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INFLUENCE OF LONG TERM LIMING AND FERTILIZATION ON THE TOTAL AND MOBILE SELENIUM CONTENT IN AN ALBIC LUVISOL

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ABSTRACT

Total and mobile selenium contents of an albic luvisol were studied in a long term experiment with lime, mineral and organic fertilizers, in relation with other soil chemical properties (reaction, organic matter content, clay content < 2μ). Statistical processing of the analytical data obtained in the laboratory showed that moderate liming, with cumulated doses that totalise 30 t·ha^{-1} calcium carbonate contributed to a significant increase of selenium content, by 16% for the total selenium and by 29% for the mobile one. Liming with total calcium carbonate doses of 60 t·ha^{-1} contributed to a significant decrease of selenium content, by 7% for the total selenium and by 25% for the mobile one. The contrasting behaviour of selenium in the differently limed soils was due to different ionic forms in which it occurs in soils in close oxidizing conditions, but different reaction conditions, acid or alkaline. The organic fertilization increased, significantly as compared to the unfertilised control, the soil selenium content, by 9% for the total selenium and by 4% for the mobile one.

Significant direct proportionality relations were established between the total and mobile selenium content of the albic luvisol, as well as between the mobile selenium content and soil reaction. Mobile selenium was in a significant reverse proportionality relation with the humus content. The relation between the mobile selenium content and soil clay < 2μ content was also reverse and significant when moderate lime doses were applied. When higher calcium carbonate doses were applied the relation was direct and significant.

Key words: selenium, albic luvisol, long term experiment, liming, fertilization.

INTRODUCTION

Selenium is a microelement with numerous functions in animal and human nutrition, and it has an anti-infectious, antioxidant role, as a component of the glutathione peroxidase enzyme, but also an anti-tumour role (Deélstra et al., 1982; Gissel-Nielsen et al., 1985). Its physiologic and biochemical role has also been highlighted in plant nutrition (Läuchli, 1993; Turakainen et al., 2005) and yield increases were obtained by administering selenium on seeds, in the soil, or on the plant (Lăcătuşu et al., 2002b).

The selenium content in the world's soils unaffected by this element's deficiency or toxicity phenomena varies between 5 and 3.500 μg·kg^{-1}, with an average value of 383 ± 255 μg·kg^{-1} (computed with data from Kabata-Pendias and Pendias, 2001).

In numerous countries all around the world (USA, China, Russia, Finland, Norway, Germany, Serbia) areas of both selenium deficiency and toxicity are found (Hartikainen, 2005; Hartfield and Bahners, 1988; Maksimović, 1992; Ermakov, 1992). Selenium was administered on the soils in some deficiency areas and an increase of this element in the yields was obtained. The Finnish experience (Yläranta, 1990; Turakainen et al., 2004; Yli-Halla, 2005, 2008) is the most relevant in this respect.

Selenium deficiency cases in animals were registered in Romania (Salanțiu, 1970; Lăcătuşu et al., 2002a; Serdaru et al., 2003; Serdaru and Giurgiu, 2007). As the major cause of these phenomena is the low selenium content of the soils and plants, a research program was initiated and developed on the selenium condition in the soil – plant system

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in different parts of the country, known as areas with significant natural (the Danube Delta) or specific handicap. In the last category the halomorphic, sandy, acid, etc. soils are included. Some of the results have been published by Lăcătuşu et al. (2009, 2010 a, b, 2011, 2012a).

In the present paper results are presented regarding the selenium contents of the acid soils located in the Romania's North-Western part, namely at the Livada Agricultural Research and Development Station, Satu Mare County. Besides the general selenium content, mineral and organic fertilization and liming influence on the total and mobile selenium contents of the albic luvisol's upper agrochemical horizons was highlighted.

MATERIAL AND METHODS

Soil samples were collected in 2009, from three agrochemical horizons, at 5-10, 25-30 and 40-45 cm soil depth, from a long term experiment which started in the autumn of 1961 on the albic luvisol at Livada. The experiment aims to assess the long term effect of mineral and organic fertilization and liming on different crops yields and on the soil characteristics.

