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Effectiveness of micronutrient mobilization from a controlled-release fertilizer in soils with different physico-chemical characteristics

Milchena Atsenova and Irena Atanassova*

Agricultural Academy, Institute of Soil Science, Agrotechnologies and Plant Protection „N. Poushkarov“, 1331 Sofia, Bulgaria
**Corresponding author:* i.d.atanassova@abv.bg

Abstract

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The present study deals with the effects of a controlled-release macro- and microelements containing fertilizer added at 50%, 100%, and 200% of the optimal rate of 90 mg/kg N on two soils of different physico-chemical characteristics at three T°, 15^{0}C, 25^{0}C and 35^{0}C for a period of two months. The fertilizer gradually releases the trace elements Cu, Zn, Fe, Mn, Mo, B, at optimal humidity, and their release depended on the temperature and the rate of addition to the soil.

The two types of soils exhibit different degree of release of the studied trace elements under controlled conditions. A weaker release of trace elements from the added fertilizer was observed in the Cinnamonic forest soil, which has a heavier texture and higher cation-exchange capacity than the Alluvial-meadow soil. For the temperatures studied, a similar change in the physico-chemical characteristics was observed, i.e. a slight decrease in pH, a decrease in the degree of base saturation and the appearance of H+ and exchangeable AI ions.

The principal component analysis (PCA) revealed a common source for the elements Cu, Zn, Fe, Mn, Mo and a different one for B in the Alluvial-meadow soil. In the Cinnamonic Forest a similar source of elements mobilization in the soil solution was found for Cu, Zn, Fe, another one for Mn, Mo and a third for B. We conclude that the source of mobilization of the microelements in solution in the Cinnamonic forest soil is mainly the soil colloidal complex, and in the case of the Alluvial meadow soil, the added fertilizer.

Keywords: controlled-release fertilizers; micronutrients; soil characteristics; incubation experiment; temperature; diffusion release

Introduction

Micronutrients are of major biological, agricultural and ecological importance. A number of physiological disturbances in plants and pathological processes in animals are associated with shortage, excess or disproportion of microelements in their tissues, as a result of which the yield and quality of plant production decrease (Stanchev et al., 1982; Stoyanov & Peneva, 1985; Kabata-Pendias & Pendias, 2001). One of the main factors influencing the mobility of heavy metals – trace elements in soil, is pH. In the adsorption-desorption studies of metals – trace elements, it was established that clay fractions isolated from main soil types in Bulgaria show pH-dependent adsorption for Cu, Zn, Cd and Ni (Atanassova & Okazaki, 1997; Atanassova, 1999).

Mansouri et al. (2023) conclude that controlled-release fertilisers are emerging products which can replace and compensate conventional fertilisers for their inefficiency (> 60% or even higher inefficiency is found for phosphorous fertilisers). The excess fertilizer will be unavailable to plants due to physico-chemical or microbial reactions in soil, and /or leaching to ground water (e.g. in the case of NO_3^-). Micronutrients are important for animal and human health and therefore micronutrient fertilization is paramount, in order to achieve adequate nutritional requirements and high crop quality. For micronutrient release, Micula et al. (2020) summarize the new fertilization technologies with consideration of micronutrients influence on the environment, focusing on four basic groups of fertilisers, e.g. low-solubility fertilizers, fertilizers with external coating, bio-based and nano-fertilizers. The authors consider that despite the structural differences, all groups of fertilizers show properties of controlled microelement release. Trace elements – heavy metals have higher bioavailability in acidic environment, and with an increase in pH, clay content and organic matter in soils, their availability decreases (Alloway, 2008; Kabata-Pendias, 2010; Atanassova & Okazaki, 1997). In particular, the elements Fe, Mn, B, Cu, and Zn are most available in the pH range 5 and 7, while Mo is more available at pH > 7 (Wang et al., 2022). Controlled-release fertilizers (CRF) improve the efficiency of their use by increasing plant growth and the efficiency and quality of nutrient uptake, while reducing application costs (Mansouri et al., 2023). The use of these fertilizers reduces both plant toxicity and stress, as well as soil and atmospheric pollution. Polymer coated fertilizers provide a gradual and consistent release of nutrients (Ali & Danafar, 2015). For some fertilizers, substrate type has been found to have no significant effect on nutrient release rates, but temperature is an important factor (Adams et al., 2013). High temperature and lack of moisture also contribute to reducing the mobility of nutrients. The dynamics of alternating drought and waterlogging can lead both to reduction in bioavailability and toxic effects on plants and groundwater pollution.

