SELENIUM IN THE ROCK – SOIL SYSTEM FROM SOUTH-EASTERN PART OF ROMANIA

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Abstract: Total and mobile selenium contents in soils and rocks was studied in the South-Eastern part of Romania, namely South and Central Dobrogea and the South-Eastern Romanian Plain. The average total selenium content in the rocks and parent materials is lower than the values presented in literature for rocks and similar materials. The total selenium content of the upper horizon (0-20 cm) of the South-Eastern Romanian Plain soils is 65% higher as compared to the content registered in the Central and South Dobrogea soils (237 and 143 $\mu g \cdot kg^{-1}$, respectively). As compared to the average value of the total selenium content in the soils all over the world considered unaffected by deficiencies or excess (383 ± 255 $\mu g \cdot kg^{-1}$), the total selenium content of the South-Eastern Romanian Plain soils is almost 40% lower and that of the Central and South Dobrogea soils 63% lower. As compared to the average mobile selenium content in the South-Eastern Romanian Plain soils (14 $\mu g \cdot kg^{-1}$), in the soils of Central and South Dobrogea 3.5 times lower average values were registered (4 $\mu g \cdot kg^{-1}$). Between the mobile and total selenium contents on one hand and the aridity index (De Martonne) on the other hand, direct proportionality relations, statistically ensured, have been established. Between the total and mobile selenium contents of the upper horizon of the soils from South-East Romania direct proportionality relations, statistically ensured have been established. The mobile selenium content is higher in the slightly acid soils as compared to the neutral or alkaline ones. Between the mobile and total selenium contents, on one hand, and the humus, total nitrogen, mobile phosphorus and potassium on the other, direct proportionality relations, statistically ensured have been established.

Introduction

Selenium is an essential micro-element for both animal and human nutrition, especially due to its presence in the glutathion-peroxidase composition, an enzyme with anti-oxidant role. Anti-infectious and anti-cancer selenium effects are also

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known (Rotruer and Poue, 1993; Deélestra, 1982). Selenium deficiency can cause animal disease, like liver necrosis with swine, white muscle disease with cattle, exudative diathesis with poultry, and selenium excess generates alkaline disease or staggering in some animals and people. Its role in plant nutrition was lately highlighted (Gissen-Nielsen et al., 1984; Läuchli, 1993; Nowak et al., 2004). Yield increases have been even obtained when administering it in soil, on the plant or on the seed (Lăcătuşu et al., 2003).

Selenium abundance in the environment is low. Thus, the average values range between 50 and 90 $\mu g \cdot kg^{-1}$ in the lithosphere, between below 100 and 2,000 $\mu g \cdot kg^{-1}$ in the pedosphere, around 0.2 $\mu g \cdot L^{-1}$ in the hydrosphere, and from less than 50 to 15,000 $\mu g \cdot kg^{-1}$ in biosphere (Kabata-Pendias and Pendias, 2001).

The low selenium content of the environment components and its relatively difficult analytical chemistry have been impeding on enriching the information regarding this micro-element. The progress registered by the physico-chemical analytical methodology and the occurrence of some selenium deficiency or excess cases in the environment components lately allowed the increased number of scientific papers regarding this micro-element on a worldwide level.

Though information regarding selenium deficiency with some animals existed in our country ever since 1970 (Salanțiu, 1970), truthful data regarding soil and plant selenium content are to be found in papers of Ababi and Dumitrescu (1973), Lăcătuşu and Ghelase (1992), Lăcătuşu et al. (2002). In the last two papers low selenium contents were highlighted in the soils of the haematurigenous areas and cases of ovine miodystrophy have been recorded in Dobrogea, at Sibioara, correlated with low selenium levels in soil and plants.

The present paper highlights the results of the research carried out in the South-Eastern part of Romania, regarding selenium abundance in the rock-soil system of the South-Eastern Romanian Plain and of Central and South.

1. Materials and method

The research had an expeditionary character, rock samples (loess, crystalline schist, carbonates) and soil samples from the upper horizon (0-20 cm) of the main soil types were collected from the mentioned areas.

