International Journal of Biological, Life and Agricultural Sciences
ISSN: 2415-6612
Vol:13, No:9, 2019

Selenium Content in Agricultural Soils and Wheat from the Balkan Peninsula

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Abstract**—**Selenium (Se) is an essential micro-nutrient for human and animals but it is highly toxic. Its organic compounds play an important role in biochemistry and nutrition of the cells. Concentration levels of this element in the different regions of the world vary considerably. This study aimed to compare the availability and levels of the Se in some rural areas of the Balkan Peninsula and relationship with the concentrations of other trace elements. For this purpose soil samples and wheat grains from different regions of Bulgaria, Serbia, Nord Macedonia, Romania, and Greece situated far from large industrial centers have been analyzed. The main methods for their determination were the atomic spectral techniques – atomic absorption and plasma atomic emission. As a result of this study, data on microelements levels from the main grain-producing regions of the Balkan Peninsula were determined and systematized. The presented results confirm the low levels of Se in this region: 0.222– 0.962 mg.kg^{-1} in soils and 0.001 - 0.005 mg.kg^{-1} in wheat grains and require measures to offset the effect of this deficiency.

Keywords**—**Agricultural soils, Balkan Peninsula, rural areas, selenium.

I. Introduction

THE main characteristic that distinguishes Se from the other essential elements is the small difference between the minimum - about 30 μg/day, and the maximum - 300 μg/day, a value of the acceptable daily intake (ADI). Deficiency of Se can cause socially significant diseases, some of which is Keshan and Kashin - Beck disease [1]. Selenosis is a disease in both animals and humans, which is due to excess Se in the body. Intake of Se can counteract the toxic effects of heavy metals in foods and helps the body rapidly and effectively eliminate them by forming complexes with them [2]. Se is involved in more than 35 enzymes which play a crucial role in controlling the regulation of the thyroid hormone, as well as the synthesis of the DNA molecule. In case of absence of Se, RNA viruses such as influenza, AIDS, hepatitis B and C develop much faster. It is considered that Se is the most important element of the antioxidant defense of the body. It is a trace element with essential biological and biochemical functions in living organisms due to its unique antioxidant properties and its ability to regulate the metabolism of the thyroid gland [3]. It is a component of glutathione peroxidase, which disposes of the most dangerous and aggressive "free radicals" that other antioxidants cannot cope with. If Se is absent the most important unit of the antioxidant protection will not work.

The distribution of Se in the lithosphere is uneven. Soils typically contain about 50 to 200 μg.kg^{-1}, but in some places, it may be outside this range. Se concentrations in different regions and its levels in different foods vary widely which has significant implications for the dietary intake. In the USA, the average daily intake of the element is 62 to 216 μg/day [4], in most European countries it is about 40 μg/day, and in some parts of China it is from 3 to 22 μg/day [5]. The substantial differences in the concentrations of Se in the same foods lead to an inability to use universal tables for food composition with an accurate assessment of Se intake. To solve this problem and evaluate the need for Se intake is used data on the average consumption of the population in the given region. This has given rise to the need to create a Se World Atlas [6]. It has been made on the basis of data from different studies, which illustrate the deficiency, adequacy or toxicity of Se.

European soils usually have low levels of Se. That is why its content in bread in Europe is lower than that in the USA. Some countries have taken steps to protect the public against the possible adverse effects of this situation. In Finland, the law requires to add Se to all fertilizers, and New Zealand farmers use Se-enriched fertilizers on pastures to combat its deficiency in livestock. Self-healing with Se supplementation is widely practiced. Increasingly, consumers are offered Se-enriched food products. European countries have extensive research related to the Se status of the continent. On the Balkans, the most significant studies on Se status are those in Greece, Serbia and Romania [7].

About the levels of Se in soils, cereals and garlic, the authors of the world atlas noted that ‘all the data suggest a serious lack of Se’. For some regions, the levels of Se in garlic, grain, human serum and hair are close to those in the low Se area of China [8]. The main nutritional source of Se for the human body in the geographic area of the Balkan Peninsula is wheat and the products from its processing – bread and bakery products [9]. In Hungary, the Se content in wheat ranged from 5 to 235 μg.kg^{-1} [10]. Low Se values have been reported from Yugoslavia [11] in the range of 3.6 to 65.5 μg.kg^{-1} with an average of 18 μg.kg^{-1}. This has led to the need for reinforcement of the wheat flour with Se or for mixing it with wheat flour obtained from other climatic zones. This study aimed to compare the availability and the levels of the Se in some rural areas of some countries from the Balkan Peninsula. The study contributes to the gathering of new

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information and additional knowledge on issues of relevance to agriculture and human health, namely: the state of soil stocks of grain-producing areas of Se and other microelements.

This study will contribute to information and additional knowledge on issues of importance to agriculture and human health, namely: environmental assessment and soil reserves of grain-producing areas of primary nutrients and micronutrients.