The aim of the present study is to evaluate the release of micronutrients from a fertilizer with with a polymer coating under controlled conditions, the formation of complexes in soil solution and free ion species, in view of evaluating the mobile and plant-available ions in soils with different physico-chemical characteristics.

Materials and Methods

For the implementation of the incubation experiments, two types of soils were studied, leached Cinnamonic Forest soil (Chromic Cambisol) in Chelopechene and Alluvial-meadow soil (Fluvisol) in Tsalapitsa from the experimental fields of "N. Poushkarov" Institute of Soil Science Agrotechnologies and Plant Protection. The soils were taken from a depth of 0–20 cm (42°44´N, 23°28´E, Chelopechene) and (42°10´N, 24°32´E, Tsalapitsa). Soils were treated at three fertilizer rates: 50%, 100%, and 200% and a control variant that did not contain fertilizer. The introduced amounts are determined in relation to nitrogen, with 90 mg/kg N accepted as the norm. The optimal fertilizer rate was calculated based on the data for the planned yield of maize (unpublished data) in relation to the stock of the soil with bioavailable nutrients (Mikhailov & Kniper, 1971; Rinkies, 1972). They were placed in containers with soil of 0.1 kg of weight, and a controlled-release fertilizer (Osmocote, 12% N, 7% P, 18% K, 1.5% Mg, 0.013% Zn, 0.045% Cu, 0.35% Fe, 0.05% Mn, 0.01% B, 0.017% Mo, 0.013% Zn). The data on the physico-chemical characteristics of the soils are presented in Table 1. In Table 2 are shown the data for the microelements extracted with 0.01 mol/l $CaCl_2$ before the start of the experiment. The dishes were placed in a Climate Chamber KK 350 Smart PRO (POL-EKO), with air humidity control at 60% at three temperatures, 15°C, 25°C, and 35°C. Soil moisture at all three temperatures is kept constant at 75% field capacity (FC) with deionized water. The concentrations of the trace elements Cu, Fe, Zn, Mn, B, Mo in 0.01 mol/l $CaCl_2$ in a soil:solution ratio (1:5) and incubation for 2 h, were recorded (Van Ranst et al., 1999).

Calcium chloride (0.01M) simulates the ionic strength of the soil solution, and is used for modelling the solid-solution partitioning of ions and assessing the mobility of a number of heavy metals in the environment (Degryse et al., 2003; Groenenberg & Lofts, 2014; Simeonova et al., 2018; Ata-

Table 1. Physico-chemical characteristics of the experimental soils

Soil	pH/H_2O	$T_{8,2}$	T_{CA}	T_A	$H_{8,2}$	Exch. Al	Exch. Ca	Exch. Mg	DBS, %	Clay <0.001 mm, %	OC, %
		cmol/kg									
Cinnamonic forest soil	6.1	30.9	26.3	4.6	4.3	0	23.2	3.5	86.08	29.5	1.50
Alluvial meadow soil	6.2	15.5	11.5	4.0	3.5	0	10.1	1.8	77.42	19.7	0.73

Table 2. Major trace elements in the two soils in 0.01 mol/l $CaCl_2$ extractant before starting the experiment

