

## SELENIUM IN ROCK-SOIL-PLANT SYSTEM IN THE SOUTH-EASTERN PART OF ROMANIA

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**Abstract:** Selenium is a trace element with multiple functions in animal and human nutrition. Deficiency in selenium reported for sheep bred in Central Dobrogea, required to initiate a comprehensive study on the abundance of total Se in parental rocks, in soil and wheat plants (the whole plant, on 5-6 stage by Feeks scale, and the grain at maturity) from the southeastern Romanian Plain and Central and South Dobrogea. 17 samples of rocks and parental materials, 101 soil samples, 83 samples of wheat during the vegetation period, and 49 samples of wheat at maturity stage, were analyzed in terms of total and mobile selenium content in rocks and soils, and the total selenium in plants. Also, other chemical properties of the collected samples were determined. Analytical results obtained, compared with similar results from literature, have shown that both in rocks and soils, the selenium content in our country is lower than in other areas of the world, unaffected by the phenomenon of deficiency or toxicity in this microelement. Thus, compared to the normal average total selenium content of the worldwide soils ( $383 \pm 255 \mu\text{g}\cdot\text{kg}^{-1}$ ), in the South-Eastern

Romanian Plain soils and in Dobrogea soils, the average total selenium content is 38%, respectively, 63% lower. Moreover, in Dobrogea deficiency phenomenon is more intense. Average content of mobile selenium, soluble  $\text{CH}_3\text{COONH}_4$ -EDTA solution at pH 7, of the Central and Southern Dobrogea soils is 3.5 times lower compared with that of the South-Eastern Romanian Plain soils ( $14 \mu\text{g}\cdot\text{kg}^{-1}$ ). If in wheat plants during the vegetation the selenium content ( $130 \text{ mg}\cdot\text{kg}^{-1}$ ) was close to normal ( $146 \mu\text{g}\cdot\text{kg}^{-1}$ ), recorded in wheat plants grown in different countries with soils that are not affected by selenium deficiency or excess, in grains of wheat obtained in the south-east of the country the selenium content was lower, and the grains of wheat, particularly those obtained on Dobrogea soils, selenium content tended to be a value below the detection limit of the method ( $0.5 \mu\text{g}\cdot\text{kg}^{-1}$ ) used for analysis. It outlines the need to bio-fortify with selenium the wheat flour obtained from Central and Southern Dobrogea wheat or mixing it with other wheat that was cultivated in other climatic zones.

**Key words:** total selenium content, mobile selenium content, loess, green schist, Chernozem, Kastanozems, wheat

### INTRODUCTION

Selenium is widely distributed in the environment and is one of the essential elements for animals and human, it plays a major role in the activity of the glutathione peroxidase enzyme, of which it is a component (ROTRUCK et al., 1973). Selenium is a trace essential chemical element, having antiviral and anti-tumor effects (DEELESTRA, 1982). It was highlighted its role in plant nutrition (LÄUCHLI, 1993, NOWAK et al., 2003), resulting in even crop increases by taking into soil, the plant or seed (LĂCĂTUȘU et al., 2003). Se content in plants is considered to reflect Se content of the soil, where the plants grow. In this context, information on the Se content in soil, especially in agriculture soil, is vital to prevent Se deficiency for human and livestock.

Romania is situated in an area of Europe with deficiency trends in this microelement. There have been recorded cases of selenium deficiency in calves, lambs, piglets and young

buffaloes in the central part of the country (SALANTIU, 1970) and in lambs in Central Dobrogea. This paper brings contributions related to the abundance of selenium in rock-soil-plant system in the southeast part of the country, including the area in which there were frequent cases of myodystrophy in sheep, caused by selenium deficiency (LĂCĂTUȘU et al., 2002).

#### MATERIAL AND METHODS

Research has an expeditionary character, during which samples from rocks, soil from the upper horizon (0-20 cm) of major soil types of investigated areas were collected (Figure 1), and samples of wheat plants, both during the vegetation period, at the 5-6 stage on the Feeks scale (aerial part) and maturity (wheat grains), were collected. Harvesting of wheat plants and wheat grains was made in the same places where soil samples were collected. Wheat was chosen as test plant because it represents an important transmission vector of selenium, and not only, especially as grain in food of animals and humans.

17 rock samples, 81 soil samples and 81 samples of plants (green plants and grains) were collected. Soil samples belonging to the main soil types existing in studied areas: Typical Chernozem, Calcareous - Kastanic Chernozem in the South-Eastern Romanian Plain and Kastanozems, Calcareous-Brownish Chernozem, Regosols and Alluvial Soils in Central and Southern Dobrogea.