The soil samples were taken from the control variant (unfertilised and unlimed), from the variants annually fertilised with $N_{100}P_{70}K_{60}$, from the variants fertilised, with 20 $t.ha^{-1}$ manure, annually until 2005, and once every four years since, and limed with calcium carbonate ($CaCO_3$) with recurrent doses that totalised, at the sampling time, 30 and 60 $t.ha^{-1}$. The total 30 $t.ha^{-1}$ dose was obtained by administering 5 $t.ha^{-1}$ each 5 years, starting 1961 and until 1998. The 60 $t.ha^{-1}$ dose was obtained by administering 10 $t.ha^{-1}$ in the same years.

The albic luvisol, unfertilised and unlimed, is a strongly acid soil (pH = 4.78), with a very low humus content (1.21%), a low total nitrogen content (0.136%), and an average supply of mobile phosphorus and potassium (31 $mg{\cdot}kg^{-1}$ P_{AL} and 90 $mg.kg^{-1}$ K_{AL}).

The soil samples were analysed in the laboratory from the general agrochemical characteristics point of view. The pH was determined by the potentiometric method, in aqueous suspension, using a double glass and calomel electrode. The humus was determined by the Walkley-Black method, modified by Gogoaşă (Daniliuc, 1981), the total nitrogen by the Kjeldahl method, and the mobile forms of phosphorus and potassium were extracted in an ammonium acetate-lactate solution at pH 3.7 (AL), after Égner-Rhiem-Domingo. The phosphorus was determined by spectrophotometry and the potassium by flame photometry.

The total selenium was determined in the hydrochloric solution obtained after soil digestion with a perchloric ($HClO_4$) and nitric (HNO_3) acids mixture, and the mobile selenium was extracted in a CH_3COONH_4-EDTA solution at pH 7 (after Lăcătuşu et al., 1987). In both solutions the selenium was determined by atomic absorption spectrometry in the boron hydride variant.

The analytical results were statistically computed, the spreading and the grouping centre parameters were determined, in order to establish the general abundance of the two selenium forms in the acid soils of that part of the country. Variance analysis was also used to establish the significance of the differences between the unfertilised and unlimed variants and the fertilised or limed ones. Correlation analysis was used to establish the relations between selenium content and some soil properties.

RESULTS AND DISCUSSIONS

Selenium abundance in the acid soils

In the Livada area, Satu Mare County, luvisols are predominant, with two sub-types: haplic and albic. The analytical data used to compute the selenium abundance refer to soil samples taken from agrochemical horizons down to 45 cm, both from unfertilised and fertilised or limed variants (Table 1).

When analysing the values ranges characteristic to the luvisols, in general, and to the Livada's agricultural land albic luvisol in particular, striking resemblances come out, both in the total and mobile selenium contents. Only the standard deviation (σ) and the coefficient of variation (cv) values differed more, as they are higher in the case of the first values range, showing a larger variation interval in the case of all samples and a much smaller variation in the case of the samples collected from the albic luvisol.

Table 1. Statistical parameters of the total and mobile selenium contents (μg·kg^{-1}) of luvisols, in general, and of the albic luvisol from Livada

Statistical parameter	Total Se		Mobile Se	
	General samples n = 153	Samples from the albic luvisol n = 36	General samples n = 153	Samples from the albic luvisol n = 36
x_{min}	326	326	14	15
x_{max}	579	574	35	34
$\overline{x}$	461	458	21	22
σ	260	58	6	6
cv (%)	56	13	29	28
x_g	458	455	20	22
Me	466	461	17	21
Mo	466	466	16	22

If we compare the average values of the total selenium contents of the analysed soils with the average 383 μg·kg^{-1} value, specific to the world's soils, computed after Kabata-Pendias and Pendias (2001), it is obvious that they are higher.

The acid soils have with 77 μg·kg^{-1} more total selenium, representing 20% more than the average total selenium content of the world's soils. In natural conditions, without liming or fertilizers, the total selenium content of the agrochemical horizons down to 45 cm depth is, on an average, 448 μg·kg^{-1}, and the mobile selenium content is, also on average, 24 μg·kg^{-1}.