№	Soil	Zn, mg/l	Cu, mg/l	Fe, mg/l	Mn, mg/l	B, mg/l	Mo, mg/l
1	Cinnamonic forest soil	0.036	0.050	0.418	1.626	0.035	0.008
2	Alluvial meadow soil	0.081	0.109	0.034	6.434	0.156	0.001

nassova et al., 2020). The elements are analysed by ICP-OES 5800 (Agilent). The following physico-chemical characteristics were determined, pH in soil-water (1:2.5), cation exchange capacity at pH 8.25; strongly acidic ion exchanger capacity (Tsa), weakly acidic ion exchanger capacity (Ta), total acidity ($H_{8.25}$), exchangeable acidity (Al), exchangeable calcium and magnesium and degree of base saturation (BS) after Ganev & Arsova (1980). Soil clay content was analyzed by the method of Kachinski, and total organic carbon (TOC) in the samples were determined by oxidation with $K_2Cr_2O_7/H_2SO_4$ by the Kononova method. In order to assess the sources and relationships between the studied elements: Cu, Zn, Fe, Mn, B, Mo principal component analysis (PCA) was performed with SPSS-IBM Statistics 26.

Results and Discussion

In Table 1 are presented the main physico-chemical soil characteristics. The soils are characterized by slightly acidic soil reaction, e.g. the soil from Chelopechene, the leached Cinnamonic forest soil is moderately colloidal with a predominant montmorillonitic mineralogy, while the Alluvial

Table 3. Physico-chemical characteristics of the soils at 15⁰C recorded on the 60th day of incubation (SD cmol.kg^{-1} 0.03−0.1), SD_{pH} (0.05–0.2)

№	Variants	pH/H_2O	$T_{8,2}$	T_{SA}	T_A	$H_{8,2}$	Exch. Al	Exch. Ca	Exch. Mg	BS, %
			cmol.kg^{-1}							
1	Cinnamonic forest soil	6.3	29.5	26	3.5	3.1	0	23.1	3.4	89.49
2	50%	6.2	29.8	26.3	3.5	3.4	0	23	3.5	88.29
3	100%	6.2	29.5	25.7	3.8	3.4	0	22.6	3.5	88.47
4	200%	6	29	25.2	3.8	3.5	0	21.8	3.4	87.93
8	Alluvial-meadow soil	6.3	15.7	12.7	3	2.8	0	10.9	2	82.27
9	50%	6.2	15.5	12.5	3	2.8	0	10.7	1.9	81.94
10	100%	6.2	15.2	12.2	3	2.8	0	10.2	2	81.58
11	200%	6	15.2	12	3.2	2.9	0	10	2	80.92

Table 4. Physicochemical characteristics of the soils at 25⁰C recorded on the 60th day of incubation (SD cmol.kg^{-1} 0.04−0.09), SD_{pH} (0.05–0.2)

№	Variants	pH/H_2O	$T_{8,2}$	T_{SA}	T_A	$H_{8,2}$	Exch. Al	Exch. Ca	Exch. Mg	BS, %
			cmol.kg^{-1}							
1	Cinnamonic forest soil	6.0	30.7	26.1	4.6	4.5	0	22.8	3.4	85.34
2	50%	5.9	30.8	26.2	4.6	4.8	0.2	22.7	3.5	84.42
3	100%	5.8	31.1	26.3	4.8	5	0.3	22.9	3.5	83.92
4	200%	5.6	31.7	26.7	5	5.4	0.5	22.9	3.6	82.97
8	Alluvial-meadow soil	6.2	15.5	11.9	3.6	3.5	0	10.1	1.8	77.42
9	50%	6.0	15.7	12	3.7	3.6	0	10.4	1.9	77.07
10	100%	5.7	15.7	12.1	3.6	3.7	0.3	10.2	1.9	76.43
11	200%	5.6	16	12.4	3.6	3.9	0.4	10.4	2	75.62

Table 5. Physicochemical characteristics of the soils at 35°C recorded on the 60th day of incubation (SD cmol.kg^{-1} 0.03−0.09) and SD_{pH} (0.05–0.2)

