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LEAD AND STRONTIUM ISOTOPE EVIDENCE FOR LOCAL HERBAL VARIETIES DUE TO THE ELEMENTAL SOIL CHEMISTRY

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ABSTRACT

The aim of this study was to evaluate lead and strontium composition (total content and isotope ratios) in several herbal species: rosemary (*Salvia Rosmarinus*), thyme (*Thymus vulgaris*), basil (*Ocimum basilicum*), sage (*Salvia officinalis*), yellow wort (*Blackstonia perfoliate*) and chamomile (*Matricaria chamomilla*) with regional occurrence in the area of the Republic of North Macedonia. Furthermore, the elements' isotope ratios were correlated with the average data for the corresponding elements in soil samples (top layer). Samples of yellow wort (*Blackstonia perfoliate*) were used for comparative analysis to the same species obtained in market in China. Several metrics has been applied for authenticity testing of the samples: total lead and strontium content, as well as lead and strontium isotopic ratios. Element content was measured with validated method for isotopic measurement with inductively coupled plasma with mass spectrometry (ICP-MS).

Keywords: Isotopic measurement, Lead, Strontium, Soil chemistry, ICP-MS

1. INTRODUCTION

Soil is an extremely complex and variable medium. Soil structure plays a significant role in determining its ability to perform its functions. Any damage to soil structure also damages other environmental media and ecosystems [1].

The soil is subjected to serious degradation. These include erosion, reduction of organic matter, local and diffuse contamination, imprinting, reduction of biodiversity, salinization, flooding, etc. In combination, all these degradations can lead, in arid and subarid climates, to desertification. The impacts on the soil caused by human activities are constantly increasing, which causes serious socio-economic consequences [2]. Thus, the soil destruction reflects as significant geochemical and anthropogenic marking in plants.

A major challenge is to prevent soil degradation. This must be achieved through special policy measures for soil protection and management. Furthermore, incorporation of soil protection issues should be introduced into other sectoral policies, that is, in agriculture, forestry, water management, transport, etc. Soils are limited natural resources. They are considered renewable because they are constantly forming [3]. Soil formation occurs at extremely slow rates. In fact, one inch of topsoil can take several hundred years or more to develop. Soil formation rates vary across the planet: the slowest rates occur in cold, dry regions, and the fastest rates are in hot, wet regions (several hundred years) [3]. For that instance, some geochemical characteristics of soils can be reflected as marks in certain plants.

Soil chemical properties can be adjusted using various methods and improvements including: organic matter, mineral composition, trace elements content, soil texture, soil solution, cation exchange capacity of the soil, soil adsorption performance, soil pH and others. The relationships between them, mutual restraint, and in the soil minerals and organic matter, as they are dominant [4].

Soil chemical properties and chemical processes that affect soil fertility are an important factor for soil health. In addition, soil acidity and redox properties have a direct impact on plant growth. Moreover, soil chemical properties, mainly through the soil cation exchange capacity and nutrient intervention status indirectly affect plant growth. On the other hand, is given on soil mineral composition, composition of organic matter, soil texture, soil moisture in the soil significantly affect on the biological activity of soil. Soil pollutants and its fate is also affected by the conversion of the soil chemical nature [5-6]. Soil physical properties, such as soil texture, and soil moisture in cohesion with soil mineral particles, impact on ions charge characteristics, redox potential. Soil organisms, especially soil microbes can affect the accumulation of organic matter in the soil, humus decomposition [7]. The specific conditions in the soil which are due to the chemical, physical and biological interactions represent characteristic conditions of the environment which is reflected in a certain way in the plants.

A modern trend is the consumption of plant food produced locally, in order to reduce energy footprint and pollution through transportation. Determination of food authenticity is an important

issue in quality control and food safety. Authenticity is a quality criterion for plantfood and is required more and more worldwide, as a result of legislative protection for regional plant food [8].