The mobile selenium represents only 4% of the total one. The total selenium content value of the albic luvisol, in natural conditions, is with 17% less than the average content of the world's soils mentioned before.

Table 2. Average contents of the total and mobile selenium contents from the upper horizons of different soils of Romania

Location	Soil type	Total Se	Mobile Se	Author
		μg·kg^{-1}		
Livada, Satu Mare County	Haplic luvisol	448	22	Lăcătuşu et al., 2012 (this paper)
Central and Southern Dobrogea	Kastanozems Chernozems	143	4	Lăcătuşu et al., 2009
South-Eastern Romanian Plain	Chernozems	237	14	Lăcătuşu et al., 2010 a, b
Danube Delta's Sireasa and Pardina dyked areas	Fluvisols	600	24	Lăcătuşu et al., 2012 a
Călmăţui and Buzău Valleys	Solonchaks Solonetz	766	18	Lăcătuşu et al., 2012 b
Făgăraş Depression	Eutric cambisols luvisols	268	15	Lăcătuşu et al., 2012 c

In comparison with other soils of Romania (Lăcătuşu et al., 2011, 2012 a, b) the albic luvisol contains three times more total selenium than the chernozems and kastanozems from Central and Southern Dobrogea, 1.9 times more than the chernozems of the Romanian Plain South-Eastern part, and 1.7 times more than the soils of Făgăraş Depression. But the Livada albic luvisol contains with 43% less total selenium than the solonchaks and solonetz of the Călmăţui and Buzău Valleys and with 25% less than the fluvisols from the Danube Delta's Sireasa and Pardina dyked areas.

The average mobile selenium content, soluble in the CH_3COONH_4-EDTA at pH 7, from all the analysed variants of the Luvisol, was high (22 µg·kg^{-1}), close to the one of the North-Eastern Danube Delta Fluvisols, but 5.5; 1.6; and 1.2 times higher than the mobile selenium of the soils from Central and Southern Dobrogea, the South-Eastern Romanian Plain, and the Solonchaks and Solonetz from the Călmățui and Buzău Valleys respectively (Table 2).

The influence of liming and mineral or organic fertilization of the albic luvisol on the total and mobile selenium contents

The albic luvisol liming was done for two pH levels, namely 6.0 and 7.6, by administering calcium carbonate ($CaCO_3$) doses of 30 and 60 t.ha^{-1} respectively, over a period of 37 years.

The total selenium contents registered in the three agrochemical horizons significantly differed, depending on liming and fertilization (Figure 1). Thus, as compared, the mineral fertilization on an unlimed background brought a significant total selenium increase only in the first agrochemical horizon, down to 10 cm, while the organic fertilization contributed to a significantly increase also in the second agrochemical horizon, down to 30 cm. in comparison with the values around 450 µg·kg^{-1} total selenium in unlimed and unfertilised control.

Liming with 30 t.ha^{-1} contributed to the significant increase of the total selenium content in all horizons and high levels were registered on organic fertilization background. Anyway the significant contribution of the organic fertilization to the soil total selenium content (Figure 1, Variant 11) can be noticed, as well as the liming contribution (Figure 1, Variant 8).

Taking into account that, as a result of liming with 30 t.ha^{-1}, pH values in soil ranged between 6.0 and 6.5, in oxidizing conditions, the selenium will still exist in soil as acid selenite ion ($HSeO_3^-$), with a low mobility, due to the easiness with which it is absorbed on the oxides and hydroxides present in such soils (Brookins, 1988; Kabata-Pendias, 1998).

Liming with double calcium carbonate ($CaCO_3$) doses, of up to 60 t.ha^{-1}, led to the registration of pH values around 7.6, range in which the selenate (SeO_4^{2-}) ions predominated, in compounds such as $CaSeO_4$, $MgSeO_4$, or K_2SeO_4. In alkaline reaction conditions and still in oxidant environment, the selenates are not adsorbed by the soils' oxides and hydroxides, have a high mobility, and easily leave the upper horizons of the soils or even the whole soil profile.