Figure 1 presents the location of the sampling points. In the South-Eastern Romanian Plain the itinerary focused on two zones. The first one is bordered by the localities: Slobozia, Drajna, Călăraşi, Feteşti, Unirea, Țăndărei, and Giurgeni, and the second one by the localities: Slobozia, Ciochina, Lehliu, Valea Argovei, Mănăstirea, Călăraşi. In Dobrogea the sampling area is bordered by the localities: Vadu Oii, Hârşova, Saraiu, Rahmanu, Casimcea, Cheia, Sibioara, Ovidiu, Agigea, Amzacea, Comana, Negru Vodă, Cobadin, Adam Clisi, Ion Corvin, Alimanu, Cochirleni.

The soil samples (0-20 cm) were collected from the following soil types: Typic Chernozem (Calcic Chernozem); Calcaric Kastanic Chernozem (Calcaro-calcic Chernozem[2]); Kastanozem[1] (Kastanozem[2]); Regosol[1] (Regosol[2]); and Aluviosols[1] (Fluvisol[2]).

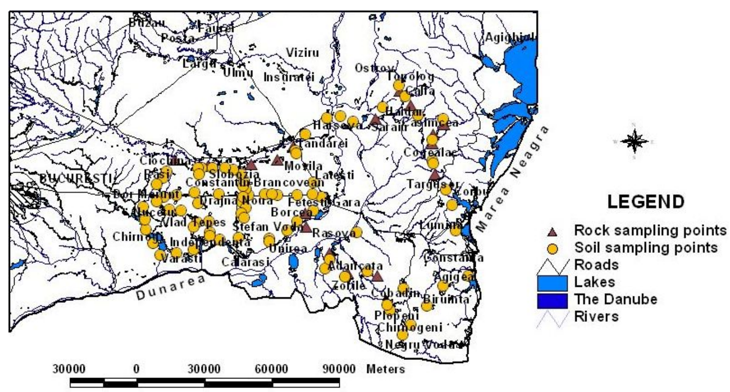

Fig. 1 – The location of the sampling points in the investigated area

The rock samples were collected from natural outcrops in the vicinity of the soil sampling points. They consisted of loess, limestone, and crystalline schist (green schist).

Total selenium contents were determined in the rock and soil samples in the laboratory. The samples were digested with a concentrated mineral acids (nitric and perchloric) and peroxide (H_2O_2) mixture. Then selenium was measured by means of atomic absorption spectrometry using the boron-hydride ($NaBH_4$) reducing procedure and the analysis of the hydrogen selenium that forms. The mobile selenium of the samples was extracted with an 1 *n* ammonium acetate (CH_3COONH_4) and 0.01 *m* ethilen-diamino-tetraacetic acid (EDTA-H_2) solution at pH = 7,0 (Lăcătuşu et al., 1987) and was measured by the already described method.

In order to characterize the soil samples fertility level the next determinations have been carried on: pH by potentiometry with double glass-calomel electrode in aqueous suspension soil:water ratio 1:5; humus content by the Walkley-Black method modified by Gogoaşă, total nitrogen content by the Kjeldahl method; and the mobile forms of phosphorus and potassium soluble in ammonium acetate-lactate, after Ègner-Rhiem-Domingo.

The analytical data were statistically computed and the spreading parameters (xmin, xmax, cv,□) and those of the grouping centre (xg, Me, and Mo) were calculated as well as the correlations of the mobile selenium content with different chemical soil characteristics. The tendency maps for the total and mobile selenium distribution have also been drawn for the research areas using the SURFER software.

2. Results and discussions

2.1 Selenium abundance in rocks and parent materials. The main rocks and parent materials on which the soils developed in the investigated areas are loess in the South-Eastern Romanian Plain, green schist and limestone in Central and South Dobrogea.

The analytical data of the total mobile selenium contents in the analyzed rocks and parent materials are presented in Table 1. Significant content differences are clearly highlighted between the rocks and parent materials of the South-Eastern Romanian Plain and of the Central and South Dobrogea. Thus, the total selenium content of the South-Eastern Romanian Plain loess is 119 $\mu g \cdot kg^{-1}$ in the Eastern part of the investigated area, and it diminishes to 75 $\mu g \cdot kg^{-1}$ in the Western part, but it increases again (100 $\mu g \cdot kg^{-1}$) in the loess from the Central Dobrogea North-Western part. In the green schist, limestone and loess from Southern Dobrogea the total selenium content oscillates in a low values interval, between 8 and 22 $\mu g \cdot kg^{-1}$. On an average, the total selenium contents is 98 $\mu g \cdot kg^{-1}$ in the Romanian Plain loess and in the loess from the Central Dobrogea North-Western part, while in the green schist, limestone, and loess from South Dobrogea the average total selenium content is only 16.7 $\mu g \cdot kg^{-1}$, 5.9 times lower than the total selenium content of the South-Eastern Romanian Plain loess.

