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SELENIUM IN THE SOIL-PLANT SYSTEM OF THE FĂGĂRAŞ DEPRESSION

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Abstract: The soil cover of the Făgăraş Depression consists of different types and sub-types belonging to the following classes: Protisols, Umbrisols, Cambisols, Luvisols, and Hydrisols. These soils are generally acid, with low humus and total nitrogen contents and low up to average mobile phosphorus and potassium contents. They have a predominantly loamy texture. The heavy metals contents are normal. The total selenium content oscillates between 12 and 587 $\mu g \cdot kg^{-1}$, with an average value of 268 $\mu g \cdot kg^{-1}$. This value is 30% lower than the average selenium content in the World's soils unaffected by deficiency or excess phenomena. The soil mobile selenium, soluble in the EDTA-CH_3COONH_4 solution at pH 7.0, oscillates between 9 and 28 $\mu g \cdot kg^{-1}$, with an average value of 15 $\mu g \cdot kg^{-1}$, comparable with the one in Central and Southern Dobrogea, where deficiency phenomena were registered with sheep. The tendency maps of the total an mobile selenium contents distribution in the Făgăraş Depression soils highlight low contents in the Northern and Central-Eastern part as well as 2-3 points of concentrated values around the localities Făgăraş, Victoria, and Mârşa. Between some of the soils chemical properties (pH, mobile potassium, heavy metals contents) and the mobile selenium contents statistically ensured correlations were registered. The average selenium content in the fodder plants of the Făgăraş Depression (19 $\mu g \cdot kg^{-1}$) is four times lower than the average selenium content of some similar plants grown in other countries. A direct correlation is highlighted between the soil deficient selenium content, the deficient selenium content in the fodder plants grown on these soils, and the selenium deficiency phenomena registered with animals.

Key words: selenium, soil-plant system, Făgăraş Depression, acid soils, tendency maps

1. INTRODUCTION

Selenium is a micro element with numerous functions in animal and human nutrition; it has an anti-infectious, anti-oxidant role, as a component of the glutathione peroxidase enzyme, and an anti-tumor role (Deélstra, 1982, Gissel-Nielsen et al., 1984 Its physiological and biochemical roles have also been outlined in plant nutrition (Läuchli, 1993; Turakainen et al., 2005), and yield increases were registered when administering selenium on the seed, in the soil, or on the plant (Lăcătuşu et al., 2002).

The selenium abundance in the environment components is low. Thus, the average content oscillates between 50 and 90 $\mu g \cdot kg^{-1}$ in the lithosphere, between less than 100 and 2,000 $\mu g \cdot kg^{-1}$ in the pedosphere, from less than 50 up to 15,000 $\mu g \cdot kg^{-1}$ in the biosphere, and around 0.2 $\mu g \cdot l^{-1}$ in the hydrosphere (Kabata-Pendias & Pendias, 2001; Kabata-Pendias & Mukherjee, 2007).

The soil selenium abundance depends on a series of chemical and physical factors, such as reaction, organic matter, macro and micro elements contents, the parent material nature. The total selenium contents interval in the World's soils is between 5 and 3,500 $\mu g \cdot kg^{-1}$, with an average value of 383 ± 255 $\mu g \cdot kg^{-1}$ (Kabata-Pendias & Pendias, 2001). The extreme values of the content interval are specific to areas with selenium deficiency, respectively toxicity. Selenium deficiency leads to some diseases occurrence in living beings, such as: sheep myodystrophy, hepatic necrosis with swine, white muscle disease with horses, exudative diathesis with poultry, and the excess determines the alkaline disease occurrence with animals and people (Gissel-Nielsen et al., 1984 Selenium deficiency with people is implied in a series of cardiovascular and digestive systems diseases and in many tumor diseases. Its major role for human health lies in the anti-oxidant effect of its compounds (Reilly, 2006).

The fact is known that large areas of the North (Finland, Sweden, Norway; Hartikainen, 2005), Central (Germany; Hartfiel & Bahners, 1988, Slovakia; Kadrabova et al., 1997), South-Eastern European countries (Serbia; Maksimovic et al., 1992) and from Russia (Ermakov, 1992) are affected by the selenium deficiency. Romania also lies in a World's area with deficient selenium contents registered with animals and even with people. Thus, Salanțiu, even since 1970 (in Ghergariu, 1980), highlighted the selenium deficiency in calves, lambs, sucking pigs, and young buffalos in large areas of the Transylvania Basin, including the Făgăraş Depression. More recently, Serdaru & Giurgiu (2007) analyzed 1,548 fodder samples, 1,175 cattle blood serum samples, 1,030 sheep blood serum samples, and 600 human blood serum samples collected from the Ardeal area and concluded that only 3.7% of the fodder samples, 5.0% of the cattle blood serum samples, none of the sheep blood serum samples, and only 3.3% of the human blood serum samples have normal contents, while the differences belong to the deficiency domain. Alike, Serdaru et al., (2003) analyzed 185 fodder samples from 41 Dobrogea localities and concluded that only 6.5% of them belong to the normal content domain, and the difference belongs to the deficiency domain. This situation required the introduction of selenium in the animal feed premixes. The deficiency level mostly occurs because of some low soil selenium contents.