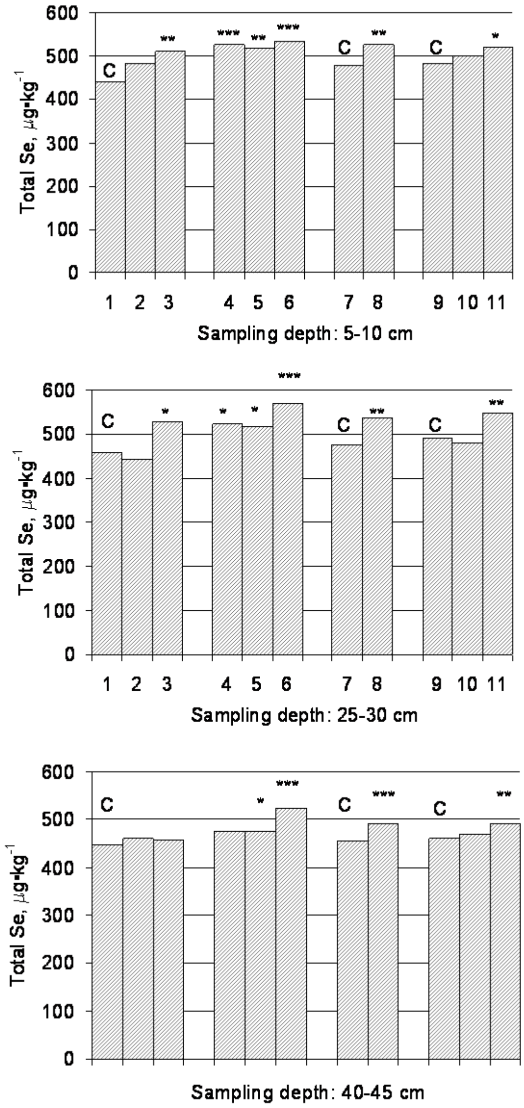

Figure 1. The influence of liming with 30 t.ha^{-1} $CaCO_3$, for pH 6.0, and of the mineral and organic fertilisation upon the total selenium content of the upper horizons of the albic luvisol

Variants: 1 – unlimed, unfertilised (C); 2 – unlimed, fertilised $N_{100}P_{70}K_{60}$; 3 – unlimed, organically fertilised 20 t.ha^{-1} manure; 4 – limed 30 t.ha^{-1}, unfertilised; 5 – limed, fertilised $N_{100}P_{70}K_{60}$; 6 – limed, organically fertilised 20 t.ha^{-1} manure; 7 – unlimed (C); 8 – limed; 9 – unfertilised (C); 10 – mineral fertilisation $N_{100}P_{70}K_{60}$; 11 – organically fertilised 20 t.ha^{-1} manure

This is the explanation for the fact that in strong liming conditions the total selenium content of the unlimed and unfertilised soil was significantly higher than in the limed and fertilised variants (Figure 2). Still, the positive effect of the liming and fertilisation, especially organic, was obvious, without taking into account the unfertilised and unlimed control.