№	Variants	pH/H_2O	$T_{8,2}$	Tsa	Ta	$H_{8,2}$	Exch. Al	Exch. Ca	Exch. Mg	BS, %
			cmol.kg^{-1}							
1	Cinnamonic forest soil	6.2	30.5	26	4.5	4	0	23.1	3.5	86.89
2	50%	5.9	30.8	26.5	4.3	4.4	0.1	22.9	3.5	85.72
3	100%	5.8	30.8	26.4	4.4	4.8	0.3	22.7	3.5	84.42
4	200%	5.7	30.7	26.2	4.5	5	0.4	22.2	3.5	83.71
8	Alluvial-meadow soil	6.2	15.5	11.9	3.6	3.2	0	10.4	1.8	79.35
9	50%	6.0	15.6	11.7	3.9	3.4	0	10.3	1.9	78.21
10	100%	5.6	15.6	12.4	3.2	3.6	0.4	10	2	76.92
11	200%	5.4	15.5	12.3	3.2	3.9	0.5	9.6	2	74.84

meadow soil from Tsalapitsa is weakly colloidal with a predominant montmorillonite-illitic mineralogy according to the classification of Ganev (1990).

The data in Table 2 indicate that the measured levels of copper, iron and manganese in solution of 0.01 mol/l $CaCl_2$ exceed the threshold values according to Ordinance 12 of June 18, 2002 for the quality requirements for surface water intended for drinking and domestic water supply in the two soils (for Cu and Mn) and in the Cinnamonic soil (for Fe).

Tables 3, 4, and 5 present the physico-chemical characteristics of the two soils at 15°C, 25°C, 35°C recorded after 60 days of maintaining constant temperature and moisture in the climate chamber.

The physico-chemical parameters of the strongly acidic (SA) and weakly acidic (WA) ion exchanger show that at 15°C there was a tendency towards acidification (pH decreases by ~ 0.3 units) with an increase in the rate of added fertilizer from 50–200%. In these soils, the hydrogen form of the weakly acidic system of the soil adsorbent predominates (Table 2), but it does not completely exhaust the exchanger, as well as the strongly acidic exchanger, i.e. no exchangeable aluminum appears. The DBS decreases accordingly, especially at the high fertilizer rates. Relatively greater acidification at 25°C (pH decreases by 0.4–0.6 units), Table 4, is noted, which is accompanied by the consumption of hydrogen ions and their entry into strongly acidic positions, leading to destruction of soil adsorbent and the appearance of exchangeable Al. Soil acidification at 35°C is the greatest and pH decreases by 0.5–0.8 units, especially in the Alluvial-meadow soil, which correlates with an increase in the exchangeable Al and a decrease in the DBS, especially in the system of the low-colloidal Alluvial-meadow soil from Tsalapitsa and the Osmocote fertilizer, which lacks Ca.

We believe that the increase in temperature to 35°C accelerates microbial activity, and respectively, the degree of mineralization of soil N, and decomposition of soil organic matter. The decrease in pH is due to nitrification of NH_4-nitrogen with the participation of soil microorganisms and release of hydrogen. With an increase in the amount of added fertilizer, respectively N, the acidifying potential of the soil increases, which correspondingly lowers the pH.

Figures 1 to 6 present the data from the trace element extraction in 0.01 mol/l $CaCl_2$ for the two experimental soils in mg/l, recorded on the 60th day of incubation by maintaining the respective T° in the climate chamber. The highest values were obtained at 25°C extraction compared to 15°C, while at 35°C there was a decrease in the concentration of some trace elements. In the Cinnamonic forest soil of heavier texture, the data for the soluble forms of the elements for the two highest temperatures are much lower than in the Alluvial meadow soil, which released more trace elements for all the three selected temperatures, especially Mn.