Plant food authentication may cover many different aspects, including mislabeling, misleading claims about origin, and adulteration. This occurrence is defined as a process by which the quality or the nature of a given substance is reduced by adding a foreign or an inferior substance and removing a vital element or characterization of the product. European Union (EU) quality schemes identify products and foodstuff farmed and produced to exacting specifications. Product designations fall into two categories: those linked to a territory and those relating to a particular production method [8]. Geographical indications and designations of origin are names identifying a product as originating in a given territory and testifying to a link between a given quality, reputation or characteristic of the product and its geographical origin [9]. The EU regulation allows the application of the following geographical indications to a food product: (1) protected designation of origin (PDO); (2) protected geographical indication (PGI); and, (3) traditional specialties guaranteed (TSG). PDO covers agricultural products that are produced, processed and prepared in a given geographical area using recognized know-how. PGI covers agricultural products and foodstuffs closely linked to the geographical area [10]. Thus, the main goal of the present research was to identify severe base-line geochemical indicators for food authentication.

Reviews of analytical methods for the determination of geographical origin of plant food and beverages have been published [11]. Methods based on elemental composition have been reviewed as well as methods based on isotope ratios [12, 13]. Strategies employed to detect adulteration have relied on instrumental techniques and have evolved through time along with technology and instrumentation. High-performance liquid chromatography (HPLC) gas chromatography (GC) nuclear magnetic resonance (NMR), infrared spectroscopy (IR) fluorescence spectroscopy capillary electrophoresis (CE), and more advanced techniques such as proton transfer reaction mass spectrometry (PTR-MS), electronic nose coupled with MS DNA technologies and sensory analysis, have been proposed for food authentication [12]. However, organic components of a food-crop production depend on various conditions (e.g., fertilization, history of the field, climatic conditions in the year of cultivation, geographic location and soil composition), so it is not always possible to determine the origin of a product by analyzing the organic components. Despite uncertainty about the organic compounds in a sample, the content of selected elements (trace and rare earth elements, REEs) in food positively reflects the growing conditions in the particular environment. For that instance, in the present research we will give focus on the inorganic compounds' identifications, due to the more stable response to the lithogenic nature of the soil-plant interaction.

In addition, multi-isotope or single-isotope ratios (e.g., strontium and lead) can provide unique, representative fingerprints that make it possible to discriminate the origin of plant food samples. Over the past decade, with the development of new advanced analytical techniques we can successfully retrieve elemental and isotopic compositions, of any given food sample and determine the geographic origin successfully. The growing concern of the consumers stimulated scientific research and publications in recent years, including multi-element and isotope-ratio methods of analysis in food authentication after statistical evaluation of the data.

1.1 Lead isotopes ratios-basics and it's applications

Due to the complex environmental chemistry, soil chemistry, transport patterns, meteorological conditions, the mixing of emissions from multiple sources, and uncertainties associated with receptor modelling, it remains difficult to quantify the relative impact of emissions from different sources on metal accumulation in plant food. The emission and deposition of hazardous trace metals such as lead (Pb) is of significant concern because it can affect human and environmental health. Lead isotope ratio analysis is important as it is used for Pb-Pb dating in geochronology, and to trace the ratio measurement can provide analytical information related to the source of lead contamination in naturally occurring samples [14]. Studies of the isotopic composition of lead are therefore commonly used in the environmental, geological and anthropological studies [15]. Small Pb abundance variations occur in nature and the isotopic composition of lead in the environment is dependent on the local pollutant source. If lead is present in the soil, a plant will take up small amounts and subsequent isotope ratio studies might provide unique means of differentiating between different plant sources of origin. Local lead level may become mixed with external source of contamination that vary with time depending on the anthropogenic activity. There are four stable isotopes of Pb with the following approximate abundances: ^{208}Pb (52.4%), ^{207}Pb (24.1%), ^{206}Pb (22.1%), and ^{204}Pb (1.4%). ^{204}Pb is non-radiogenic and was not measured in this study because of its low relative abundance. ^{208}Pb , ^{207}Pb , and ^{206}Pb are formed by the radioactive decay of ^{232}Th (half-life=14 billion years), ^{235}U (half-life=0.7 billion years), and ^{238}U (half-life=4.5 billion years), respectively[15]. Inductively coupled plasma mass spectrometry (ICP-MS) has been increasingly used in isotope ratio measurements in recent years. Lead isotope measurements provide analytical information relating to the source of lead contamination in naturally occurring samples [15]. Concentration measurements cannot provide this kind of information. Studies of the isotopic composition of lead are therefore commonly used environmental sciences and geological sciences as well.