Among the first data regarding total selenium content in Romania's soils there are those referring to the Oriental Carpathians Mountain soils and some river sediments (Ababi & Dumitrescu, 1973; Lăcătuşu & Ghelase, 1992). The authors found 640 $\mu g \cdot kg^{-1}$, respectively 380 $\mu g \cdot kg^{-1}$ average values, the latter in areas with haematuria incidence. Determinations carried out in Dobrogea soils highlighted total selenium concentrations between 211 and 585 $\mu g \cdot kg^{-1}$, with an average value of 314 $\mu g \cdot kg^{-1}$, and mobile selenium concentrations, soluble in the EDTA-CH_3COONH_4 solution with pH = 3.7, between 0.9 and 74 $\mu g \cdot kg^{-1}$, with an average value of 4 $\mu g \cdot kg^{-1}$ (Lăcătuşu et al., 2009, 2010 a, b). In the Central-Eastern part of Dobrogea, in the Sibioara area, where cases of sheep myodystrophy have been registered, the average total and mobile selenium contents, soluble in AL, were 140 $\mu g \cdot kg^{-1}$, respectively 5 $\mu g \cdot kg^{-1}$ (Lăcătuşu et al., 2002). Total selenium determinations carried out in samples of the upper horizon of the soils from the South-Eastern part of the Romanian Plain, predominantly Chernozems, highlighted higher values than those of the Dobrogea soils, with 64%, on an average (Lăcătuşu et al., 2010 a, b). Unlike these ones, in the Solonchaks and Solonetz of the Buzău and Călmățui Valleys, Lăcătuşu et al. (2011) determined total selenium contents with values around 800 $\mu g \cdot kg^{-1}$, twice as much as the average of the selenium contents from many non-halomorphic soils of the World and three up to five times more than the total selenium content of the upper horizon of the South-Eastern Romanian Plain or Dobrogea soils. The highest values of selenium content in Romania soils have been registered so far in the Danube Delta soils of the dyked precincts Sireasa and Pardina: total contents of up to 1,776 $\mu g \cdot kg^{-1}$, with an average value of 600 $\mu g \cdot kg^{-1}$, 1.6 times higher than the total selenium content in the World's soils which is 383 ± 255 $\mu g \cdot kg^{-1}$ (Kabata-Pendias & Pendias, 2001), and mobile contents up to 29 $\mu g \cdot kg^{-1}$, with an average value of 19 $\mu g \cdot kg^{-1}$.

Continuing the researches regarding selenium abundance in the Romania's soils the present paper highlights this chemical element's contents in the soils of the Făgăraş Depression, where selenium deficiency cases were registered with animals (Salanțiu, 1970, in Ghergariu, 1980).

2. MATERIAL AND METHODS

The researches had an expeditionary character; soil samples were collected from 50 test pits by the 0-20; 20-40 and 40-60 cm depths (Fig. 1). Plant samples were taken from around the test pits, especially from the soils under fodder plants crops and from pastures and hay fields.

The soil samples were analyzed in the laboratory from the point of view of general chemical properties, using standardized methods. Thus, pH was determined in aqueous suspension by the potentiometric method, with double glass and calomel electrode; the humus content by Walkley-Black method modified by Gogoaşă; total nitrogen content by the Kjeldahl method; mobile phosphorus and potassium, soluble in the ammonium acetate-lactate solution at pH 3.7, after Ègner-Rhiem-Domingo, were determined by spectral photometric, respectively flame photometric methods.