For Cu, Zn, Fe and Mn (Figures 1–4), increase in the concentration was observed with increase of the fertilizer

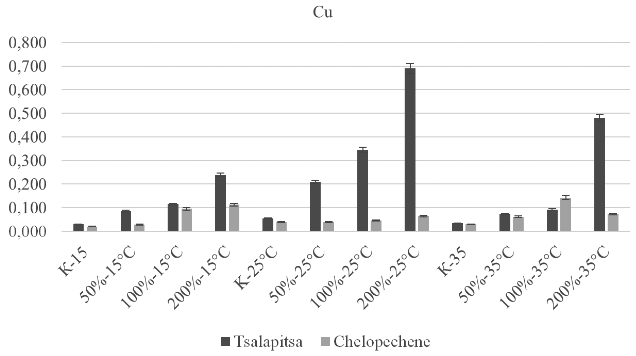

Fig. 1. Copper content (mg.l^{-1}) in the extracts of 0.01M $CaCI_2$ in the Alluvial meadow soil and the Cinnamonic forest soil

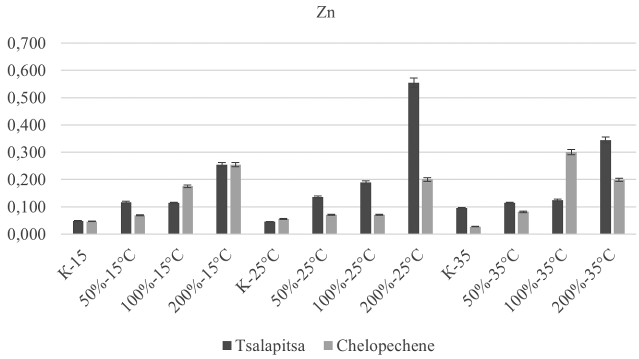

Fig. 2. Zinc content (mg.l^{-1}) in the extracts of 0.01M $CaCI_2$ in the Alluvial meadow soil and the Cinnamonic forest soil

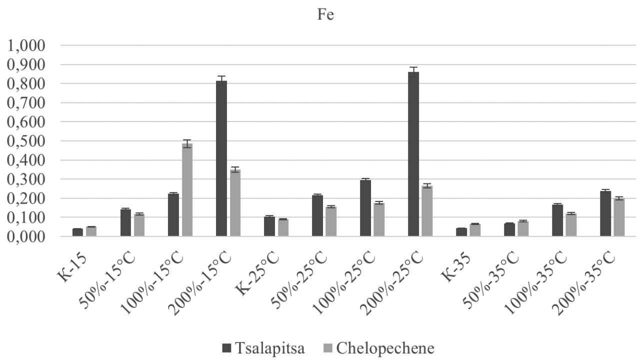

Fig. 3. Iron content (mg.l^{-1}) in the extracts of 0.01M $CaCI_2$ in the Alluvial meadow soil and the Cinnamonic forest soil

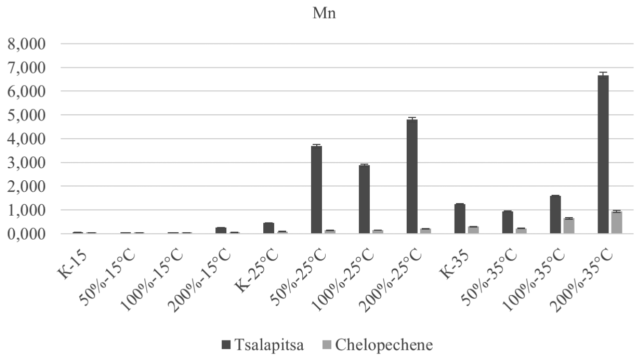

Fig. 4. Manganese content (mg.l^{-1}) in the extracts of 0.01M $CaCI_2$ in the Alluvial-meadow soil and the Cinnamonic forest soil

