Research Article

Selenium Content in Soil and Wheat Grain in Bulgaria

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Abstract

Selenium (Se) is an essential but highly toxic element. Its organic compounds play an important role in biochemistry and nutrition of the cells. Shortage or surplus of this element leads to the occurrence of socially significant diseases. Se concentrations in different regions of the world and its levels in different foods vary widely. Bulgaria does not appear in the World Atlas of Se, and the scarcity of data about the neighboring countries shows serious lack of Se, causing concern about human health in the region. As a result of the present study, data on the status of selenium in soils and wheat from 60 points from the main grain-producing regions of Bulgaria. The results show that there is a significant deficiency of selenium in the soil and especially in the grain of wheat, which is a major source of selenium and its entry into the human body for our geographical areas through the bread.

Keywords: *Selenium; Status; Soil; Concentration; Wheat Grain*

Introduction

Selenium is an essential, yet highly toxic element. Its organic compounds play an essential role in the biochemistry and nutrition of the cells. Two main characteristics distinguish selenium from the other essential elements: a 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 selenium can cause socially significant diseases, some of which are Keshan and Kashin - Beck diseases [1]. Selenosis is a disease in both animals and humans, which is due to an excess of selenium in the body. Intake of selenium can counteract the toxic effects of heavy metals in foods and helps the body to rapidly and effectively eliminate them by forming complexes with them [2]. Selenium 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 selenium, RNA viruses such as influenza, AIDS, hepatitis B and C develop much faster. It is considered

that selenium 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 selenium is absent or present, but in small concentrations, the most important unit of the antioxidant protection will not work.

The distribution of selenium 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 foods lead to an inability to use universal tables for food composition with an accurate assessment of selenium intake. To solve this problem and evaluate the need for selenium 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 Selenium World Atlas [6]. It has been made based on data from different studies, which illustrate the deficit, adequacy or toxicity of selenium. 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 selenium-enriched fertilizers on pastures to combat its deficiency in livestock. Self-healing with selenium supplementation is widely practiced. Increasingly, consumers are offered selenium-enriched food products. European countries have extensive research related to the selenium status of the continent. Among them are the countries of Western Europe, Scandinavia and Russia. On the Balkans, the most significant studies on selenium status are those in Greece, Serbia and Romania [7]. About the levels of selenium in soils, cereals and garlic, the authors of the world atlas noted that 'all the data suggest a serious lack of selenium'. For some regions, the levels of Se in garlic, grain, human serum and hair are close to those in the low selenium area of China [8]. The main nutritional source of selenium for the human body in our geographic area is wheat and the products from its processing – bread and bakery products. In Hungary, the Se content in wheat ranged from 5 to 235 μg.kg^{-1} [9]. Low Se values have been reported from Yugoslavia [10] in the range of 3.6 to 65.5 μg.kg^{-1} with an average of 18 μg.kg^{-1}. The most extreme values for the Se content of wheat were reported from Sweden, Germany, Scotland and Norway and ranged from 9 to 34 μg.kg^{-1} [11].