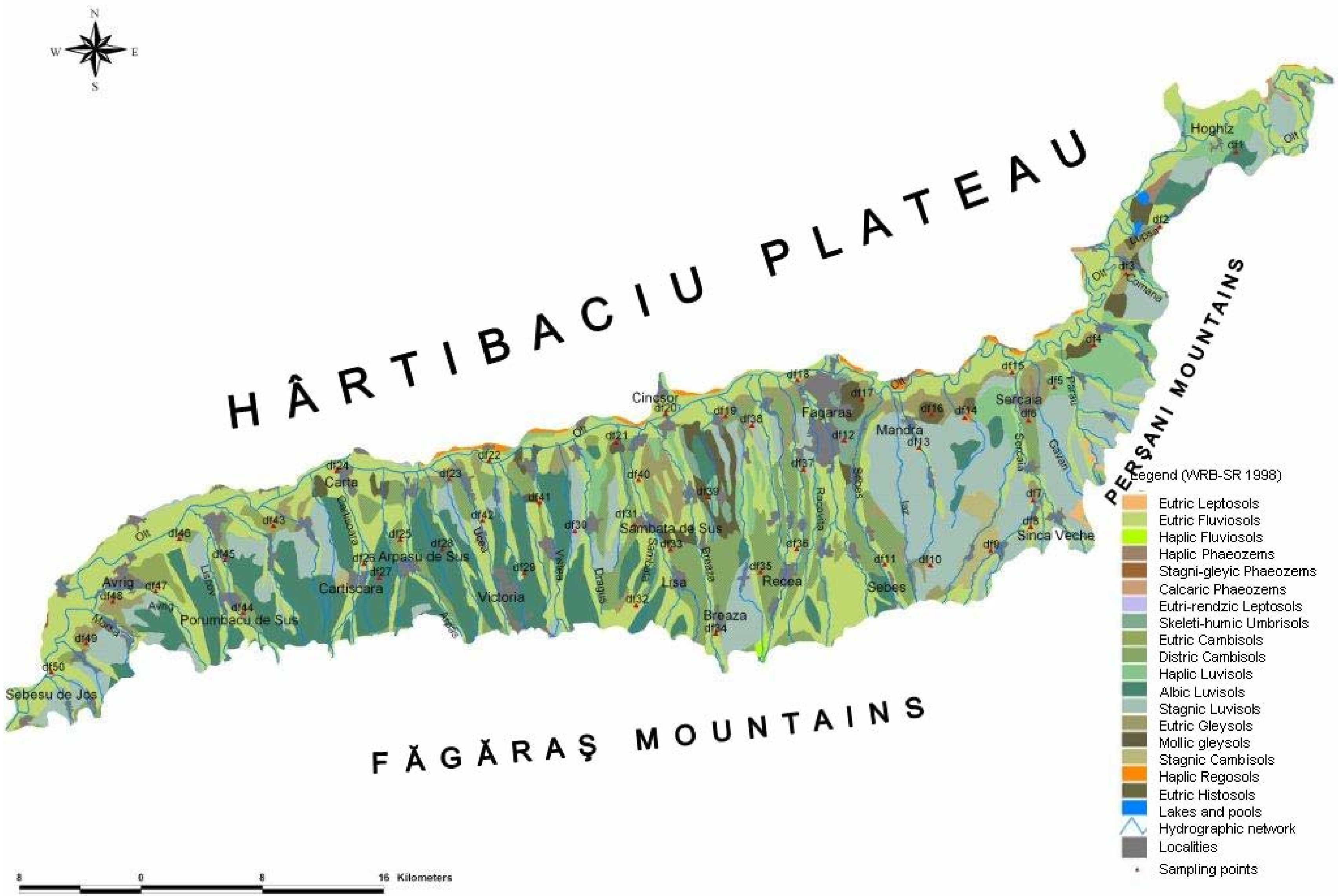

Figure 1. Soil map of the Făgăraş Depression, adaptation after the Romania Soil Map, scale 1:200,000, Braşov and Sibiu sheets (Bălăceanu et al., 1971 and 1975) and sampling points location

The heavy metals contents were determined by atomic absorption spectrometry, the total forms in the hydrochloric solution obtained after soil digestion with strong mineral acids (nitric, HNO_3, and perchloric, $HClO_4$), and the mobile ones in the extracting CH_3COONH_4-EDTA solution at pH 7 (after Lăcătuşu et al., 1987).

Total and mobile selenium contents were determined in the same solutions. Concentration measurements were carried out by atomic adsorption spectrometry too but using the boron hydride variant. The same method was used to determine selenium contents in plant samples.

The analytical data were statistically computed, the spreading (minimum value x_{min}, maximum value x_{max}, coefficient of variation cv, and standard deviation σ) and grouping centre parameters (arithmetic average $\overline{x}$, geometric average x_g, median Me and module Mo) were determined. Moreover, Kurtosis and Skewness coefficients were calculated. Also, correlations between different analytical values categories were drawn. Microsoft Excel Programme was used to this end. The tendency maps of the selenium distribution in soils were obtained by the Kriging method in a Surfer Programme.

3. RESULTS AND DISCUSSIONS

3.1. The investigated soils and their general characteristics

The investigated soils in the Făgăraş Depression belong to the following classes: Protisols, Umbrisols, Cambisols, Luvisols, and Hydrisols[1]. Of the **Protisols** class the *Calcaric Fluvisols, Eutric, Eutric and Gleyic, and Eutric and Skeletic Fluvisols*, and *Dystric Fluvisols*[2] are to be noticed.