Food 'fingerprinting' is the process of identifying a unique isotopic imprint of an ingredient using mass isotope ratio spectrometry (IRMS). This imprint consists of the relationship to the key elements (carbon, nitrogen, oxygen, hydrogen and sulfur), because each of them is

influenced by the source material, production process and environmental conditions specific to the place of origin. Therefore, it is unique for each ingredient and can be used to determine where it was produced and to which it was subjected. Taking a 'footprint' of food can be used to: confirmation of the geographical origin of the ingredient; examining the authenticity of ingredients listed as natural; identification of undeclared additives, such as sugar; detection of the use of synthetic fertilizers in organic products. Thus way, it can help to: prevent food fraud; reduce risks; maintain full control of the supply chain; you strengthen your reputation; increase customer loyalty.

1.2 Multi-isotope ratio

Investigations of the ratios of stable isotopes and the contents of unstable isotopes (radioisotopes), especially heavy elements (e.g., uranium, strontium, thorium or lead) have been used primarily in geological sciences for age determination [15, 16]. For heavier elements (e.g., Pb and Sr), fractionation is insignificant compared to the original isotopic ratios because the nuclides have high mass compared to the mass differences of the isotopes. In this case, stable isotopic ratios depend essentially upon the origin of the orebody and can be used for identification of the source of a material or characterization of its transportation history (e.g., $^{208}\text{Pb}/^{207}\text{Pb}$). Strontium is the commonly used heavy metal for isotope-ratio analysis. Clearly, the present $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is greater for samples that have greater ages, t , and samples with larger Rb/Sr ratios. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio therefore varies between different rock types and formations. Since Rb is an alkali metal and Sr is an alkaline earth, these elements behave differently in geological processes, creating large variations in Rb/Sr, and, so, large variations in $^{87}\text{Sr}/^{86}\text{Sr}$. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio has been shown to vary widely in surface rocks, so any Sr released into soils, rivers, and groundwaters has an isotopic signature that reflects its source. Sr isotopes have also been used to trace agricultural products, which have incorporated Sr, along with Ca, from soils incorporating the Sr-isotope ratios of the underlying rocks [15, 16].

1.3 Isotopes ratios – measurement challenges

Whichever methodology is selected, the natural or “common lead” ^{204}Pb isotope is measured as a reference to calculate the original (primordial) level of the other (mainly radiogenic) Pb isotopes, so accurate measurement of ^{204}Pb is essential [17]. Unfortunately, for measurements made using inductively coupled plasma mass spectrometry (ICP-MS), ^{204}Pb suffers an isobaric interference from ^{204}Hg (an isobaric overlap is where isotopes of different elements occur at the same nominal mass) meaning that any mercury present as a contamination or as a component of the sample would bias the measurement of ^{204}Pb [18].

2. MATERIALS AND METHODS

The aim of this case study was to evaluate lead and strontium composition (total content and isotope ratios) in several herbal species: rosemary (*Salvia Rosmarinus*), thyme (*Thymus vulgaris*), basil (*Ocimum basilicum*), sage (*Salvia officinalis*), yellow wort (*Blackstonia perfoliate*) and chamomile (*Matricaria chamomilla*) with regional occurrence in the area of the Republic of North Macedonia. Furthermore, the elements' isotope ratios were correlated with the average data for the corresponding elements in soil samples (top layer). Samples of yellow wort (*Blackstonia perfoliate*) were used for comparative analysis to the same species obtained in market in China. Several metrics have been applied for authenticity testing of the samples: total lead and strontium content, characterization with clustering, and lead and strontium isotopic ratios.