This has led to the need for reinforcement of the wheat flour with selenium or for mixing it with wheat flour obtained from other climatic zones. Unfortunately, the name of Bulgaria on the selenium world atlas is not present. From the scant information about selenium levels in Bulgaria, it can be concluded that there may be a shortage of selenium in the national diet. This defines the main objective of our investigate - research into the soil and wheat grain selenium content in the major grain-producing regions in Bulgaria and the levels of selenium which enters the human body through bread and bakery products. This study will contribute to new 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.
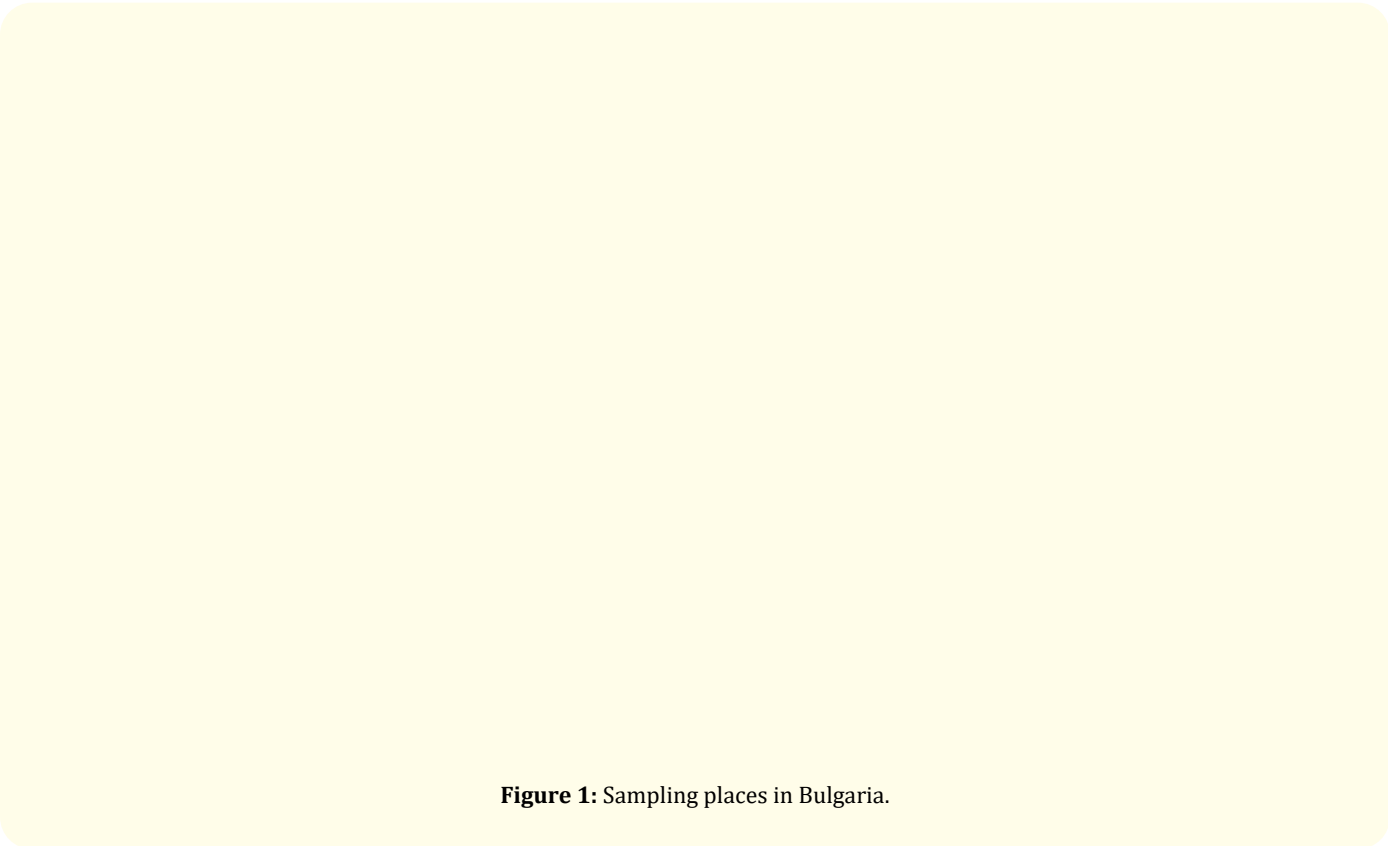
Materials and Methods
Sampling

When we choose the areas for sampling, we take into consideration the current location of the main arable areas for industrial grain production in Bulgaria. Most of those regions characterized by soils of chernozem type. The total number of points for soil sampling is 60 from the major grain-producing area in Bulgaria (Figure 1). The sampling was carried out following the Bulgarian state standard (BDS). From each point, three parallel samples were taken from a depth of 0 - 20 cm. The results were processed using statistical methods. The sampling points were described in adequate coordinates using the GPS. The locations for the sampling of wheat grain match those from which the soil samples were taken. The grain samples were taken during the period of technical maturity which in Bulgaria is from 15th June to 25th July, depending on the weather conditions. The transportation, homogenization and taking an average sample for analysis were done following the requirements of BDS.