Except for the Calcaric Fluvisols, which have a slightly alkaline reaction (pH 7.28-8.18), the other Fluvisols have a slight up to moderate acid reaction, with pH in aqueous suspension values ranging from 4.91 to 6.65. The Fluvisols' humus and total nitrogen contents are low up to medium, with values ranging in the 1.62-4.64%, respectively 0.054-0.192% intervals. Mobile phosphorus and potassium supply is generally low, with few exceptions registered in the Calcaric and Eutric Fluvisols.

Umbrisols are represented by *Umbrisols*. These soils are moderate-strongly acid, with a high humus content but a low up to medium total nitrogen one. Mobile phosphorus and potassium supply is diverse, from low values to high values.

Cambisols are represented by *Eutric Cambisols* and *Distric Cambisols*. The first, in their turn, include *Fluvi-eutric Cambisols* and *Lepti-eutric and Fluvi-eutric Cambisols*. Both types are slightly up to moderate acid, have low up to high contents of both humus and total nitrogen. Mobile phosphorus and potassium supply is generally low up to medium. The same subtypes as the Eutric Cambisols are to be encountered for the Distric Cambisols too. The reaction, the humus and total nitrogen contents, and the mobile phosphorus and potassium supply are similar to those of the Eutric Cambisols.

Of the **Luvisols class** in the Făgăraş Depression *Stagnic Luvisols*, *Albic and Stagnic-albic Luvisols* occur. They all have moderate-strongly acid reaction, the humus content is low up to medium, the total nitrogen one too. The mobile phosphorus and potassium supply is diverse, from extremely low to medium.

Table 1. Statistical parameters of the main soil chemical properties

Statistical parameters	pH_{H_2O}	Humus	Nt		P_{AL}	K_{AL}
		%		C/N	mg·kg^{-1}	
n	135	135	135	135	135	135
x_{min}	4.32	0.84	0.040	4.2	1	23
x_{max}	8.18	22.80	0.613	52.4	128	356
$\overline{x}$	5.84	3.19	0.140	15.5	24	89
σ	0.94	2.36	0.076	4.6	27	58
x_g	5.77	2.70	0.125	15.0	13	74
c.v. (%)	16	74	54	30	113	65
Me	5.58	2.82	0.133	15.1	14	77
Mo	5.45	2.46	0.130	13.7	11	61

In the end, the last class of the soils occurring in the Făgăraş Depression, **Hydrisols**, are: *drained Mollic Gleysols* and *Histic Gleysols*. Their reaction is slightly-moderate acid. But humus and total nitrogen contents are different, namely low-medium for the first soil category and high, even very high, for the second. Mobile phosphorus and potassium supply is similar, namely low up to medium.

In an overall assessment, the major chemical properties of the Făgăraş Depression soils (Table 1) highlight the fact that they are acid, have low humus and total nitrogen contents, and a predominantly

[1] SRTS, (Florea et Munteanu 2003, 2012)

[2] WRB-SR, (FAO, 1998)

loamy texture. And the mobile phosphorus and potassium supply is low up to medium.

3.2. Total and mobile selenium contents

The statistical parameters of the total selenium content in the analyzed soils (Table 2) highlight a values interval between 12 and 587 μg·kg^{-1}, with average values of: 268 μg·kg^{-1} (arithmetic average $\bar{x}$); 218 μg·kg^{-1} (geometric average x_g); 295 μg·kg^{-1} (median Me), and 359 μg·kg^{-1} (module Mo). When comparing the 268 μg·kg^{-1} average total selenium content value of the Făgăraş Depression soils with the 383 μg·kg^{-1} average total selenium content of the World's soils unaffected by deficiency phenomena (Kabata-Pendias & Pendias, 2001), it comes out that the first is 30% lower.

The frequency histogram of the total selenium content distribution in the analyzed soils, in the horizons down to 60 cm depth (Fig. 2a) shows a normal distribution with a slightly right asymmetry, with two Module values, one in the 83-154 μg·kg^{-1} interval with a 13% frequency, and one in the 296-367 μg·kg^{-1} interval with a 21.6% frequency.

Table 2. Statistical parameters of the total and mobile selenium contents (μg·kg^{-1})

Statistical Parameter	Total Se	Mobile Se
n	135	135
x_{min}	12	9
x_{max}	587	28
$\bar{x}$	268	15
σ	133	3
x_g	218	15
cv (%)	50	20
Me	295	14
Mo	359	14
Kurtosis	-0.83	0.67
Skewness	-0.19	0.98

The negative value of the Kurtosis coefficient shows the presence of a platicurtic type distribution. The high value of the coefficient of variation (50%) shows that the median represents the significant value of the grouping centre parameters.

On the other hand, the mobile selenium histogram (Fig. 2b) shows a clearly left asymmetry with a 22.6% frequency at the 14 μg·kg^{-1} Module value. At the same time, the Skewness indicates a normal distribution and Kurtosis a leptocurtic type distribution, with a medium spreading of the data; the arithmetic and geometric averages are representative values for the grouping centre parameters.

