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THE AVAILABILITY OF BASE ELEMENTS (CA, MG, NA, K) IN SOME IMPORTANT SOIL TYPES IN SERBIA

ABSTRACT: In this paper results are presented of agrochemical and mineralogical analyses of 14 types of important soils in Serbia (Vojvodina and Central Serbia) and total content and availability of base alkali elements (Ca, Mg, Na, K) are determined. Total element content was as follows: Ca 2.22%; K 1.77%; Na 0.85% and Mg 0.61%. Total content of alkali metals in the soils investigated and their variations within and between the soil types, is in very good/close correlation with contents of primary and secondary minerals as well as their rates of weathering. Taking in account the average availabilities the most abundant is calcium with 947 mg/100 g, whilst the averages of the other elements (Mg, K and Na) are quite similar and are about of 40 mg/100 g of soil. The results obtained have shown that the soils investigated are well to moderate provided with K, Ca and Mg and that their deficit could not be expected in plant nutrition, apart for some plants/cultures in the case of magnesium due to occasionally higher Ca/Mg and K/Mg ratios.

KEY WORDS: soil, alkali metals, total and available contents

INTRODUCTION

According to Haby et al. (1990) from all alkali metals found in soils: K, Ca, Mg and Na, the most important in plant nutrition is potassium and it is occasionally found in plants in higher percentages than nitrogen. Most of agricultural plants, under optimal yield condition, would take up between 100 and 300 kg of potassium per hectare from soils. Calcium is following one in the significance amongst the alkali metals, which is usually in soils in ample supply for plant nutrition. Its contents in plants are about less then half of that of potassium. Third in significance is magnesium, which is present in plants about less then half of calcium, but in soils it is frequently found in deficit for plant nutrition. Sodium is common constituent in plants, but it is not an essential element, although for some plants (e.g. sugar beet) is an important element to achieve high yields.

Total content of potassium in soils varies within wide limits from 0.01% up to 4%, with most common values of about 1% and an average content between 1—2% (W i l d, 1988). In soils and many rocks, potassium occurs as major constituent of many rock-forming primary minerals, particularly in the alkali feldspars group: orthoclase and microcline, also as mica group: muscovite and biotite as well as secondary minerals, particularly illite. Principal source of available potassium in soils is its concentration in soils solution, which could be refreshed by cation exchange with adsorbed potassium ions, and which is also affected by content of fixed potassium (strongly bonded and non-exchangeable).

As with potassium, other three alkali metals (Ca, Mg and Na) are also present in silicate rock-forming minerals and later are transferred into mineral fraction of soils. Their contents depend on the rate of mineral weathering and the rate of leaching of weathered products. Principal source of Ca and Na are plagioclase group minerals: anortite and albite, whilst Mg is present in a few silicate minerals ouch as: biotite, pyroxenes and amphiboles. All mentioned minerals are weathered faster than potassium minerals. Beside that magnesium is also present in many secondary minerals (hydrobiotite, vermiculite and montmorillonite). Available forms of Ca, Mg and Na, as with potassium, are their exchangeable cations and various salts in soil solution.

With respect to content and state of potassium in our soils, during the last twenty years (decades) large number of papers was published, but the most of them were dealing with potassium availability and only a few were related to its state and chemical speciation in soils. With regards to the problems of the other three alkali elements there are much less available data and it is occasionally said they seam as ignored elements in soil chemistry investigations. All available data are presented as general chemical soil properties as well as in CEC analyses or in soil solution analyses (B o g d a n o v i c et al. 1973; J a k o v l j e v i c and B l a g o j e v i c, 1997). However, up to now there was no data dealing with spatial distribution of alkali metals in our soils, apart from a comprehensive/extensive paper by K o s t i c et al. (2001), about content, concentrations, spatial distribution and chemical speciation as well as mineralogy of magnesium in our soils.

MATERIAL AND METHODS

During a large scale sample collecting for the project, financed by the Ministry of Science and technology and Fund for Land Use, Protection and Organisation of the Republic of Serbia, an orthogonal regular grid was used to avoid bias in site location. For financial reasons sample collection was restricted to the layer 0—20 cm depth. Sampling was based on a 5 x 5 km cell and samples were collected. From this set of samples a selection of samples from Vojvodina, Šumadija and Northern Pomoravlje was taken to represent the most important (14) soil types and the number of 100 samples was obtained.

Total and available contents of the elements (Ca, Mg, K and Na) were determined. Total contents were analyzed after grinding of sample and digesting it in a mixture of aqua regia and HF in Pt crucible. Ca and Mg contents, after taken into solution and addition of lanthanum, were determined by AAS, whilst the K and Na contents were determined by a flame-photometric method. The available contents of alkali metals were determined by the same methods, but after the 1M NH_4OAc (pH 7.0) extraction.