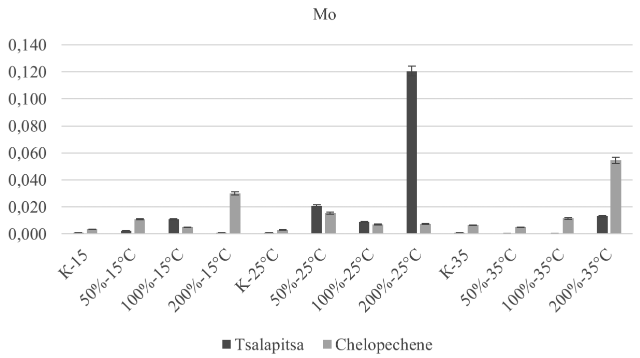

Fig. 5. Molybdenum (mg.l^{-1}) content in the extracts of 0.01M $CaCI_2$ in the Alluvial-meadow soil and the Cinnamonic forest soil

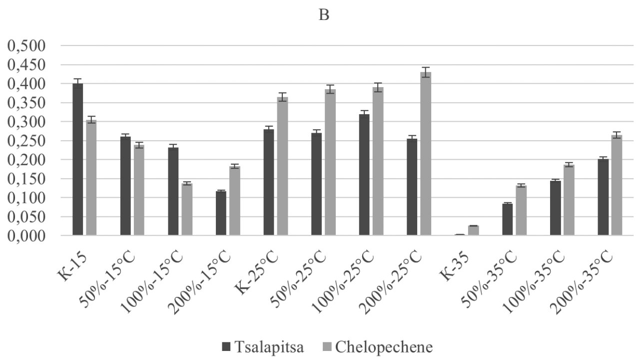

Fig. 6. Boron content (mg.l^{-1}) in the extracts of 0.01M $CaCI_2$ in the Alluvial-meadow soil and the Cinnamonic forest soil

rate in both soils, however the rate was higher in the Alluvial meadow soil. We consider that the early release of the microelements, especially in the Alluvial meadow soil with a lighter texture, can also be a cause of plant toxicity.

For B and Mo different trends in the solubility were found in the two soils, i.e. higher release in the Cinnamonic forest soil than in the Alluvial meadow soil and depended on the amount and nature of the clay content (Table 1). The trends were consistent with boron and molybdenum behavior in noncalcareous soils (Stanchev et al., 1982). For instance, for B adsorption was assumed to occur by means of ligand exchange with aluminol groups at the edges of the clay particles and was found to increase at low pH, peak at 8 to 10, and decrease at high pH (Goldberg & Glaubig, 1986). Molybdenum adsorption in noncalcareous soils exhibits a peak near pH 3 to 4 and decreases with increasing pH up to pH 7 (Goldberg et al., 1996). The main source of boron in soils is the mineralization of soil organic matter. Plant-available boron is present in the soil solution mainly as undissociated boric acid (H_3BO_3), which is a neutral molecule and is not attracted to negatively charged soil colloids in soils.

For all the trace elements, lower ranges of concentrations in the extracts and greater fixation was observed in the Cinnamonic forest soil with the heavier texture and higher sorption capacity, compared to the Alluvial meadow soil. In the Alluvial-meadow soil, the most favorable temperature for the diffusion of the microelements for the studied period of two months was found at 25°C when higher concentrations were reached, while e.g. at 35°C the solubility of the trace elements decreased.

Sources of trace elements and relationships in treated soils

Principal component analysis was applied to the data from the soluble forms of microelements in the two soils, in order to identify the sources of the elements, the interrelationships between them, and distinguish groups of elements with different behavior. Each principal component identified (factor) is a linear combination of the output variables, the trace elements Cu, Zn, Fe, Mn, B, Mo. The method allows the simultaneous study of several parameters and explains the variance in the data in the process of reducing them to unrelated components (factors).

Extracted factors were those with an eigenvalue > 1. We also conducted a cluster analysis, with the individual parameters hierarchically grouped using the weighted mean relationship between groups and Pearson's correlation. Principal component analysis is based on the six trace elements as principal variables.