Decomposition of soil samples

We have used the method of microwave mineralization [12,13]. 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 selenium, 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 (a ramp) for a maximum temperature of 160°C and decomposition time of 15 minutes. After completion of the procedure, first, the vessels were cooled to room temperature for about 30 minutes, then weighed and finally opened and their content was transferred quantitatively into a volumetric flask and made up to the nominal volume (100 cm^3). The undissolved components were separated by filtration or centrifugation.

Decomposition of wheat grain samples

Here again, we have used the method of microwave mineralization following the procedure below: 2g of ground, homogenized

Figure 1: Sampling places in Bulgaria.

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.

Quantitative measurement of the concentration of elements. We have used the method of ICP-OES. The quantification was made using the method of the calibration line. 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.

Descriptive statistics, correlation and regression analysis were performed using the SPSS program for Windows.

Results and Discussion

The results of the study on the content of selenium in soils and wheat grains are presented in table 1. The exact sampling coordinates and the area of the settlement are marked. The highest values of selenium in the soil were found in the lands of Ovcharovo, Svoboda, Zmeevo, Kremena and Dropla. Geographically these settlements are located in the northeast of the town of Dobrich. The content of selenium was in the range of 0.6 - 0.96 mg.kg^{-1}. The lowest values were found in the area of Geshanovo, Lovchantsi, Miladinovci and Tervel. In the other results, cardinal conclusions cannot be drawn to localize the selenium content by a geographic point of view. The data from table 2 shows that the selenium content of the tested soils was in the range of 0.007 to 0.962 mg.kg^{-1}. The variation coefficient was 43,8526%. The results of the analysis for selenium content in wheat grains indicated extremely low values of 0,3 to 6 µg.kg^{-1}, which in most cases correlate with the soil content. Comparison with similar research in neighboring Romania and Serbia [7,10] shows similar levels but slightly higher than those found in Bulgaria. The variation coefficient for the selenium content of wheat was close to that for soils - 53.3333%.