Total selenium and mobile content in rocks and soil, and total selenium content of plants in vegetation and in grain at maturity was determined in the laboratory. For determination of total selenium in rocks and soil, disaggregating of samples was made with a mixture of concentrated mineral acids ( $\text{HNO}_3$  and  $\text{HClO}_4$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). Mobile selenium from rocks and soil was extracted with  $\text{CH}_3\text{COONH}_4$ -EDTA solution, at pH 7.0 (after Lăcătușu et al., 1987). Total selenium in plant was dozed in hydrochloric solutions resulted after solubilization of the ash obtained at  $475^\circ\text{C}$ . All dosages of selenium have been performed by atomic absorption spectrometry method, as a result of carrying away in air-acetylene flame of hydrogen selenate, formed as a result of reduction reaction of selenium with sodium boron hydride.

Analytical results were processed statistically, for scattering parameters (standard deviation, minimum and maximum values) and grouping centre parameters (arithmetic mean, geometric mean, and median).

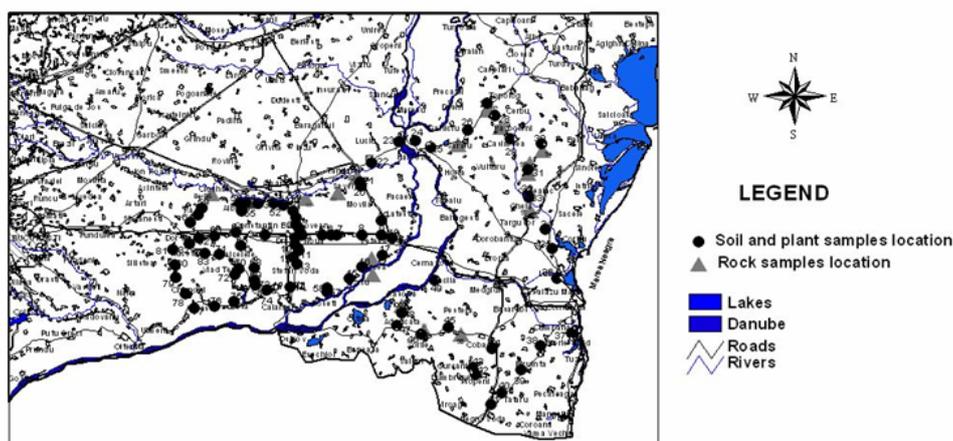


Figure 1. Location of sampling points of rock, soil and plant

## RESULTS AND DISCUSSION

### Selenium abundance in the rocks and parental materials

The main parental rocks and materials that were developed soils investigated are: loess (Romanian Plain), and loess, green schist and limestone (Central and Southern Dobrogea). Samples were taken from natural openings.

Analytical data of the total selenium content determined in rocks and parental material presents low values, lower than  $100 \mu\text{g}\cdot\text{kg}^{-1}$ . Although loess from southern Dobrogea has a slightly lower content of total selenium, however, the values determined in the three areas of investigation are close (Table 1), which may prove genetic unity of loess in these areas.

Table 1.

Medium total and mobile selenium content ( $\mu\text{g}\cdot\text{kg}^{-1}$ ) in rocks and parental materials on which the soil formed in South-Eastern Romanian Plane and Central and Southern Dobrogea

Areas	Rock type	total Se	mobile Se
South-Eastern Romanian Plane	loess	$97 \pm 22$	$9,4 \pm 2,6$
	loess	$100 \pm 15$	$4,6 \pm 0,5$
Central Dobrogea	green schist	$22 \pm 7$	$4,6 \pm 1,0$
	Jurassic limestone	$20 \pm 3$	$30 \pm 0,8$
Southern Dobrogea	loess	$84 \pm 18$	$4,8 \pm 1,3$

Total Se in clay ( $400-600 \mu\text{g}\cdot\text{kg}^{-1}$ ), sandstone ( $50-80 \mu\text{g}\cdot\text{kg}^{-1}$ ), limestone ( $30-100 \mu\text{g}\cdot\text{kg}^{-1}$ ) in Kabata – Pendias and Pendias (2001).

If we compare these values with analytical data on total Se content in similar types rocks (clay, sandstone, in Kabata-Pendias and Pendias, 2005), results that in the loess located in the south-eastern part of the country, including green schist and limestone from the Dobrogea, total Se content is much lower.

