

## SELENIUM STATUS IN SOIL AND WHEAT GRAIN OF NORTHEAST REGION OF BULGARIA

Stefan Krustev<sup>1\*</sup>, Violina Angelova<sup>1</sup>, Penka Zaprjanova<sup>1</sup>, Margarita Nankova<sup>2</sup>, Krasimir Ivanov<sup>1</sup>

<sup>1</sup>Agricultural University – Plovdiv

<sup>2</sup>Dobroudzha Agricultural Institute – General Toshevo

\*Email: f104@avb.bg

### Abstract Abstract

Selenium (Se) is an essential but highly toxic element. Its organic compounds play an important role in the 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 neighbouring 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 27 points from the main grain-producing region of Bulgaria – *Dobroudzha* was obtained. 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 for the human body supplied by bread consumption for our geographical areas.

**Keywords:** selenium, 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 (Ge and Yang, 1993). 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 (Rosenfeld et al., 1964). 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 defence 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 (Magos and Webb, 1980). 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<sup>-1</sup>, 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 (Gerla, 2010), in most European countries it is about 40 µg/day, and in some parts of China, it is from 3 to 22 µg/day (Tan et al., 2002). 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 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 (Oldfield, 2002). It has been made on the basis of 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 practised. 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 (Lakatusu et al., 2010). 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 (Xing et al., 2015). 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  $\mu\text{g}\cdot\text{kg}^{-1}$  (Alfthan et al., 1992). Low Se values have been reported from Yugoslavia (Maksimovic et al. 1992) in the range of 3.6 to 65.5  $\mu\text{g}\cdot\text{kg}^{-1}$  with an average of 18  $\mu\text{g}\cdot\text{kg}^{-1}$ . The most extreme values for the Se content of wheat were reported from Sweden, Germany, Scotland and Norway and ranged from 9 to 34  $\mu\text{g}\cdot\text{kg}^{-1}$  (Kumpulainen et al., 1993).

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 region in Bulgaria – Dobroudzha 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

**1. 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. This is the region of Dobroudzha, northeast Bulgaria, characterized by soils of chernozem type. The total number of points for soil sampling was 27 from the major grain producing area in Bulgaria – region of Dobroudzha

(Fig. 1). The sampling was carried out in accordance with BS. 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 system. The locations for the sampling of wheat grain match those from which the soil samples were taken. The grain samples are taken during the period of technical maturity which in Bulgaria is from 15<sup>th</sup> June to 15<sup>th</sup> July, depending on the weather conditions. The transportation, homogenization and taking an average sample for analysis are done in accordance with the requirements of BS.

**2. Decomposition of soil samples.** We have used the method of microwave mineralization (*EPA method*, 1996). 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  $\text{cm}^3$ ). The undissolved components were separated by filtration or centrifugation.

**3. Decomposition of wheat grain samples.** Here again, we have used the method of microwave mineralization following the procedure below: 2g of ground, homogenized and air-dry sample was transferred to a Teflon reaction vessel. Then 15  $\text{cm}^3$  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  $\text{cm}^3$ ). The undissolved components were separated by centrifugation or filtration.

**4. 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<sup>3</sup> aqua regia.

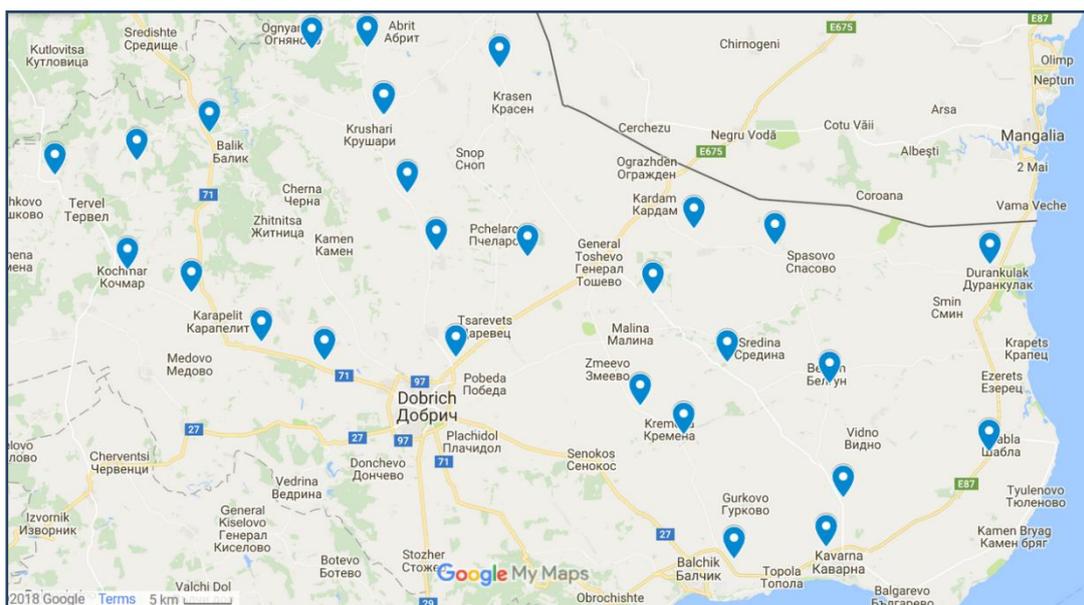
**5. Descriptive statistics, correlation and regression analysis were performed using the SPSS program for Windows.**