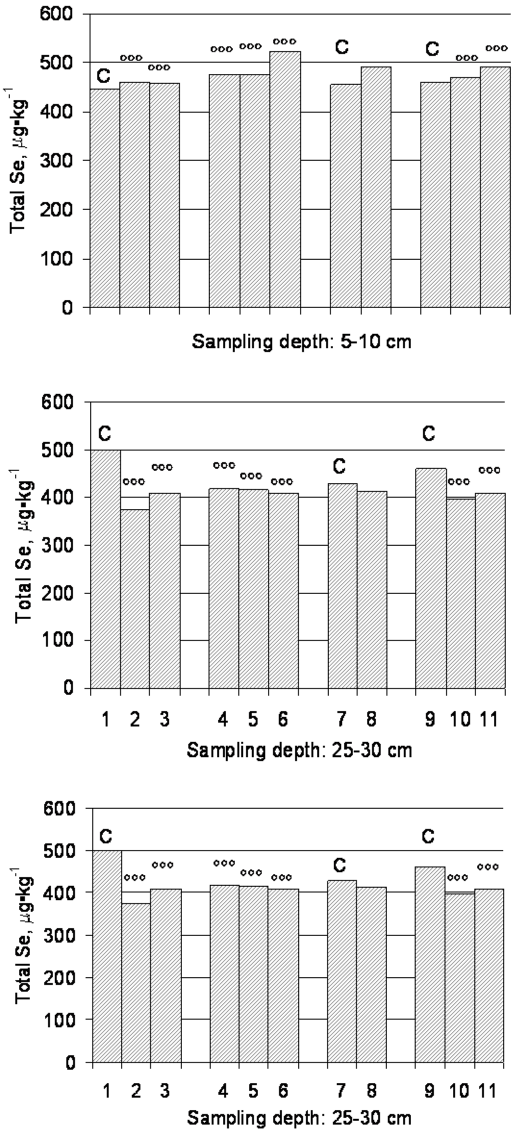

Figure 2. The influence of liming with 60 t.ha^{-1} $CaCO_3$, for pH 7.6, and of the mineral and organic fertilization upon the total selenium content of the upper horizons of the albic luvisol

(Variants: 1 – unlimed, unfertilised (C); 2 – unlimed, fertilised $N_{100}P_{70}K_{60}$; 3 – unlimed, organically fertilised 20 t.ha^{-1} manure; 4 – limed 30 t.ha^{-1}, unfertilised; 5 – limed, fertilised $N_{100}P_{70}K_{60}$; 6 – limed, organically fertilised 20 t.ha^{-1} manure; 7 – unlimed (C); 8 – limed; 9 – unfertilized (C); 10 – mineral fertilization $N_{100}P_{70}K_{60}$; 11 – organically fertilized 20 t.ha^{-1} manure)

The data regarding the liming and fertilisation effect on the mobile selenium content of the albic luvisol (Table 3) highlighted again the positive effect of liming, of a higher intensity in the case of applying 30 t.ha^{-1} $CaCO_3$, and the significant negative effect in the case of applying 60 t.ha^{-1} $CaCO_3$, as compared to the unlimed control. Therefore, over liming determined a decrease of selenium mobility.

Table 3. The influence of liming and fertilization upon the mobile selenium content (µg·kg^{-1}) of the upper horizons of the albic luvisol

Sampling depth cm	Fertilization	Liming $CaCO_3$, t/ha		
		0 (C)	30	60
5-10	0 $N_{100}P_{70}K_{60}$ 20 t.ha^{-1} manure	23 25 23	31 *** 31 *** 29 ***	17 °°° 18 °°° 18 °°°
25-30	0 $N_{100}P_{70}K_{60}$ 20 t.ha^{-1} manure	24 26 25	30 *** 29 *** 31 ***	17 °°° 19 °°° 19 °°°
40-45	0 $N_{100}P_{70}K_{60}$ 20 t.ha^{-1} manure	24 25 26	32 *** 32 *** 33 ***	18 °°° 19 °°° 17 °°°
	DL 5%		2	1
	DL 1%		4	2
	DL 0,1%		5	3

Correlations involving Selenium content

Between the mobile and total selenium contents of the analysed albic luvisol statistically ensured direct proportionality relations were established, described by a first degree equation in the case of liming with 30 t.ha^{-1} $CaCO_3$ and by a second degree equation in the case of 60 t.ha^{-1} $CaCO_3$ liming, up to a 7.6 pH. In the latter case the values were placed on both sides of a parabola arch with the maximum value corresponding to 440 µg·kg^{-1} total selenium and 17 µg·kg^{-1} mobile selenium. Up to these values the dependence between the two parameters was direct and beyond these values, where most points are, the dependence was indirect. On the whole it can be stated that the mobile selenium content increased as the total selenium one did. The two functions were verified at lower values in the case of liming with 60 $t.ha^{-1}$ $CaCO_3$ and at higher, almost double values in the case of liming with 30 $t.ha^{-1}$ $CaCO_3$ (Figure 3).