II. Materials and Methods

A. Sampling

When we choose the areas for sampling, we take into consideration the current location of the main arable areas for industrial grain production. Three parallel samples were taken from each point a depth of 0-20 cm. The results were processed using statistical methods. The sampling points were described in adequate coordinates using the GPS system. Wheat grain sampling places are the same from which soil samples were taken. The grain samples were taken during the period of technical maturity from 15^{th} June to 15^{th} July, depending on the weather conditions.

B. Decomposition of Soil Samples

We have used the EPA method of microwave mineralization [12]. The soil samples were placed in a pressure-resistant vessel for decomposition, made of a suitable fluorinated polymeric material (PTFE/Teflon), and then to them were added a mixture of mineral acids. To achieve a decomposition temperature above the atmospheric boiling point and to avoid the loss of Se, the vessels were sealed hermetically. The dissolution of the samples was performed on a microwave system for mineralization using a program with a set temperature and time for degradation. Typically it comprises a stage for a maximum temperature of 160 °C and decomposition time of 15 minutes. After completion of the procedure, the vessels are cooled to room temperature for about 30 minutes, then opened and their contents are quantitatively transferred to a volumetric flask and made up to nominal volume (100 cm^3). The undissolved components were separated by filtration or centrifugation.

C. Decomposition of Wheat Grain Samples

Here again, we have used the method of microwave mineralization following the procedure: 2 g of ground, homogenized and air-dry sample was transferred to a teflon reaction vessel. Then 15 cm^3 of aqua regia was added to the sample, and the vessels were closed, sealed, weighed and placed on the rotor in the microwave system and the program for decomposition got started. After completion of the procedure, the vessels were cooled to room temperature. Finally, the reaction vessels were opened, and their content was quantitatively transferred to a volumetric flask and made up to the nominal volume (100 cm^3). The undissolved components were separated by centrifugation or filtration.

D. Quantitative Analysis

Quantitative analysis of solutions from soils were used an inductively coupled plasma atomic emission spectrometer Prodigy 7. The quantification was made using the method of the calibration line [13]. For this purpose, we used a multi-element standard solution, from which, after various levels of dilution, were obtained five working standard solutions. To conform to the matrix, to all standard solutions was added about 25 cm^3 aqua regia.

E. Descriptive Statistics

Correlation and regression analysis were performed using the SPSS program for Windows.

III. Result and Discussion

TABLE I
Observed Concentrations of Se in Different Places of the Balkan Peninsula

Place	GPS coordinates	Se in soil ($mg.kg^{-1}$)	Se in wheat grain ($mg.kg^{-1}$)
Zmeevo, Bulgaria	43.6086, 28.0705	0,810	0,005
Dropla, Bulgaria	43.5719, 28.0902	0,740	0,005
Kremena, Bulgaria	43.5461, 28.14389	0,765	0,005
Topola, Bulgaria	43.4350, 28.2058	0,666	0,003
Kavarna, Bulgaria	43.4531, 28.3241	0,580	0,002
Belgun, Bulgaria	43.5922, 28.3233	0,553	0,003
Vasilevo, Bulgaria	43.6111, 28.1972	0,484	0,003
Dubovnik, Bulgaria	43.7058, 27.9511	0,528	0,003
Krasen, Bulgaria	43.8741, 27.9166	0,512	0,003
Kardam, Bulgaria	43.7308, 28.1569	0,485	0,002
Rogozina, Bulgaria	43.7163, 28.2566	0,550	0,003
Shabla, Bulgaria	43.5308, 28.5205	0,460	0,002
Sokolovo, Bulgaria	43.4897, 28.3411	0,682	0,005
Dobrich, Bulgaria	43.6158, 27.8627	0,754	0,004
Ovcharovo, Bulgaria	43.7111, 27.8386	0,962	0,005
Svoboda, Bulgaria	43.7625, 27.8030	0,920	0,005
Krushari, Bulgaria	43.8322, 27.7738	0,440	0,003
Ognur, Bulgaria	43.8166, 27.5588	0,720	0,005
Mali izvor, Bulgaria	43.7913, 27.4688	0,333	0,002
Tervel, Bulgaria	43.7783, 27.3683	0,222	0,001
Kochmar, Bulgaria	43.6938, 27.4575	0,444	0,001
Geshanovo Bulgaria	43.6733, 27.5363	0,260	0,001
Yambol, Bulgaria	42.5031, 26.4650	0,548	0,004
Glavaci, Bulgaria	43.3087, 23.3655	0,620	0,005
Sadovo, Bulgaria	42.0790, 24.9704	0,555	0,003
Novaci, N. Macedonia	41.0552, 21.4276	0,670	0,005
Kumanovo, N. Macedonia	42.1314, 21.7557	0,322	0,002
Pageo, Greece	40.9803, 24.1198	0,460	0,002
Felotas, Greece	40.6788, 21.7913	0,628	0,004
Kavala, Greece	43.3087, 23.3655	0,615	-
Calarasi, Romania	44.2948, 27.3512	0,762	0,005
Punghina, Romania	44.2996, 22.9190	0,820	0,005
Backa Topola, Serbia	45.8228, 19.6892	0,540	0,003
Deveti Maj, Serbia	43.3244, 21.8100	0,585	0,004
Bisko selo, Croatia	45.1550, 18.1868	0,622	0,005
Edirne, Turkey	41.6615, 26.6973	0,495	0,002