## RESULTS AND DISCUSSION

The results of the study on the content of selenium in soils and wheat grains are presented in the 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 central part of Dobroudzha, northeast of the town of Dobrich. The content of selenium was in the range of 0.6 - 0.96 mg.kg<sup>-1</sup>. The lowest values were found in the area of Geshanovo, Lovchantsi, Miladinovci and Tervel. All of them are located in the western part of Dobroudzha, about 20–30 km west of the city of Dobrich. 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<sup>-1</sup>. The variation coefficient was 50.58%. The results of the analysis of selenium content in wheat grains indicated extremely low values of 3 to 5 µg.kg<sup>-1</sup>, which in most cases correlate with the soil content. Probably we have a weakly selective form of selenium that is

difficult to assimilate from plants. Comparison with similar research in neighbouring Romania and Serbia (Lakatusu, 2010 and Maksimovic, 1992) 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 – 47.059% (Table 2). When performing the descriptive statistics for Se in the plants, the last two points were excluded – the villages of Miladinovci and Lovchanci, where the concentration of Se in wheat was below the detection limit. In the same settlements, the content of Se in the soil was also very low.

A correlation and regression analysis were made between selenium content in soil and wheat (Figure 2). The correlation coefficient (0.809) indicated the existence of a very good correlation between the concentration of Se in soils and wheat. The coefficient of determination indicated that about 66% 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 power model adequately reflects the studied relationship (the empirical characteristic was:  $F = 41,782$  and the observed level of significance had a very small value  $\alpha_s = 0,0003$ ). 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 power model had the following specific analytical form:  $y = 0,0064x^{1,2211}$ . The model can be used to predict selenium content in wheat based on soil selenium content.



**Fig. 1. Sampling places in northeastern Bulgaria – region Dobroudzha**

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

Place	GPS coordinates	Se in soil (mg.kg <sup>-1</sup> )	Se in wheat grain (mg.kg <sup>-1</sup> )
Zmeevo	43.6086, 28.0705	0,810	0,005
Dropla	43.5719, 28.0902	0,740	0,005
Kremena	43.5461, 28.14389	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

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

Statistical parameters	Se in soil	Se in wheat grains
Mean	0,5069	0,0034
Std. Deviation	0,2564	0,0016
Range	0,955	0,004
Minimum	0,007	0,001
Maximum	0,962	0,005
CV, %	50,582	47,059

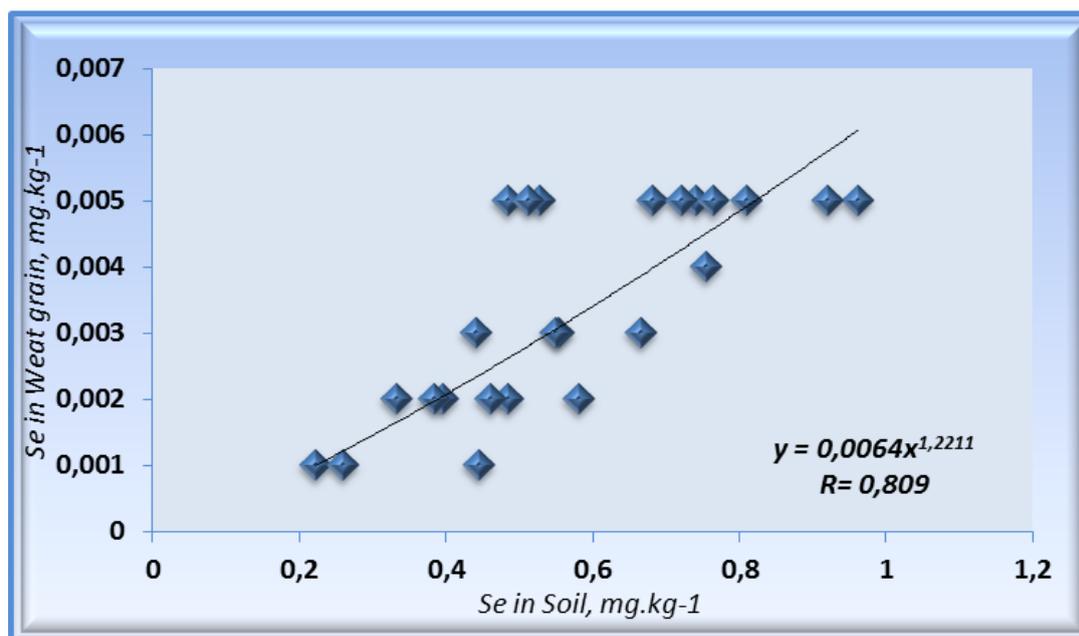


Fig. 2. Correlation between selenium concentration in soils and wheat

## CONCLUSIONS

1. 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 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 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.

2. A significant selenium deficiency in soil ranging from 0.1 to 0.9 mg.kg<sup>-1</sup> was found to be commensurate with the values measured in the neighbouring regions of Romania.

3. 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<sup>-1</sup>.

4. 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. In many countries, it is widely practised to feed selenium feed supplements to food and bakery products to compensate for the selenium deficiency.

## Acknowledgement

This work is supported by the Bulgarian Ministry of Education, Project DFNI 06/21.

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