Besides the content differences due to the nature of the rocks and parent materials another difference occurs induced by the sampling points' geographic position, namely: the samples from the Western whole investigated area, even from the same type of rock (loess), have higher contents than those from the East.

Concomitantly with the total selenium content values a similitude was registered of the mobile selenium contents decrease (Table 1). In this case, as compared to the average mobile selenium content of the Romanian Plain loess, of 9.4 $\mu g \cdot kg^{-1}$, the average mobile selenium contents of the rocks and parent materials from Central and South Dobrogea were three times lower.

One can conclude that the South Eastern Romanian Plain Loess has, on an average, a total selenium content (98 $\mu g \cdot kg^{-1}$) of almost six times higher than the average total selenium content of the rocks and parent materials from Central and South Dobrogea. Alike, the average mobile selenium content is three times higher in the South-Eastern Romanian Plain loess.

Comparing the obtained analytical values with those mentioned in literature (Adriano, 2001; Kabata-Pendias and Pendias, 2001) regarding total selenium content in similar rocks (tab. 1), it can be noticed that generally they belong to a poor content domain.

Tab. 1 – The average values of total and mobile selenium content ($\mu g \cdot kg^{-1}$) in the rocks and parent materials of soils from South-Eastern Romanian Plain and Central and South Dobrogea, as compared to the average total selenium content of different rocks

Area	Zone number	Rock nature	Total Se		Mobile Se	
			$\bar{x}$	σ	$\bar{x}$	σ
S-E Romanian Plain (the Slobozia – Călăraşi – Feteşti – Ţăndărei – Giurgeni zone)	1	Loess	75	21	10,0	0,8
S-E Romanian Plain (the Slobozia – Ciochina – Lehliu – Mănăstirea – Călăraşi zone)	2	Loess	119	23	8,8	4,5
Central Dobrogea (Vadu Oii, Hârşova, Saraiu zone)	3	Loess	100	15	4,6	0,5
Central Dobrogea (Rahmanu – Casimcea – Râmnicu zone)	4	green schist	22	7	1,0	0,1
Central Dobrogea (Cheia – Sibioara – Ovidiu zone)	5	limestone	20	10	2,0	0,1
South Dobrogea (Amzacea – Comana – Negru Vodă – Cobadin – Pietreni – Ion Corvin – Alimanu – Cochirleni zone)	6	Loess	8	1	4,6	1,3
From Kabata-Pendias and Pendias (2001)		acid rocks clay sandstone limestone	10-50 400-600 50-80 30-100			

3.2 Total selenium abundance in the soils' upper horizon (0-20 cm). The statistical data regarding the total selenium content of the soils upper horizon in the investigated area support the conclusion resulted from the rocks selenium content analysis with respect to the selenium content decrease from West to East. Indeed, all the grouping centre parameters values (Me, and Mo) and even the variation intervals limits diminish from West (Area 2 of the South-Eastern Romanian Plain) to East (Dobrogea). Thus, as compared to the average value of the selenium content from the Area 2, total soil selenium content in Dobrogea is lower by 47%, and lower by 24% as compared to the average total selenium content of the Area 1 (Table 2).

The significant differences between soil total selenium contents of the two areas are highlighted by the frequency histograms presented in fig. 2 and by the total selenium contents tendency map (fig. 3). In the latter the higher intensity of the color on the left side (West) of the image highlights the higher total selenium concentration.

Tab. 2 – Statistical parameters of the total selenium contents (μg·kg^{-1}) of the upper horizon (0-20 cm) of the South-Eastern Romanian Plain and of South and Central Dobrogea soils

Statistical parameters	Romanian Plain			Dobrogea
	Zone 1	Zone 2	Zone 3	
n	23	34	57	26
x_{min}	1	177	1	6
x_{max}	329	382	382	306
$\bar{x}$	189	270	237	143
σ	104	42	83	76
x_g	119	266	192	104
cv (%)	55	16	35	53
Me	199	269	256	166
Mo	203	276	273	177