The results of the study on the content of Se in soils and wheat grains are presented in Table. I. The exact sampling coordinates and the area of the settlement are marked. The highest values of Se in the soil were found in the lands of Ovcharovo and Svoboda, Bulgaria. The lowest values were found in the area of Geshanovo and Tervel. All of them are located in the northeastern Bulgaria. In the other results, cardinal conclusions cannot be drawn to localize the Se content by a geographic point of view. The data from Table I show that the Se content of the tested soils was in the range 0.222– 0.962 $mg.kg^{-1}$. The variation coefficient was 28.956%. The results of the analysis for Se content in wheat grains indicated extremely low values of 1 to 5 $\mu g.kg^{-1}$, which in most cases correlate with the soil content. Comparison with similar research in neighboring Romania and Serbia [10] shows similar levels but slightly higher than those found in Bulgaria. The variation coefficient for the Se content of wheat is slightly higher than in the soils - 41.176 % (Table II). In the same settlements, the content of Se in the soil was also very low.

A correlation and regression analysis was made between Se content in soil and wheat (Fig. 1). The correlation coefficient (0.859) indicated the existence of a very good correlation between the concentration of Se in soils and wheat. The coefficient of determination indicated that about 74% of the Se content of the plants was due to its concentration in the soil. Regression coefficients were statistically significant at a critical level of significance of 0.01. The observed level of significance for these coefficients was less than the critical level of significance ($\alpha_s < \alpha$). The linear model had the following specific analytical form: $y = 0,0069x – 0,0006$. The model can be used to predict Se content in wheat based on soil Se content.

TABLE II
STATISTICAL ANALYSIS OF RESULTS FOR SE CONTENT IN SOILS AND WHEAT GRAINS

Statistical parameters	Se in soil	Se in wheat grains
Mean	0,5864	0,0034
Std. Deviation	0,1698	0,0014
Range	0,740	0,004
Minimum	0,220	0,001
Maximum	0,960	0,005
CV, %	28,956	41,176

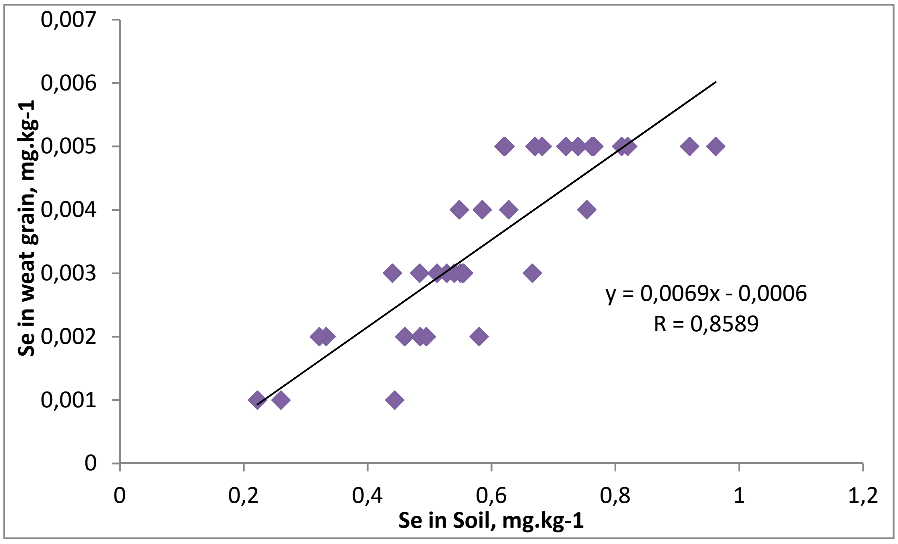

Fig. 1 Correlation between Se concentration in soils and wheat

IV. CONCLUSIONS

The results of the presented scientific research are extremely important for the region of the Balkan Peninsula and especially for northeastern Bulgaria, which is a major grain-producing region for the country. The presented results give knowledge; fill in missing "white spots" about the availability and stock of Se soils. It is a chemical element of immense importance and impact on the health status of the population, ecology, nutrition of the population and having a direct connection with social policy as the main source of Se in the human organism for this geographical area is wheat and products from its processing - bread and bakery products. A significant Se deficiency in soil ranging from 0.1 to 0.9 $mg.kg^{-1}$ was found to be commensurate with the values measured in the neighboring regions of Romania. The Se content of wheat grains is within the range of minimum detectable concentrations by these methods and was in the range of 0.001 to 0.005 $mg.kg^{-1}$. Statistical analyses showed a correlation between the content of Se in the soil and its content in wheat grains. The data confirm trends and require measures to be taken to offset the effects of this deficit, which may be by encouraging farmers to use Se-enriched fertilizers or reinforcement of wheat flour with Se or mixing with wheat flour produced in other climatic zones. Recently, there has been practice adding nutritional supplements containing Se to bakery products to compensate for the deficiency of Se.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support by the Bulgarian National Science Fund (Projects DFNI 06/1).

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