Histograms of the frequency distribution and summary consisting of the mean, quartiles and range in a normal distribution of the concentrations of each element were made using STATISTICA for Windows 4.3b program. Experience in geochemical research has shown that analysing and mapping data by using the box-plot provide the best realization. The classes used to represent the data on the map were chosen from the box and wiskers analysis, as proposed by Kuerzl (1986). So, the map has the 5 classes. Raster map showing the distribution of the elements was drawn by computer, by using UNIRAS subroutine. Each square on the map represents the result from one 10 km grid scale.

RESULTS AND DISCUSSION

The results obtained during this investigation are given in the Table 1., where they are presented as total and available contents of analyzed alkali elements as well as average values and range of minimum and maximum arranged according to various soil types and as summary for all soils. In the soils investigated calcium is the most abundant alkali element with the average content of 2.25%, which is much higher value than the average (1.37%) for the soils in the world. The highest total calcium content is found in chernozem and semigley (3.4%), and the lowest in soil types: pseudogley, luvisol, dystric cambisol and vertisol (about 0.5%). This result have shown that soil types with higher calcium content have a very good correlation with soil mineral composition of primary and secondary minerals bearing calcium, such as: calcite, dolomite, plagioclas, smectite and mixed-layer-silicates (MSS 10—14). The soil types with low calcium content have mineral composition with dominant quartz, and lower content of calcium bearing minerals, particularly calcite and dolomite, as presented in the Table 2.

The average content of available calcium in our soil types is 947 mg/100 g, but it is present in very wide range limits between 93 and 2000 mg/100 g. However, only a limited number of samples of very acid pseudogley soil types have available calcium below 100 mg/100 g, when they could show signs of calcium deficit in plant nutrition, whilst the majority of soil types investigated have shown high contents of available calcium of about 1000 mg/100 g. In acid soil types content of available calcium is lower, but very close to the average contents of available calcium in soils investigated with about 300 mg/100 g. With regards to the afore mentioned, it imply that our soils contain ample/adequate supply of both total and available calcium for plant nutrition, which is evenly distributed over the area investigated, as could be seen from the map presented in Figure 1.

The average content of magnesium in our soils shows entirely adequate values for its average content in pedosphere. Its total content averages show

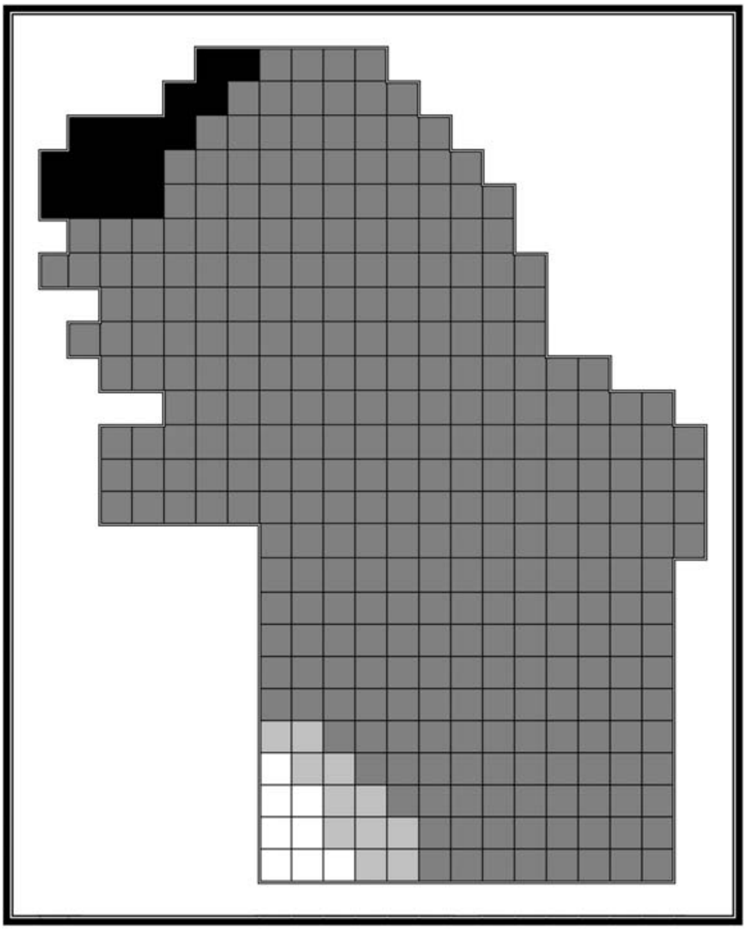
Table 1 — Total (%) and available (mg/100 gr) contents of alkali elements in the investigated soils