Between the mobile selenium content and the main soil components (clay below 2µ and humus content) direct proportionality relations were also established in the case of liming with 60 $t.ha^{-1}$ $CaCO_3$ (Figure 4b) and indirect in the case of liming with 30 $t.ha^{-1}$ $CaCO_3$ (Figure 4a). Differences occurred regarding the values variation interval, of 5 $µg·kg^{-1}$ in the case of the strongly limed soil and 16 $µg·kg^{-1}$ in the case of the soil limed with 30 $t.ha^{-1}$ $CaCO_3$, for the differences between the clay content below 2µ limits of 11%, respectively 15%.

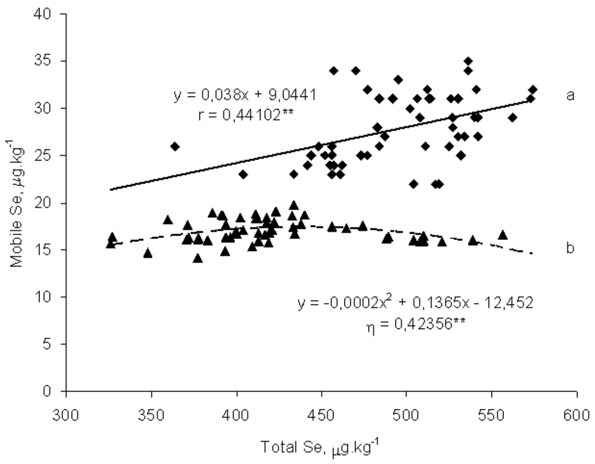

Figure 3. The relationships between the mobile selenium contents of the albic luvisol limed with 30 $t.ha^{-1}$ $CaCO_3$ (a) and 60 $t.ha^{-1}$ $CaCO_3$ (b)

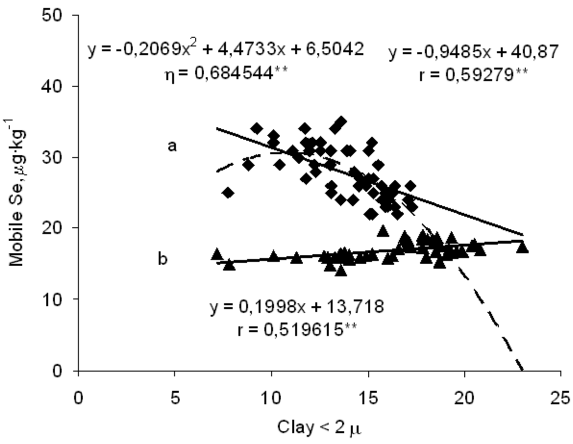

Figure 4. The relationships between the mobile selenium content of the Albic Luvisol and the clay < 2 µ, in conditions of liming with 30 $t.ha^{-1}$ (a) and 60 $t.ha^{-1}$ $CaCO_3$ (b)

The humus influence on the mobile selenium content was significant and between the two parameters a reverse proportionality relation was established (Figure 5) with a much more obvious decrease of the mobile selenium content beginning with the 1% humus content.

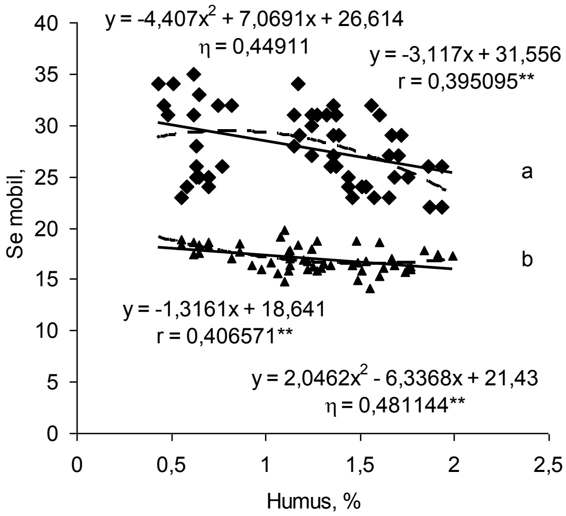

Figure 5. The relationships between the mobile selenium content of the albic luvisol and the humus content, in conditions of liming with 30 $t.ha^{-1}$ (a) and 60 $t.ha^{-1}$ $CaCO_3$ (b)

Direct proportionality relations were established between the albic luvisol reaction (pH_{H_2O}) and the mobile selenium content in both liming variants (Figure 6).