The soils of the Făgăraş Depression have comparable total selenium contents to the ones of the South Eastern Romanian Plain.

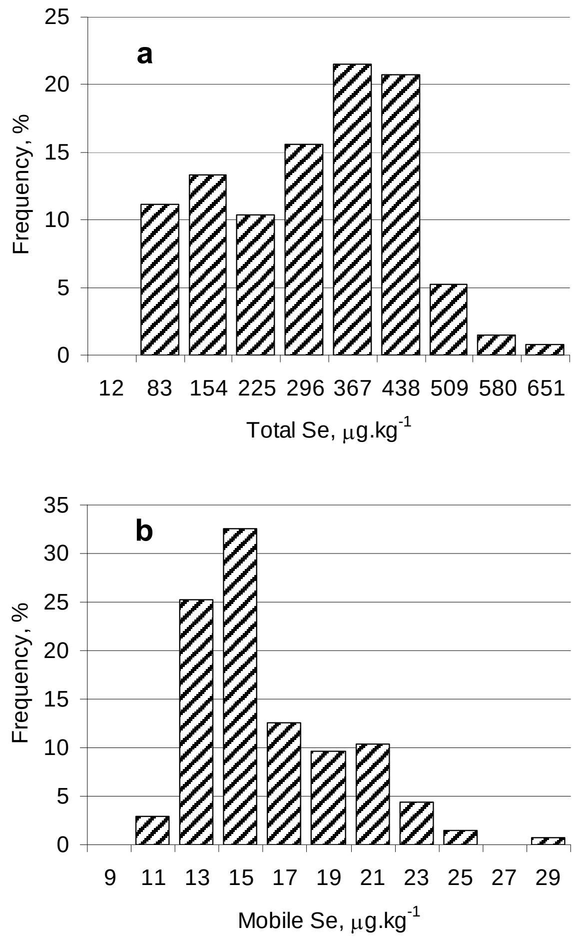

Figure 2. Frequency histograms of the total (**a**) and mobile (**b**) selenium contents in the Făgăraş Depression soils in the upper 60 cm layer.

The statistical parameters of the mobile selenium content, soluble in the EDTA-CH_3COONH_4 solution at pH 7.0, (Table 2) highlight a low content domain, from 9 to 28 μg·kg^{-1}, with average values of 15 μg·kg^{-1} ($\bar{x}$, x_g) and 14 μg·kg^{-1} (Me, Mo). These values are very low, comparable to the ones registered in Central and South Dobrogea (14 μg·kg^{-1}) where selenium deficiency in animals have been reported. Therefore, selenium mobility in the Făgăraş Depression is low and determines a low translocation too in the fodder plants and further in the animals' bodies.

