distribution compared to the li concentration, with high values of the quartile range for river waters, approved, and non-approved waters, and from a geographical point of view, the development regions W Transylvania, N-W Transylvania, N-E Moldova. Moreover, there are differences in the quartile range between approved waters (20.615) and non-approved waters (3.429).

The concentration of Li is relatively inhomogeneous, which makes the isotopic ratio present relatively homogeneous values. Thus, the quartile interval is larger in the case of approved waters compared to non-approved waters. In the case of the isotopic ratio, it is noted that these sources of provenance of the samples have relatively close values of the quartile interval. Also, the organic material shows a degree of Li concentration dispersion but the smallest variation in the isotopic ratio.

Regarding the degree of dispersion of the isotopic ratio, that of the Central Transylvania region is relatively equal to that of the S-W Muntenia region (the quartile interval is almost 6 times larger)

Another aspect to note is that the distribution of the Li concentration and the isotopic ratio values is not normal, highlighted by statistical normality tests. In this case, the median was used to express the central trend of the evolution and for comparisons, non-parametric tests.

The spring waters have high isotopic ratio values, and the approved waters have high lithium concentrations. the Krusal Wallis test highlighted the fact that there are significant differences from a statistical point of view, both from the perspective of the sources of provenance of the evidence and from the point of view of the geographical approach. The highest lithium concentration was found in the approved waters (4.83 μg/L), compared to the river waters with the lowest concentration (1.18 μg/L). The isotopic ratio is high in the case of foreign waters and low in the organic material. the median value of the isotopic ratio is 0.0872 compared to the maximum reference value.

The determination of the median values was based on the bootstrap method, a fact that allowed the identification of high values of the standard errors in the case of li concentration in the approved waters and the organic material. In the case of the isotopic ratio, the standard errors are small, the highest value being found in foreign waters. The waters of Southern Muntenia presented significantly different values compared to all other regions, having the lowest concentration of Li (0.446 μg/L) but having the highest isotopic ratio (0.1015). The waters of the S-W Oltenia and Central Transylvania regions have the highest concentrations of Li, respectively 10.4597 μg/L and 10.0321 μg/L, much lower than the values of the other regions.

The isotopic ratio has a value close to the median value of the 104 samples in the Central Transylvania region. It has the lowest value in the samples from S-W Oltenia (0.0750).

In conclusion, it can be said that there is an inversely proportional relationship between the Li concentration and the Li isotopic ratio, and the median value of the 104 samples does not differ significantly from the reference value.

This study represents a first step in carrying out a larger study that would include a more representative sampling of sources, allowing more in-depth observations regarding the relationship between Li content and Li isotopic ratio.

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