2.1 Chemometric tools applied

Sample collection has been conducted in the South-eastern region in the country. For collection of each plant species, we have chosen 5 network points, from each location two different samples were collected. In total, 2 samples from each location, we collected 10 samples for each species. The samples have been cleaned from dust, air-dried to constant mass, then homogenized and subjected to acid digestion. For digestion of samples, the microwave digestion system (model Mars, CEM) was applied. Precisely was measured 0.5 g of each sample and placed in Teflon digestion vessels. In total, 5 mL concentrated nitric acid, HNO₃ (69%, 108 m/V) and 2 mL hydrogen peroxide, H₂O₂ (30%, m/V) were added. The Teflon vessels were carefully closed and placed in microwave digestion system. Samples were digested in two steps for total dissolving at 180°C. After the digestion method was finished, digested samples were quantitatively transferred into 25 mL volumetric flasks, following the protocol of EPA METHOD 3052. The isotope analysis was conducted with application of inductively coupled plasma with mass spectrometry (ICP-MS), following the protocol provided in the EPA METHOD 6020. Technical characterization and the optimized values are given in Table 1. ICP-MS technique was used due to the high sensitivity (LOD <0.1 ppb), as well for the improved accuracy and reproducibility in isotope measurements.

Table 1: The optimized conditions of the instrument ICP-MS, model 7850, Agilent Technologies

Peristaltic pump	10-roller, 3 channels
Nebulizer	MicroMist (borosilicate glass)
Spray chamber	Scott-type double-pass (quartz)
Torch	Dimension 2.5 mm id injector, ShieldTorch system Horizontal and vertical position: ± 2 mm, in 0.1 mm steps : Sampling depth: 3 to 28 mm, in 0.1 mm steps
Ion lens	Extraction lens, off-axis Omega lens
Octopole reaction system	He collision cell gas line
Mass analyzer	Quadrupole, frequency 3 MHz hyperbolic rod profile with mass range 2-260 u
Vacuum system	Three-stage differential vacuum system
Isotope ratio Precision $^{107}\text{Ag}/^{109}\text{Ag}$	<0.05% RSD
Stability 20 min/2 hr	<2.0% RSD/<3.0% RSD
Background m/z 9	<0.2 cps
Interference reduction factor (Performed in a matrix of 2% HNO_3 + 0.5% HCl .) $^{59}\text{Co}/^{51}\text{ClO}$ >30	

2.2 Model testing and implementation

The samples were prepared according to a validated procedure for multi-element chemical analysis. Optimization of ICP-MS with standard tuning solution (contains 1 $\mu\text{g/L}$ each of Li, Mg, Y, Ce, Tl and Co in a matrix of 2% HNO_3). Comparative analysis has been applied between the two groups of samples (geographical regions). As criteria for the implementation of the procedure will be set: limit of detection, limit of quantification, linearity, reproducibility, accuracy, precision, working range and measurement uncertainty. A set of multi-element certified standards as well as certified reference materials is used for the implementation of the validation process. To determine the limit of detection a blank sample was used (blank, 2 mL H_2O_2 and 5 mL HNO_3 , totally diluted to a final volume of 25 mL), 10 repetitions with 3 repetitions of each individual measurement. The $3 \times \text{SD}$ method was used to determine the LOD.

3. RESULTS AND DISCUSION

3.1 Method validation for isotopic measurement

To confirm that Pb does not undergo a charge-transfer reaction (and to check if any cluster ions

are formed), 20 µg/L Pb solution was aspirated and a mass scan was performed. The sum of the signal for these clusters amounted to <0.5% of the total Pb signal (the sum of the unreacted precursor and reacted product Pb ions); at this level the product ions can be considered negligible and ignored (Fig.1). Pb did not appear to undergo any charge transfer reaction, as the Pb signal with argon gas in the cell remained at practically the same level as with no reaction gas. Very good sensitivity was obtained for ^{206}Pb , ^{207}Pb and ^{208}Pb isotopes concentration measurements (Fig. 2). Satisfactory linearity (R) was obtained in the range from 5 to 100 µg/L (Fig.2). The instrumental detection limits for the three isotopes (^{206}Pb , ^{207}Pb and ^{208}Pb) were calculated as 0.35, 2.86 and 0.85 µg/L, respectively. Strontium isotopes did not show characteristic isobaric interferences.