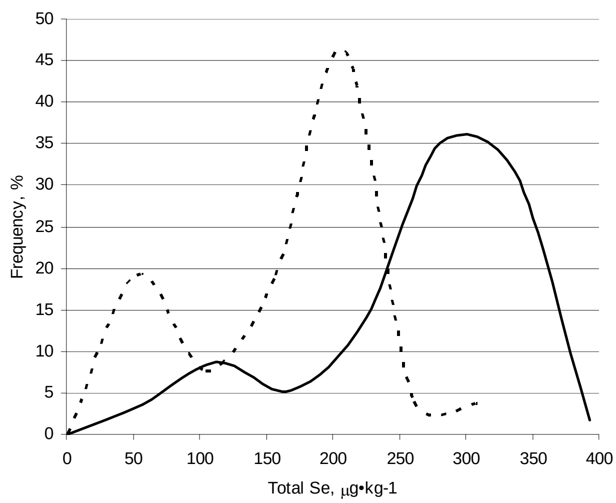

Fig. 2 – Frequency histograms of the total selenium content in the soils (0-20 cm) of the South-Eastern Romanian Plain (▬) and of the Central and South Dobrogea (‒ ‒)

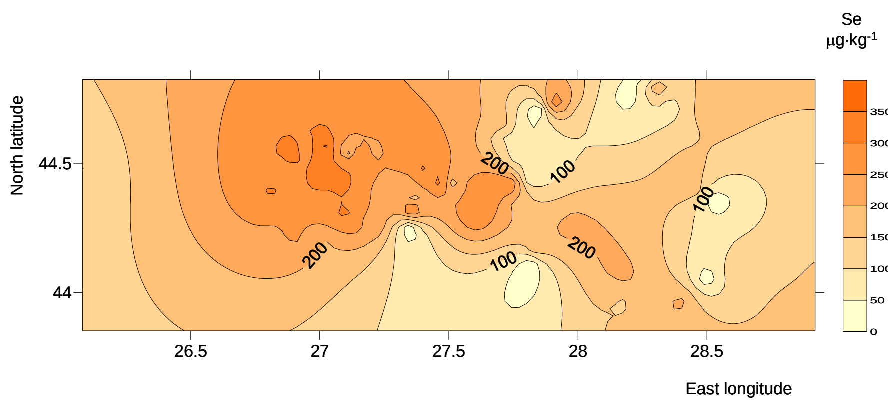

Fig. 3 – Tendency maps of the distribution of total selenium in the upper horizon (0-20 cm) of the South-East Romanian Plain and Central and South Dobrogea soils

Tab. 3 – Content intervals and average values of total selenium in the upper horizon (0-20 cm) of the soils depending of the soil type and location

Soil type	Location	x_{min}	x_{max}	$\bar{x}$	σ	*cv (%)*
Typic Chernozem (CZ ti)	SE Romanian Plain	94	325	239	90	38
	Central and South Dobrogea	178	209	192	16	8
Calcaric Kastanic Chernozems (CZka-kz)	SE Romanian Plain	67	305	198	93	47
	Central and South Dobrogea	12	209	139	64	46
Aluviosols (AS)	SE Romanian Plain	1	185			
	Central and South Dobrogea	219	306			
Kastanozems (KZ)	Central and South Dobrogea	19	129			

Soil grouping by type and sub-type also points out that the same soil types have higher selenium contents in the South-Eastern Romanian Plain as compared to Central and South Dobrogea (tab. 3). Thus, the Typic Chernozem from South Dobrogea has total selenium content 20% lower than the Typic Chernozem of the South-Eastern Romanian Plain. Alike, the Calcaric Kastanic Chernozem from Central and South Dobrogea contains 30% less total selenium than the same soil type from the South-Eastern Romanian Plain. The Kastanozems, soil types specific to Central Dobrogea, have low total selenium content. Aluviosols are an exception as a small number (5) of samples showed higher total selenium concentrations (tab. 3)

Tab. 4 – Statistical parameters of the mobile selenium content (µg·kg^{-1}) in the upper horizon (0-20 cm) of the South-Eastern Romanian Plain and Central and South Dobrogea soils

Statistical parameters	Romanian Plain			Dobrogea
	Zone 1	Zone 2	Zone 3	Total
n	23	34	57	26
x_{min}	3	15	3	2
x_{max}	9	26	26	6
$\bar{x}$	6	20	14	4
σ	2	2	7	1
x_g	6	20	7	4
cv (%)	33	10	50	25
Me	6	20	20	4
Mo	6	21	19	4

Fig. 4 - Presents the mobile selenium distribution tendency map.