In the Alluvial-meadow soil, it turns out that two main components with eigenvalues > 1 were identified, reflecting 65.3% (PC1) and 17.3% (PC2) of the total variance of 82.6%, respectively. The correlation matrix and the component matrix are presented in Tables 6 and 7. The first com-

Table 6. Component matrix for the Alluvial-meadow soil

Rotated Component Matrix[a]		
	Component	
	1	2
Cu	,975	,129
Zn	,989	-,061
Fe	,807	-,148
Mn	,751	,111
Mo	,871	,150
B	,040	,986

Table 7. Correlation matrix for the Alluvial-meadow soil

		Cu	Zn	Fe	Mn	Mo	B
Correlation	Cu	1,000	,960	,731	,815	,804	,159
	Zn	,960	1,000	,810	,716	,840	-,015
	Fe	,731	,810	1,000	,293	,667	-,024
	Mn	,815	,716	,293	1,000	,530	,058
	Mo	,804	,840	,667	,530	1,000	,171
	B	,159	-,015	-,024	,058	,171	1,000

ponent PC1 was loaded with the elements Cu, Zn, Fe, Mn, Mo, and the second with B. The results of the multifactorial analysis show that Cu, Zn, Fe, Mn, Mo have a similar source (reservoir in this soil) and bioavailability behavior, estimated by desorption with 0.01M $CaCl_2$. The second component was loaded by the element B and indicates a different source.

The dendrogram in Figure 7 from the Cluster analysis indicates the presence of two main groups (branches). The first group consists of the five trace elements Cu, Zn, Fe, Mn, Mo without the participation of the element boron. The second

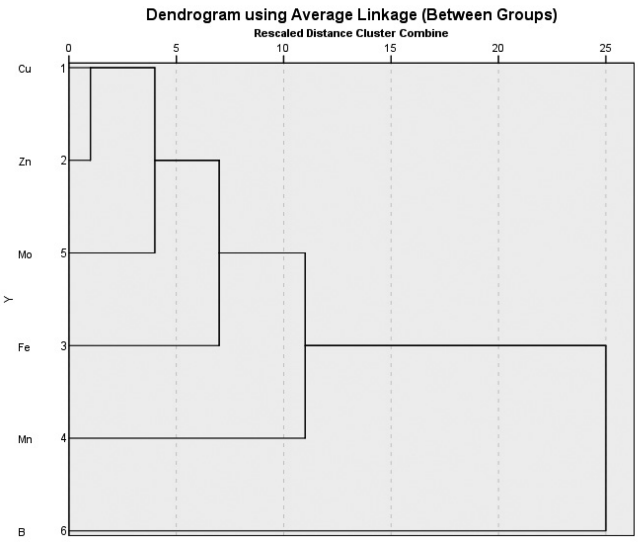

Fig. 7. Dendrogram for the Alluvial-meadow soil

main group consists of the element B. The first main group can be divided into two subgroups: subgroup 1: Cu, Zn, Fe, Mo; subgroup 2: Mn. Manganese shows greater solubility in this soil than the other elements. The cluster analysis confirms the finding of a similar source (reservoir) of Cu, Zn, Fe, Mo, i.e. the soil-fertilizer adsorption complex, the weaker iron-manganese bond and another source of B, the apparently added fertilizer. It should be emphasized that the extraction in 0.01 M $CaCl_2$ is calibrated for bioavailable forms of boron in soils, unlike the other trace metals for which also other extractants have been proved to describe availability to plants, e.g. EDTA, DTPA (Lindsay & Norvell, 1978).

In the case of the Cinnamonic forest soil, three main components (Tables 8 and 9) are sufficient to explain the total variance (87.4%), PC1, 48%, PC2, 22.4%, PC3, 17%, respectively. The first component is occupied by the elements Cu, Zn, Fe, the second by Mn, Mo and the third by B.

Table 8. Correlation matrix for the Cinnamonic forest soil

Correlation Matrix							
		Cu	Zn	Fe	Mn	Mo	B
Correlation	Cu	1.000	.935	.523	.394	.305	-.273
	Zn	.935	1.000	.547	.461	.462	-.086
	Fe	.523	.547	1.000	-.137	.213	-.054
	Mn	.394	.461	-.137	1.000	.681	-.127
	Mo	.305	.462	.213	.681	1.000	-.012
	B	-.273	-.086	-.054	-.127	-.012	1.000

Table 9. Component matrix for the Cinnamonic forest soil

Component Matrix[a]	
	Component
	1
Cu	.984
Zn	.970
Fe	.771
Mn	.740
Mo	.881
B	.360

The dendrogram (Figure 8) includes two main branches, the first being occupied by B and the second main by the remaining elements, but subdivided into two separate branches – the first is occupied by the elements Cu, Zn, Fe, and the second by Mn and Mo.