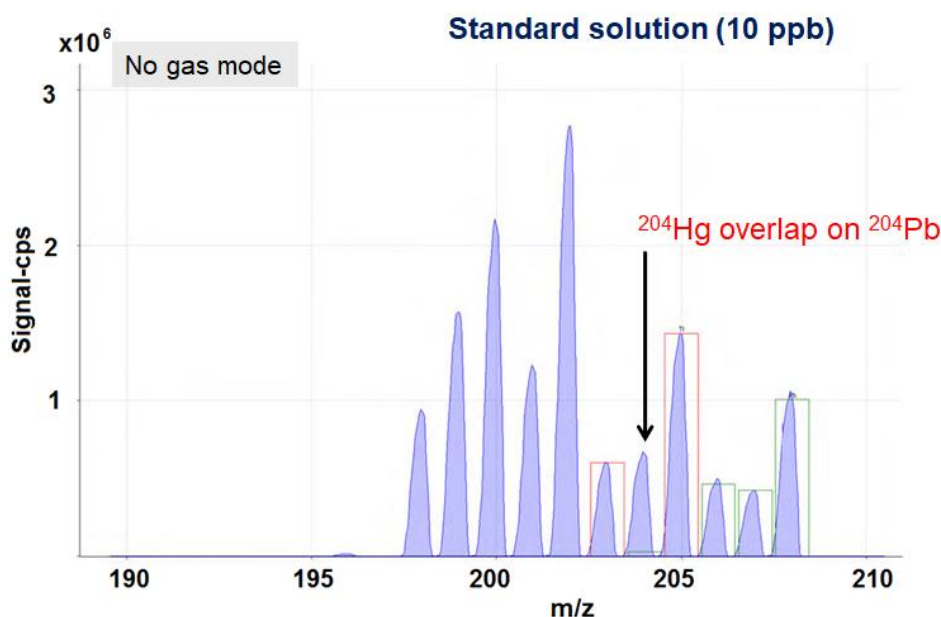


Fig. 1: Mass scan with ICP-MS, sensitivity for Pb, with overlap indication due to the of ^{204}Pb with mercury isotope (^{204}Hg)

The only limiting factor in the measurement of lead is the isobaric interference amu 204. Despite the recommendations used for the deviation of these isobaric interferences, however, by applying this method, a satisfactory sensitivity for the lead isotope Pb^{204} was not obtained. On the other hand, for lead isotopes, the target masses were strontium 86, 87 and 88. In the validation process, no significant interference occurred that could affect the sensitivity of the measurement of these two strontium isotopes.