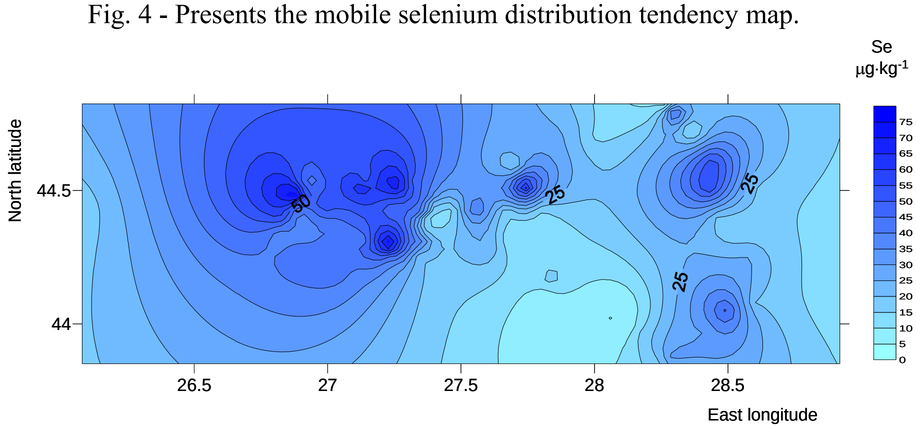

Fig. 4 - Tendency map of the distribution of mobile selenium contents in the upper horizon (0-20 cm) of the South-East Romanian Plain and Central and South Dobrogea soils

3.3 Mobile selenium abundance in the soils upper horizon (0-20 cm). As compared to the soils total selenium content the mobile selenium content, soluble in the CH_3COONH_4 – EDTA solution at pH = 7,0 is, on an average, 17 times lower in the soils of the South-Eastern part of the Romanian Plain and 30 times lower in the Dobrogea soils (tab. 4). Therefore, besides lower total selenium content in the

Dobrogea soils, its mobility is lower compared to the soils of the South-Western part of the Romanian Plain

*3.4 Selenium correlations***.** Taking into account the decrease of the selenium in the investigated area soils from West to the East, on one hand, and the aridity phenomenon in this region (Păltineanu et al., 2007) the soil (0-20 cm) total and mobile selenium contents were correlated with the aridity index (Iar; after De Martonne) values. Direct proportionality relations statistically ensured were obtained (fig. 5).

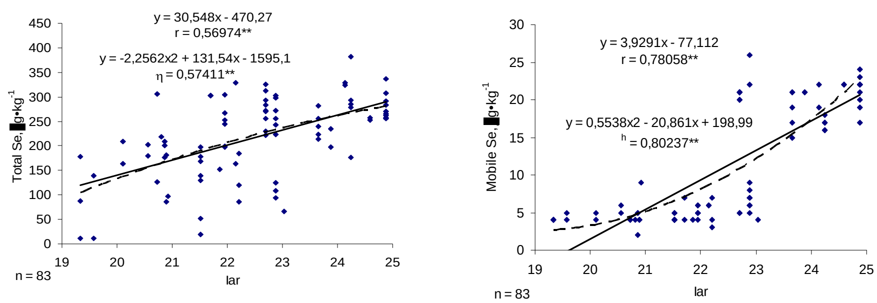

Fig. 5 – Correlations between the aridity index (Iar; after De Martonne) and total and mobile selenium soil contents of the upper horizon (0-20 cm) of the South-Eastern Romania soils

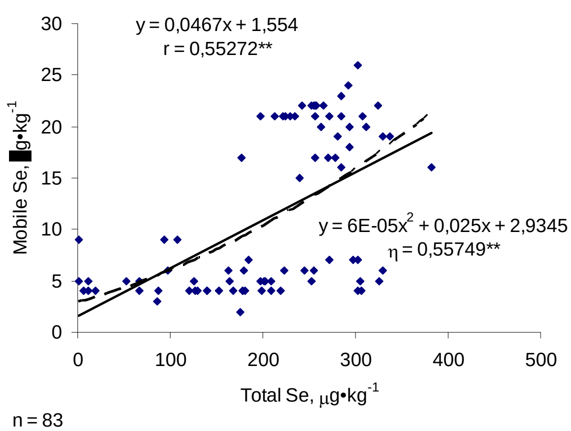

Fig. 6 – The correlation between total and mobile selenium contents of the upper horizon (0-20 cm) of the South-Eastern Romania soils