Place	GPS coordinates	Se in soil (mg.kg^{-1})	Se in wheat grain (mg.kg^{-1})
Zmeevo	43.6086, 28.0705	0,810	0,005
Dropla	43.5719, 28.0902	0,740	0,005
Kremena	43.5461, 28.1438	0,765	0,005
Topola	43.4350, 28.2058	0,666	0,003
Kavarna	43.4531, 28.3241	0,580	0,002
Belgun	43.5922, 28.3233	0,553	0,003
Vasilevo	43.6111, 28.1972	0,484	0,005
Dubovnik	43.7058, 27.9511	0,528	0,005
Krasen	43.8741, 27.9166	0,512	0,005
Kardam	43.7308, 28.1569	0,485	0,002
Rogozina	43.7163, 28.2566	0,550	0,003
Durankulak	43.6988, 28.5213	0,022	0,005
Shabla	43.5308, 28.5205	0,460	0,002
Sokolovo	43.4897, 28.3411	0,682	0,005
Dobrich-Paskal	43.6158, 27.8627	0,754	0,004
Ovcharovo	43.7111, 27.8386	0,962	0,005
Svoboda	43.7625, 27.8030	0,920	0,005
Krushari	43.8322, 27.7738	0,440	0,003
Alexandriya	43.8925, 27.7533	0,395	0,002
Ognyanovo	43.8905, 27.6844	0,383	0,002
Ognur	43.8166, 27.5588	0,720	0,005
Mali izvor	43.7913, 27.4688	0,333	0,002
Tervel	43.7783, 27.3683	0,222	0,001
Kochmar	43.6938, 27.4575	0,444	0,001
Geshanovo	43.6733, 27.5363	0,260	0,001
Miladinovci	43.6294, 27.6233	0,008	<0,001
Lovchanci	43.6127, 27.7011	0,007	<0,001
Momcilgrad	41.5147, 25.4115	0,340	0,003
Duvanlii	42.3789, 24.7180	0,342	0,002
Tsaratsovo	42.2015, 24.6937	0,411	0,005
Vetren	42.2649, 24.0646	0,180	0,004
Zhitosvyat	42.4754, 26.9744	0,333	0,005
Susam	41.9562, 25.3481	0,380	0,005
Kolenec	41.8500, 25.3309	0,324	0,003
Asenovgrad	42.0264, 24.9465	0,370	0,002
Spahievo	41.8915, 25.3321	0,333	0,002
Hadjidimovo	41.5085, 23.8614	0,422	0,005
Pazardzik	42.1827, 24.2630	0,371	0,002
Septemvri	42.1919, 24.1403	0,364	0,001
Kaloyanovo	42.3193, 24.7034	0,368	0,001
Plovdiv	42.1485, 24.8252	0,366	0,001
Sredets	42.2311, 25.6605	0,350	0,001
Mednikarovo	42.1322, 25.9621	0,155	0,001
Bryast	42.1236, 25.6382	0,640	0,005
Opan	42.2039, 25.7241	0,360	0,003
Plodovitovo	42.1858, 25.2028	0,344	0,003
Gorski Izvor	42.0119, 25.4452	0,370	0,002
Galabovo	42.1434, 25.8444	0,388	0,003
Gradina	42.1711, 25.1842	0,360	0,003
Haskovo	41.9746, 25.5402	0,414	0,005
Kirilovo	42.3734, 25.5471	0,366	0,002
Bijala Reka	42.0572, 25.2910	0,390	0,003
Ivanovo	43.7309, 26.0443	0,366	0,002
Karnobat	42.5875, 27.1201	0,322	0,002
Burgas	42.4313, 27.6375	0,366	0,002
Vinarovo	42.2847, 25.4463	0,340	0,002
Yambol	42.5031, 26.4650	0,940	0,006
Glavaci	43.3087, 23.3655	0,620	0,005
Sadovo	42.0790, 24.9704	0,555	0,004
Kamenar	43.4568, 26.6540	0,440	0,002
Stamboliiski	42.1168, 24.5248	0,380	0,003

Table 1: Observed concentrations of selenium in different places from Bulgaria.

Statistical parameters	Se in soil	Se in wheat grains
Mean	0,4506	0,0030
Std. Deviation	0,1976	0,0016
Range	0,9550	0,0057
Minimum	0,0070	0,0003
Maximum	0,9620	0,0060
CV, %	43,8526	53,3333

Table 2: Statistical analysis of results for selenium content in soils and wheat grains.

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A correlation and regression analysis were made between selenium content in soil and wheat (Figure 2). The correlation coefficient (0.6891) indicated the existence of a good correlation between the concentration of Se in soils and wheat. The correlation coefficient was statistically significant at a critical level of significance of 0.01. The observed level of significance for this coefficient was less than the critical level of significance ($\alpha_s < \alpha$). The coefficient of determination indicated that about 47% of the selenium content of the plants was due to its concentration in the soil. The results of the F-test application showed that the Linear model adequately reflects the studied relationship (the empirical characteristic was: F = 52,465 and the observed level of significance had a very small value α_s = 0,0004). The Linear model had the following specific analytical form: y = 0,0054.X + 0,0006.

Figure 2: Correlation between selenium concentration in soils and wheat.

Conclusion

The results of the presented scientific research are extremely important for the region of the Balkan Peninsula and especially for Bulgaria. The presented results give new knowledge, fill in missing "white spots" about the availability and stock of selenium 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 the social policy as the main source of selenium in the human organism for this geographical area is wheat and products from its processing - bread and bakery products. A significant selenium 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 and Serbia. The

selenium 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 selenium in the soil and its content in wheat grains. This data confirms trends and requires measures to be taken to offset the effects of this deficit, which may be by encouraging farmers to use selenium-enriched fertilizers or reinforcement of wheat flour with selenium or mixing with wheat flour produced in other climatic zones. Recently, there has been practice adding nutritional supplements containing selenium to bakery products to compensate for the deficiency of selenium.

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