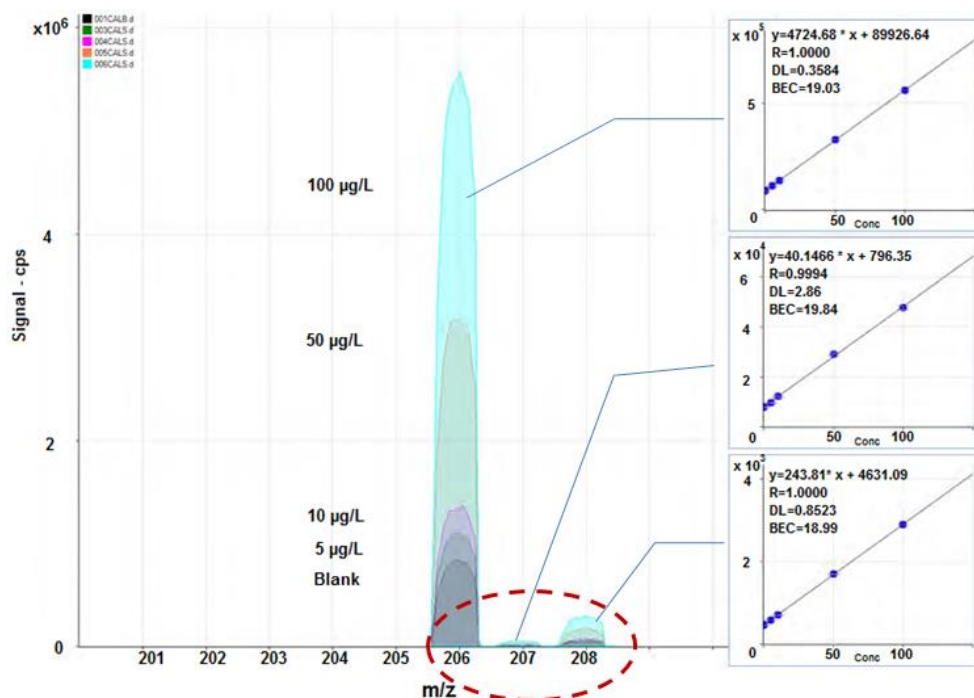


Fig. 2: Calibration data for ^{206}Pb , ^{207}Pb and ^{208}Pb isotopes, within the range of 5 $\mu\text{g/L}$ to 100 $\mu\text{g/L}$. The cps signals of 1 $\mu\text{g/L}$ calibration standard, didn't indicate stability for CCV Recovery (>80%)

The optimization parameters of the applied method are given in Table 3. Standard QA/QC variables were used to prove the validity of the method. All set parameters indicate satisfactory analytical sensitivity, accuracy and precision of analysis. During the measurements, dual gas phases were used for the analytes: a) normal mode using basic carrier gas argon and b) helium mode, using optional helium gas. From the parameters obtained, it can be determined that the first analytical mode provides greater sensitivity and linearity of the applied method.

Table 3: Data summary of the instrumental condition and validation of the applied methodology

Element	Isotope	ORSmode	IntegrationTime (s)	Linear range($\mu\text{g/L}$)	Slope	Intercept	R	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)
Sr	86	Normal	0.1	1-50	1.526	10.93	0.9998	0.27	0.872
Sr	86	Helium	0.5	1-100	0.0092	-6.271	0.9994	0.15	0.519
Sr	87	Normal	0.1	1-100	2.125	391.2	0.9999	0.12	0.401
Sr	87	Helium	0.5	0.5-50	1.150	2.483	0.9992	0.096	0.321
Sr	88	Normal	0.1	5-50	1.680	10.27	0.9995	0.77	2.572
Sr	88	Helium	0.5	1-50	2.019	-5.94	0.9991	0.10	0.334
Pb	206	Normal	0.1	1-100	0.058	-0.0063	0.9994	0.29	0.969
Pb	206	Helium	0.5	0.1-10	0.0079	0.0022	0.9991	0.0033	0.011
Pb	207	Normal	0.1	0.2-50	2.019	-5.94	1.0000	0.062	0.207
Pb	207	Helium	0.5	0.5-10	1.36	5.998	0.9989	0.12	0.401
Pb	208	Normal	0.1	0.1-100	0.023	0.0647	0.9991	0.019	0.063
Pb	208	Helium	0.5	0.1-1	0.038	10.47	0.9984	0.054	0.180

The total content of lead and strontium was determined in the samples of herbal species collected in Macedonia. A comparative analysis was made on the species Yellow wort (*Blackstonia perfoliat*), available in Macedonia vs. China. In order to determine the potential of soil enrichment with lead and strontium in the soil and the influence of the contents of these elements in the biaccumulation, the average values for these two elements in the soil are given in comparison in both countries. From the data on the content of lead and strontium in the soil, it indicates a greater enrichment of these elements in the soils in Macedonia, compared to the soils in China (Table 4). However, the elemental analysis of the comparative species does not indicate an increased bioaccumulation of these two elements in the Yellow wort species, respectively. The bioaccumulative indices were calculated for each species separately as a ratio of the average concentration in the plant versus the average concentration in the soil *Salvia Rosmarinus* (0.014), *Thymus vulgaris* (0.0026), *Ocimum basilicum* (0.028), *Matricaria chamomilla* (0.049), *Blackstonia perfoliate* NMK (0.039) and *Blackstonia perfoliate* Ch(0.19).