The mobile Se content, soluble in  $\text{CH}_3\text{COONH}_4$ -EDTA solution at pH 7.0, represents about 10% of total Se. It is noted that mobile Se in loess of south-eastern Romanian Plate is double that those existing in the loess or green schist or Jurassic limestone from Dobrogea (Table 1).

Considering both low total content of Se in green schist and limestone from Dobrogea, and low mobile selenium content of these Dobrogea rocks and loess, any soil that could not inherit in Dobrogea a satisfactory level of selenium for plant nutrition and transfer of this microelement in plant nutrition and hence on the food chain in animals and humans.

### Selenium abundance in soils

The values of statistical parameters of total and mobile Se content in soils of two investigated areas are contrasting, for the purposes of reporting to higher values in soils of South-eastern Romanian Plain soils compared to those of Central and Southern Dobrogea (table 2). Thus, the average of total Se content in Dobrogea soils is only 60% of the total Se content of soils in the South-Eastern Romanian Plain. Similarly, the mobile Se content of Dobrogea soils is only 28% of existing mobile Se content in soils of South-Eastern Romanian Plain. If we compare the average values of total Se content in soils of both areas (Table 2) with the mean of  $383 \pm 255 \mu\text{g}\cdot\text{kg}^{-1}$ , representing the total selenium in the upper horizons of many soils in different countries (KABATA-PENDIAS AND PENDIAS, 2001), result that the total selenium in soils of both Romanian areas is only 62% (South-Eastern Romanian Plain), and 38% (Central and Southern Dobrogea) of this value. Therefore, it is confirmed that our country is located in an area with low selenium levels. Of the two investigated areas, Dobrogea is

distinguished by much lower values, which could be related to the incidence of myodystrophy disease in sheep.

*Table 2.*  
Statistical parameters of total and mobile Se contents ( $\mu\text{g}\cdot\text{kg}^{-1}$ ) in the upper horizon (0-20cm) of soils from South-Eastern Romanian Plane and Central and Southern Dobrogea (cultivated with wheat - agricultural year 2007/2008)

Statistical parameter	South-Eastern Romanian Plate		Central and Southern Dobrogea	
	total Se	mobile Se	total Se	mobile Se
n (number of samples)	57	57	26	26
Xmin (Minimum)	5	3	6	2
Xmax (Maximum)	382	26	306	6
X (arithmetic mean)	237	14	143	4
$\sigma$ (standard deviation)	83	7	76	1
Xg (geometric mean)	192	7	104	4
CV% (variation coefficient)	35	50	53	25
Me (Median)	256	20	166	4
Mo (Module)	273	5;21	177	4

#### Selenium in green wheat plants and wheat grain

As a consequence of contrasting content of selenium, especially mobile selenium, existing in soils of investigated areas, the selenium content of wheat plants was also different. Although green wheat plants grown on soils of Dobrogea has accumulated a certain amount of selenium, it was, on average, almost 50% less than that of green wheat grown on soils of South-Eastern Romanian Plain. Marked differentiation was achieved in grain (Table 3). Basically, wheat grown in Dobrogea not accumulated selenium, while the grains of wheat grown on soils of south-eastern Romanian Plain, selenium has been gained, however, at slightly below the average value ( $146 \pm 189 \mu\text{g}\cdot\text{kg}^{-1}$ ), characteristic for wheat grains harvested from 13 wheat-growing countries of the world (KABATA-PENDIAS, PENDIAS, 2001).

*Table 3.*  
Statistical parameters of total Se contents ( $\mu\text{g}\cdot\text{kg}^{-1}$ ) in green wheat plants, at the 5- 6 stage on the Feeks scale, and in wheat grains cultivated on soils from South-Eastern Romanian Plane and Central and Southern Dobrogea (agricultural year 2007/2008)

Statistical parameter	South-Eastern Romanian Plate		Central and Southern Dobrogea	
	green plants	grain	green plants	grain
n	57		26	26
Xmin	10	0	6	under method detection limit ( $0,5 \mu\text{g}\cdot\text{kg}^{-1}$ )
X max	80	312	55	
X	39	130	22	
$\sigma$	18	111	14	
Xg	34	18	18	
CV%	46	85	64	
Me	40	126	18	
Mo	17; 45	39	13	

A comparative representation of the selenium content in rock-soil-plant system in the two investigated areas is shown in Figure 2.