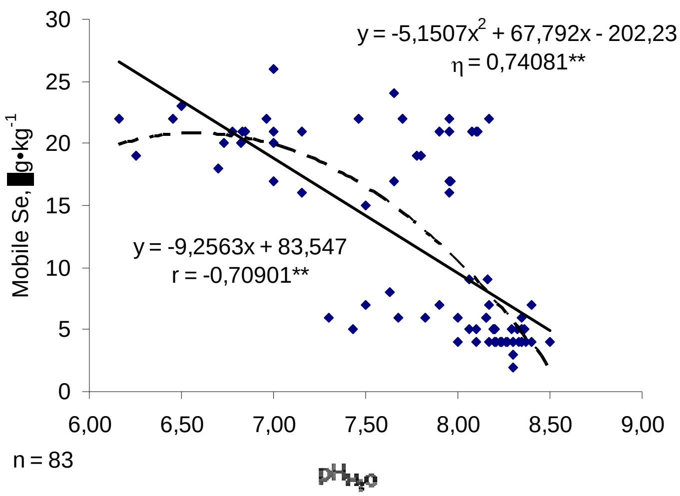

Fig. 7 – The correlation between the soil (0-20 cm) mobile selenium content and its reaction in the South-Eastern part of Romania

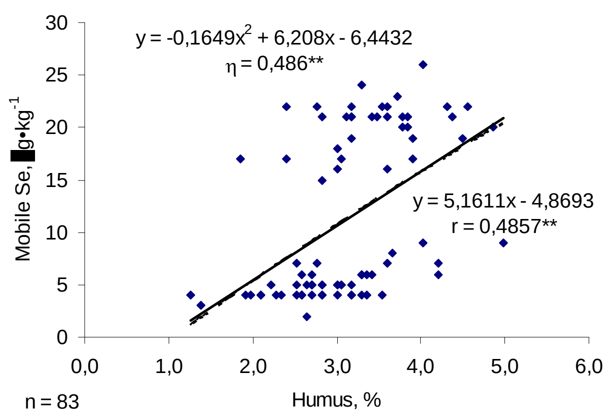

Fig. 8 – The correlation between the soil (0-20 cm) mobile selenium content and its humus content in the South-Eastern part of Romania

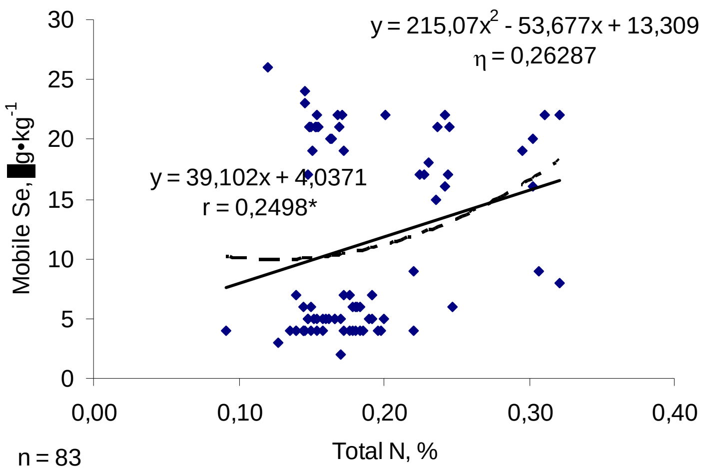

Fig. 9 – The correlation between the soil (0-20 cm) mobile selenium content and its total nitrogen content in the South-Eastern part of Romania

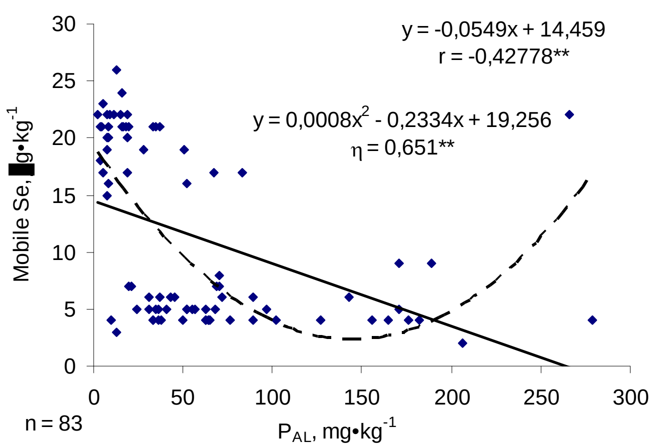

Fig. 10 – The correlation between the soil (0-20 cm) mobile selenium content and its mobile phosphorus content in the South-Eastern part of Romania