If the control soils are excluded from the analysis, no differences were noted for the Cinnamonic Forest soil in the identified components, groups and interrelationships between the investigated parameters, while for the Alluvial-meadow soil all the elements load only one component

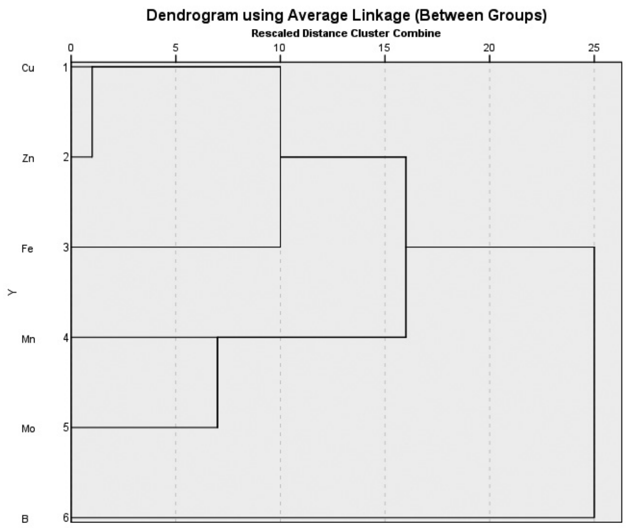

Fig. 8. Dendrogram for the Cinnamonic forest soil

Table 10. Component matrix with presence of only 1 component (Alluvial meadow soil)

Rotated Component Matrix[a]			
	Component		
	1	2	3
Cu	.834	.332	-.285
Zn	.840	.453	-.071
Fe	.880	-.159	.091
Mn	.023	.946	-.150
Mo	.220	.837	.114
B	-.072	-.009	.974

(Table 10). This is a very important finding which shows, that in the Alluvial meadow soil, the mobilization of the elements is mainly caused by the added fertilizer and no significant interaction the fertilizer-soil colloidal complex, has, yet taken place. We assume, that the reason for this finding is the lesser and insufficient interaction in the fertilizer-colloidal complex in the Alluvial meadow soil, due to the lower content of colloids, evidenced by the lower clay and organic carbon contents.

Conclusions

Two soils of different physico-chemical characteristics were treated with various rates of a macro- and microelements containing controlled-release fertiliser. The fertilizer gradually releases the trace elements Cu, Zn, Fe, Mn, Mo, B, at optimal humidity, and their diffusion depended on the temperature and the time of equilibration of the soil-fertilizer system.

The two types of soils exhibit different adsorption capacities and degree of release of the studied trace elements under controlled conditions. A weaker release of the trace elements from the added fertilizer was observed in the Cinnamonic forest soil, which has a heavier texture and higher sorption capacity than the Alluvial-meadow soil. The PCA analysis carried out on the two soils shows a common source for the elements Cu, Zn, Fe, Mn, Mo and a different one for B in the Alluvial-meadow soil, and in the Cinnamonic Forest a similar source of mobilization in the soil solution for Cu, Zn, Fe, another for Mn, Mo and a third for B.

At both temperatures, a similar change in the physicochemical characteristics was observed, a slight decrease in pH, a decrease in the degree of base saturation and the appearance of exchangeable aluminum. The PCA analysis shows that in a two-month period, equilibrium is reached in the fertilizer-soil system, and the source of mobilization of the microelements in the soil solution in the Cinnamonic forest soil is mainly the soil colloidal complex, and in the case of the Alluvial meadow soil, the added fertilizer.

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