Table 4: Total content of lead and strontium in herbal samples-comparative analysis (N=10, for each plant species)

Herbal type	Specie	Pb (mg/kg)		Sr (mg/kg)	
		Range	Average	Range	Average
Rosemary	<i>Salvia Rosmarinus</i>	0.038 – 2.15	1.34	0.21 – 9.22	1.72
Thyme	<i>Thymus vulgaris</i>	0.019 – 1.04	0.25	1.78 – 98.7	25.7
Basil	<i>Ocimum basilicum</i>	<0.001 – 4.12	2.68	2.33 – 177	59.3
Chamomile	<i>Matricaria chamomilla</i>	0.016 – 9.03	4.72	0.86 – 344.7	17.3
Yellow wort - NMK	<i>Blackstonia perfoliat</i>	<0.001- 5.88	3.79	10.8 – 210	77.4
Yellow wort - Ch	<i>Blackstonia perfoliat</i>	0.056-12.3	8.53	29.7 – 413	116
Soil data – North Macedonia, NMK	Data for automorphic soil for North Macedonia [19]	1.2->10000	95	21-1400	140
Soil data - China, CH	Data for agricultural soil in China [20-22]	32 -94.5	44	67.3–116	98.6

Geochemical markers of isotopic ratios of lead and strontium were determined in order to determine the degree of dependence of the bioaccumulation of lead and strontium in relation to the specific soil chemistry in different regions (North Macedonia vs. China), for the *Blackstonia perfoliate* herbal specie. According to the obtained results, there is a significant difference in the isotopic ratios of lead and strontium isotopes (Table 5). This indicates that these parameters can represent significant segments in determining the geographic origin of species.

Table 5: Data summary for the Pb and Sr isotopes ratios (comparative analysis)

Sample	N	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{86}\text{Sr}/^{87}\text{Sr}$	$^{87}\text{Sr}/^{88}\text{Sr}$
Yellow wort - NMK	10	0.974 ± 0.22	1.352 ± 0.11	0.811 ± 0.16	2.087 ± 0.22
Yellow wort – Ch, [20]	10	0.862 ± 0.15	2.574 ± 0.29	0.872 ± 0.25	1.903 ± 0.18

There is still limited data on the validation of these authentication methods. Numerous scientific approaches have been published to authenticate the geographical origin of food [23-27]. However, a certification guide has not been established, which will ensure the unification of the geo-chemical approach in the identification of the authenticity of plant food.

4. CONCLUSION

Geochemical markers represent a significant factor in determining the geographical authenticity of plant foods. This research was aimed at the possibility of using lead and strontium isotopes as typical indicative markers in correlation with soil chemistry. The analysis indicated that the

natural and anthropogenic indication of these two elements in the soil does not provide significant geochemical marking for the plant species. Herbal plants that have been confirmed as typical metal bio-accumulators were used. The total content of lead and strontium in plant herbal spices did not show specificity with the geographical region. The isotopic ratios of lead ($^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$) and strontium ($^{86}\text{Sr}/^{87}\text{Sr}$ and $^{87}\text{Sr}/^{88}\text{Sr}$) showed a significant difference in the same species and different geographical region. This indicates that isotopic ratios of lead and strontium can be used as a geochemical marker to determine the geographical authenticity of herbal species. However, isotopic ratios, by themselves, do not represent an isolated geochemical marker. This indicates the multi-cluster nature in determining the geographic origin of plant foods.

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