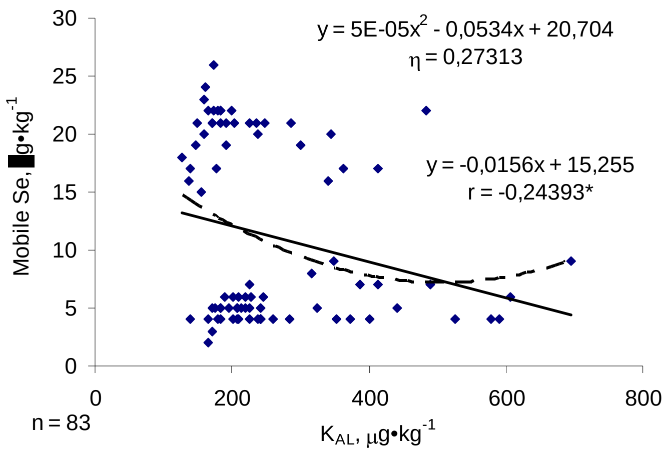

Fig. 11 – The correlation between the soil (0-20 cm) mobile selenium content and its mobile potassium content in the South-Eastern part of Romania

The correlations clearly highlight that the aridity phenomenon contributes to the decrease of selenium soil mobility, corroborated with a lower selenium native background.

The proportionality between soil mobile and total selenium is well highlighted in Figure 6 with values of the correlation coefficient (r) and ratio (□) statistically ensured.

Between the mobile selenium content of the investigated soils and their chemical characteristics (pH, humus content, total nitrogen content, phosphorus and potassium mobile forms) proportionality relations have also been established, partly statistically ensured. Between mobile selenium and soil reaction the relation is negative (fig. 7).

The mobile selenium relations with the others soil chemical characteristics are of direct proportionality (fig. 8, 9, 10, and 11). It can be noticed that the closest relations are those with humus and total nitrogen, especially for the samples collected from the Romanian Plain South-Eastern part.

Conclusions

The average total selenium content in the rocks and parent materials of the South-Eastern Romanian Plain and Central and south Dobrogea soils is inferior to the values presented in the literature for rocks and similar materials.

The average total selenium contents in the Romanian Plain and Central and South Dobrogea loess are practically equal ((97 and 92 $\mu g \cdot kg^{-1}$, respectively), while the mobile selenium content is double in the South-Eastern Romanian Plain loess as compared to Central and South Dobrogea (94 and 46 μg·kg^{-1}, respectively).

The total selenium content of the upper horizon (0-20 cm) of the South-Eastern Romanian Plain soils is 65% higher as compared to the content registered in the Central and South Dobrogea soils (237 and 143 μg·kg^{-1}, respectively).

As compared to the average value of the total selenium content in the soils all over the world considered unaffected by deficiencies or excess (383 ± 255 μg·kg^{-1}), the total selenium content of the South-Eastern Romanian Plain soils is lower by almost 40% and that of the Central and South Dobrogea soils by 63% lower.

The total selenium abundance in the soils of the investigated area diminishes in the succession: Typic Chernozem → Calcaric Kastanic Chernozem → Kastanozem.

The total selenium content in the South-Eastern Romanian Plain and Central and South Dobrogea has a maximum frequency (35%) in the intervals 225-281 μg·kg^{-1}, respectively 157-209 μg·kg^{-1}.

As compared to the average mobile selenium content in the South-Eastern Romanian Plain soils (14 μg·kg^{-1}), in the soils of Central and South Dobrogea 3.5 times lower average values were registered (4 μg·kg^{-1}).

Between the mobile and total selenium contents and the aridity index (after De Martonne) direct proportionality relations have been established.

Between the total and mobile selenium contents of the upper horizon of the soils from South-East Romania direct proportionality relations have been established.

The mobile selenium content is higher in the slightly acid soils as compared to the neutral or alkaline ones.

Between mobile and total selenium contents, on one hand, and the humus, total nitrogen, mobile phosphorus and potassium on the other, direct proportionality relations have been established.

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