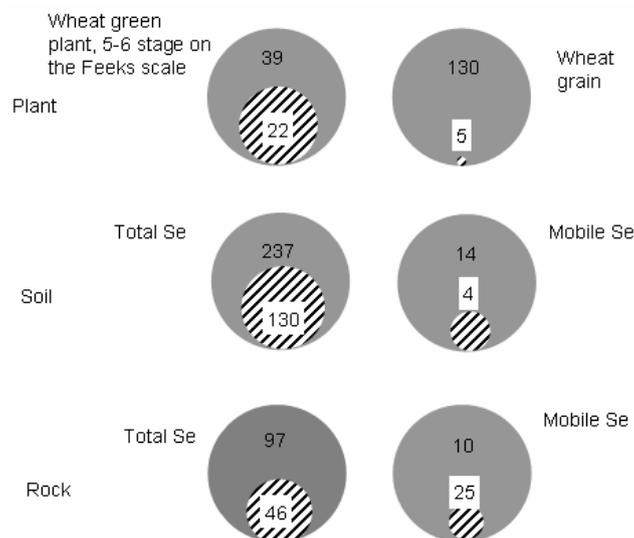


Figure 2. Comparative representation of the selenium contents (medium values,  $\mu\text{g}\cdot\text{kg}^{-1}$ ) in the rock - soil - plant system of Central and Southern Dobrogea (▨) and of the South-Eastern Romanian Plain (●)

### CONCLUSIONS

Average total selenium content of rocks and parental materials from South-Eastern Romanian Plain and Central and Southern Dobrogea is less than that quoted in the literature for rocks and similar materials.

Compared with the average total selenium content in world's soils ( $383 \pm 255 \mu\text{g}\cdot\text{kg}^{-1}$ ) non-affected by this micro-nutrient deficiency or excess, the total content of selenium in soils of South-Eastern Romanian Plain is 38% lower, and in the Central and Southern Dobrogea soils is 62% less.

Average content of mobile selenium, soluble in  $\text{CH}_3\text{COONH}_4$ -EDTA solution at pH 7, in the Central and Southern Dobrogea soils was 3.5 times lower than in the South-Eastern Romanian Plain soils.

Compared to the average of  $146 \mu\text{g}\cdot\text{kg}^{-1}$ , considered representative value for selenium content of the grain of wheat cultivated in different world soils, selenium concentration in wheat grains grown in the South-Eastern Romanian Plain was by 11% lower, while grains wheat grown in Central and South Dobrogea, it was almost zero, however, lower than detection limit of the device ( $<0.5 \mu\text{g}\cdot\text{kg}^{-1}$ ).

It outlines the need to selenium biofortificate the flour produced by wheat cultivated in Central and Southern Dobrogea, or mix this wheat with grains obtained in other pedo-climatic areas.

### BIBLIOGRAPHY

1. DEÉLSTRA H (1982). Sélénium et cancer, la situation en Belgique. *Med. Biol. Environ.*, 10, 29-34
2. KABATA-PENDIAS A, PENDIAS H (2001). *Trace Elements in Soils and Plants*, CRC Press, Boca-Raton - London - New York - Washington D.C.
3. LĂCĂTUȘU R., KOVACSOVICI B., GĂȚĂ GH., ALEXANDRESCU A., (1987), Utilisation of ammonium acetate – EDTA by simultaneous extraction of Zn, Cu, Mn and Fe from soil, *Pub. SNRSS*, 23B, 1-11 (published in Romanian)

4. LĂCĂTUȘU R., TRIPĂDUS I., LUNGU M., CÂRSTEA S., KOVACSOVICS B., CRĂCIUN L. (2002), Selenium abundance in some soils of Dobrogea (Romania) and ovine myodystrophy incidence, Trans. of 21 Workshop "Macro- and Trace Elements", Jena, Germany, 114-119
5. LĂCĂTUȘU R., KOVACSOVICS B., LUNGU M., CÂRSTEA S., LAZĂR R. (2004). Enriching alfalfa in selenium, Trans. of 21 Workshop "Macro- and Trace Elements", Jena, Germany, First volume, 399-410
6. LÄUCHLI A. (1993), Selenium in plants: uptake, functions and environmental toxicity, Bot. Acta, 106, 455-468
7. NOWAK J., KAKLEWSKI K., LIGOCKI M (2004) Influence of selenium on oxidoreductases enzymes activity in soil and plants, Soil Biology and Biochemistry, 36, 1553-1558
8. ROTRUCK J.T., POPE A.L., GANTHER H.E., SWANSON A.B., HAFERMAN D.G., HOEKSTRA W.G., (1973). Selenium: biochemical role as a component of glutathione peroxides, Science, 179, 588-589.
9. SALANȚIU V. (1993), Selenium deficiency by calves, lambs, piglets and young buffalos, PhD Thesis, Agronomic Institute Cluj (published in Romanian).