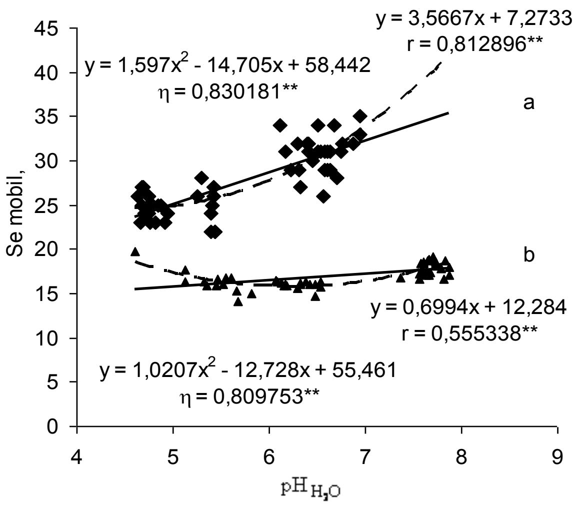

Figure 6. The relationships between the mobile selenium content of the albic luvisol and the soil reaction in aqueous solution, in conditions of liming with 30 $t.ha^{-1}$ (a) and 60 $t.ha^{-1}$ $CaCO_3$ (b)

The proportionality relation was tighter in the case of 60 $t.ha^{-1}$ $CaCO_3$ liming, as the points were arranged on a parabola arch with the descendent branch ranging in the pH_{H_2O} values domain up to 6.0. In this case, the variation interval of the mobile selenium content was only 4 $\mu g \cdot kg^{-1}$, from 14 to 18 $\mu g \cdot kg^{-1}$, unlike the values interval specific to the samples collected from the 30 $t.ha^{-1}$ $CaCO_3$ limed variants, which was 14 $\mu g \cdot kg^{-1}$, with the limits at 22 and 36 $\mu g \cdot kg^{-1}$.

CONCLUSION

The average total selenium content of the albic luvisol was 458 $\mu g \cdot kg^{-1}$, and of the mobile one 22 $\mu g \cdot kg^{-1}$. The mobile selenium represented 5% of the total selenium content. The total selenium content of this soil was with 17% higher than the total selenium content of the world's soils unaffected by deficiency or toxicity phenomena.

Liming the albic luvisol with total calcium carbonate ($CaCO_3$) doses of 30 $t.ha^{-1}$ contributed to a significant increase of the selenium content, with 16% for the total selenium content and with 29% for the mobile one.

Liming with total calcium carbonate ($CaCO_3$) doses of 60 $t.ha^{-1}$ contributed to a significant decrease of the selenium content, with 7% for the total selenium content and with 25% for the mobile one.

The contrasting behaviour of selenium in the differently limed soils was due to the different ionic forms (acid selenite, $HSeO_3^-$, selenite, SeO_3^{2-}, selenate, SeO_4^{2-}) in which it occurs in soil in similar oxidizing, but different reaction conditions, namely acid, respectively alkaline.

Organic fertilization increased significantly the soil selenium content, with 9% for the total selenium content and with 4% for the mobile one, as compared to the unfertilised control.

Between the total and mobile selenium contents of the albic luvisol, as well as between the mobile selenium content and soil reaction, significant direct proportionality relations were established. The mobile selenium was in a significant reverse proportionality relation with the humus content.

The correlation of the mobile selenium content with soil clay <2μ was very significant, indirect in the case of moderate liming, and direct in the case when higher calcium carbonate doses were applied.

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