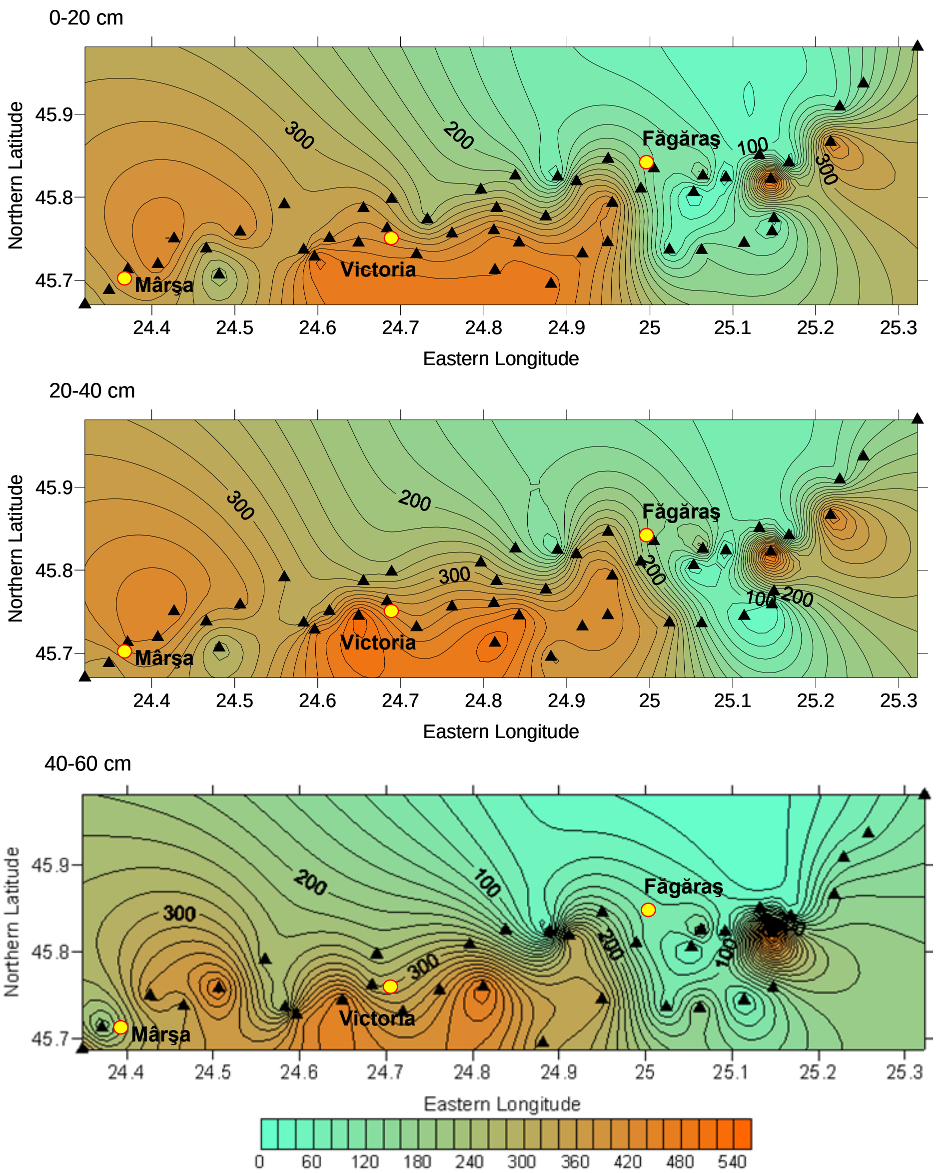

Figure 3. Tendecncy maps of the total selenium (μg·kg^{-1}) distribution on the three geometrical horizons of the Făgăraş Depression soils

3.3. Tendency maps of the Făgăraş Depression soils selenium distribution

In figures 3 and 4 the tendency maps of the total and mobile selenium contents are presented by the three analyzed depths (0-20; 20-40; and 40-60 cm). From the total selenium distribution the fact can be noticed that it concentrates more on the Western and South-Western parts, while in the North-Eastern and Central-Eastern parts the lowest contents were registered of below 10 μg·kg^{-1}. The phenomenon is more accented at the 40-60 cm depth. It can be stated from the three charts analysis that the total selenium content decreases on the soil profile. Moreover another phenomenon occurs, namely high total selenium contents around the Făgăraş and Victoria localities. Or in these localities worked and are still partially working chemical factories from which emissions could have occurred that contained selenium amongst other chemical elements.

Mobile selenium distribution emphasized by the tendency maps (Fig. 4) highlights again the very low values, below 1 μg·kg^{-1}, on a high surface but with lower surfaces with higher values of over 20 μg·kg^{-1} located around the Victoria and Mârşa localities. In the case of mobile selenium too the chemical element's content decreases on the soil profile depth. The areas with the lowest values are the same at 20-40 and 40-60 cm depth.

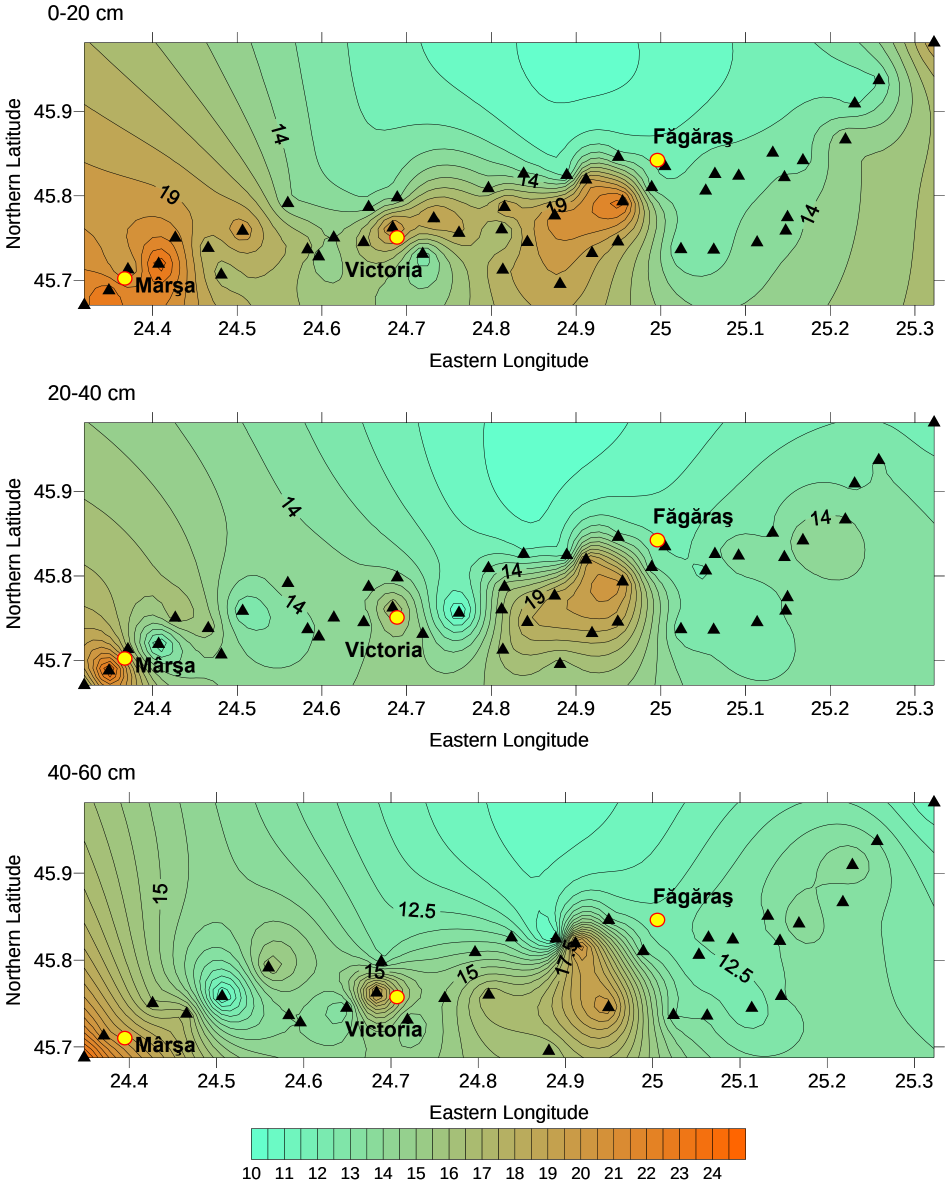

Figure 4. Tendency maps of the mobile selenium (μg·kg^{-1}) distribution in the three geometric horizons of the Făgăraş Depression soils

3.4. Selenium correlations in the Făgăraş Depression soils

A reverse statistically ensured correlation was computed between the soil mobile selenium content and the pH values determined in aqueous suspension for the points cloud included in the 4-8 pH values interval and 10 la 29 μg·kg^{-1} mobile selenium values interval (Fig. 5). The phenomenon of selenium mobility decrease with the acidity decrease and alkalinity increase was also highlighted in other soil types.

The mobile selenium content directly and very significantly correlates to the total one (Fig. 6). The two parameters can also be linked

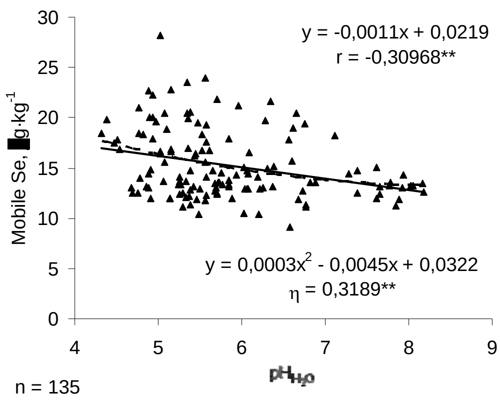

Figure 5. The correlation between mobile selenium and soil reaction in the Făgăraş Depression

by a second degree equation with very significant correlation ratio too.

Among the other major chemical characteristics (humus, total nitrogen, mobile phosphorus and potassium contents, except for the latter) and the mobile selenium content the correlations are not statistically ensured.

But statistically ensured correlations have been computed between the total selenium contents on one hand and the total heavy metals ones on the other hand, both linear and polynomial (Table 3). The high values of the correlation coefficients and ratios stand out for cadmium (Cd), cobalt (Co), and chromium (Cr) in relation with both total and mobile selenium. The correlations have theoretical value as the total heavy metals contents in the Făgăraş Depression are normal. Hence their geogenic origin as well as the selenium's.

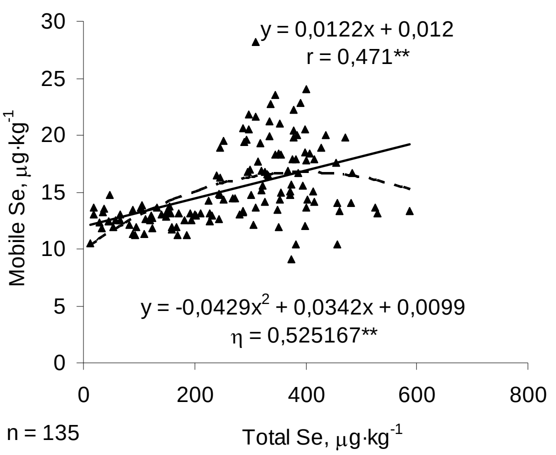

Figure 6. The correlation between the mobile and total selenium contents in the Făgăraş Depression soils

3.5. Selenium in the fodder plants of the Făgăraş Depression

Plant samples (aerial part) were taken from each soil sampling point consisting of alfalfa, mixed samples of plants grown in pastures and hay fields, and bristle grass (*Settaria* species) samples from the straw cereals' stubble fields.

The statistical parameters of the selenium content in the analyzed plants (Table 4) reveal values up to 67 µg·kg^{-1} with average values of 19 ($\bar{x}$, Mo) and 17 (Me) µg·kg^{-1}. If we compare these values to the average 73 µg·kg^{-1} selenium in the fodder plants of ten countries of the World, reported by Kabata-Pendias and Pendias (2001) it comes out that the fodder plants of the Făgăraş Depression accumulated 4 times less selenium thant the ones grown in other World's regions.

Table 4. Statistical parameters of the selenium content (µg·kg^{-1}) in the fodder plants of the Făgăraş Depression

Statistical Parameters	Values
n	50
x_{min}	0
x_{max}	67
$\bar{x}$	19
σ	14
c.v. (%)	74
Me	17
Mo	19
Kurtosis	0.98
Skewness	0.82

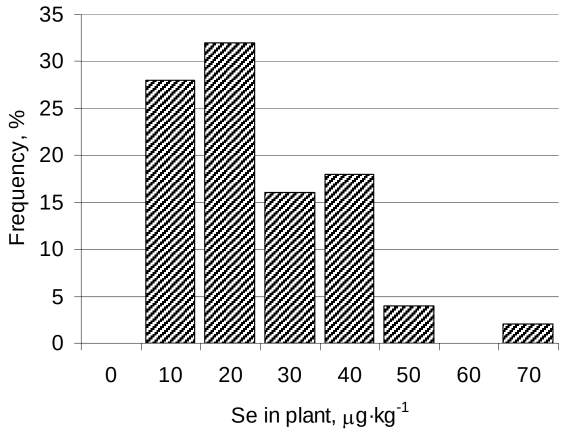

Figure 7. Frequency histogram of the selenium content in the fodder plants sampled in the Făgăraş Depression (n = 50)

Table 3. The correlation coefficients (r) and ratios (η) of the total and mobile selenium (n = 135) with the heavy metals in the Făgăraş Depression soils

		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Total Se	r	0,650**	0,663**	0,486**	0,115	0,445**	-0,190	0,030	0,383**	0,291**
	η	0,724**	0,695**	0,487**	0,129	0,346**	0,335**	0,220	0,439**	0,314**
Mobile Se	r	0,704**	0,621**	0,295**	0,062	0,052	-0,282**	-0,065	0,327**	0,114
	η	0,704**	0,626**	0,298**	0,068	0,052	0,286**	0,066	0,442**	0,137

If we also analyze the selenium distribution histogram in the fodder plants of the Făgăraş Depression (Fig. 7) a left asymmetry is noticed which is specific to areas with more low content values. The carriage of this histogram resembles the one of the soil mobile selenium (Fig. 2)

The low selenium values in the fodder plant correlate with the low soil mobile selenium contents and this correlation explains the selenium deficiency phenomena registered with animals.

4. CONCLUSIONS

The soil cover of the Făgăraş Depression consists of different types and sub-types belonging to the following classes: Protisols, Umbrisols, Cambisols, Luvisols, and Hydrisols.

Generally the Făgăraş Depression soils are acid, have low humus and total nitrogen contents and low up to average mobile phosphorus and potassium ones. Their texture is predominantly loamy. The Făgăraş Depression heavy metals contents are normal.

The total selenium content oscillates between 12 and 587 $\mu g \cdot kg^{-1}$ with a 268 $\mu g \cdot kg^{-1}$ average value. This value is 30% lower than the average selenium content in the World's soils unaffected by deficiency or excess phenomena.

The soil mobile selenium, soluble in the EDTA-CH_3COONH_4 solution at 7.0 pH, oscillates between 9 and 28 $\mu g \cdot kg^{-1}$ with a 15 $\mu g \cdot kg^{-1}$ average value, comparable to the one of the Central and Southern Dobrogea, where deficiency phenomena have been registered with sheep.

The tendency maps of the total selenium distribution in the Făgăraş Depression soils highlights low contents in the Northern and Central-Eastern parts as well as 2-3 points of concentrated values around the Făgăraş, Victoria, and Mârşa localities. It is possible that these concentrations have an anthropic origin and that they proceed from the chemical and mechanic industrial works of those regions.

Between some of the soils' chemical characteristics (pH, mobile potassium, heavy metals contends) and mobile selenium contents statistically ensured correlations have been registered.

The average selenium content in the fodder plants of the Făgăraş Depression (19 $\mu g \cdot kg^{-1}$) is four times lower than the average selenium content of plants grown in other countries.

A direct link is highlighted between the soil deficient selenium content, the deficient selenium content of the plants grown on these soils, and the selenium deficiency registered with animals.

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