	Magnesium		Calcium		Potassium		Sodium	
Soil type	Total	available	Total	available	Total	available	Total	available
Chernozem	0.67* (0.25–1.00)	42 (27–65)	3.41 (0.87–7.90)	1475 (478–2000)	1.68 (0.84–2.20)	49 (17–90)	0.87 (0.71–1.04)	40 (30–51)
Semigley	0.74 (0.26–1.25)	43 (20–75)	3.29 (0.54–10.40)	1132 (333–1925)	1.77 (1.37–2.14)	45 (17–113)	0.83 (0.43–1.19)	40 (26–54)
Humogley and eugley	0.61 (0.20–1.00)	58 (22–93)	2.40 (0.25–6.00)	984 (225–1950)	1.84 (1.02–2.26)	56 (21–115)	0.94 (0.40–1.58)	43 (32–57)
Halomorphic Soils	0.57 (0.35–0.85)	37 (25–53)	2.05 (0.96–3.30)	1060 (390–1775)	1.85 (1.44–2.22)	83 (36–122)	0.97 (0.34–1.29)	33 (28–42)
Fluvisol	0.75 (0.44–1.00)	51 (32–80)	2.14 (0.61–7.50)	832 (308–1900)	1.81 (0.86–2.30)	26 (14–46)	0.92 (0.60–1.47)	51 (34–130)
Pseudogley	0.42 (0.25–0.57)	32 (10–45)	0.55 (0.17–1.17)	334 (93–703)	1.80 (1.58–2.00)	26 (23–32)	0.69 (0.42–0.81)	32 (18–39)
Eutric Cambisol	0.48 (0.26–1.25)	43 (20–75)	1.07 (0.42–3.51)	592 (275–1908)	1.74 (1.14–2.09)	32 (21–56)	0.76 (0.36–1.26)	37 (23–45)
Vertisol	0.35 (0.20–0.52)	27 (15–38)	0.68 (0.30–0.91)	340 (175–570)	1.94 (1.60–2.85)	31 (22–40)	0.91 (0.34–1.29)	33 (28–47)
Luvisol and Distr. Cambisol	0.36 (0.32–0.43)	30 (22–40)	0.51 (0.40–0.65)	274 (180–378)	1.69 (1.51–1.96)	28 (26–30)	0.75 (0.50–0.91)	36 (33–39)
Ranker and regosol	0.65 (0.39–1.26)	23 (12–38)	1.86 (0.20–4.05)	963 (160–1685)	1.72 (0.95–2.60)	23 (18–26)	0.80 (0.44–1.07)	36 (22–44)
All soils	0.60 (0.20–1.26)	41 (10–93)	2.25 (0.17–10.40)	947 (93–2000)	1.76 (0.84–2.85)	41 (14–122)	0.85 (0.34–1.58)	40 (18–130)

N. B. * Average (min-max)

Table 2 — Average mineral composition (%) of the bulk samples of the soils investigated

	Quartz	Plagio clase	Ortho clase	Chlorite	Mica + Illite	Smectite + Verm.	Mixed Layers	Kaoli-nite	Calcite	Dolo-mite	Goetite
Chernozem	53.8	8.7	0.7	6.0	19.0	0.9	0.3	1.0	4.5	4.9	0.2
Halomorphic soils	57.3	10.4	0.7	4.7	20.6	0.5	0.4	1.1	1.2	2.3	0.2
Semigley	52.5	8.5	0.6	5.4	19.8	1.8	0.2	1.5	4.3	5.1	0.2
Humo- + Eugley	52.9	11.2	0.7	5.3	21.7	2.6	0.3	1.7	1.7	1.5	0.3
Fluvisol	51.2	10.4	0.6	5.7	22.4	3.3	0.2	2.2	2.3	1.7	0.2
Pseudogley	67.6	6.4	0.5	4.6	16.5	1.3	1.3	1.1	0.1	0.1	0.1
Eutric Cambisol	63.5	8.9	0.8	3.7	16.5	2.3	0.2	2.3	0.8	0.2	0.3
Vertisol	70.3	8.8	1.4	2.5	10.8	4.0	0.3	1.1	0.2	0.0	0.3
Distric Cambisol + Luvisol	69.1	7.4	0.8	4.7	13.5	2.3	0.3	1.3	0.3	0.0	0.4
Regosol + Ranker	58.9	6.9	0.8	4.7	18.9	2.5	0.4	1.9	2.5	2.1	0.4
All soils	57.6	8.8	0.7	5.0	18.7	2.0	0.3	1.6	2.5	2.6	0.2

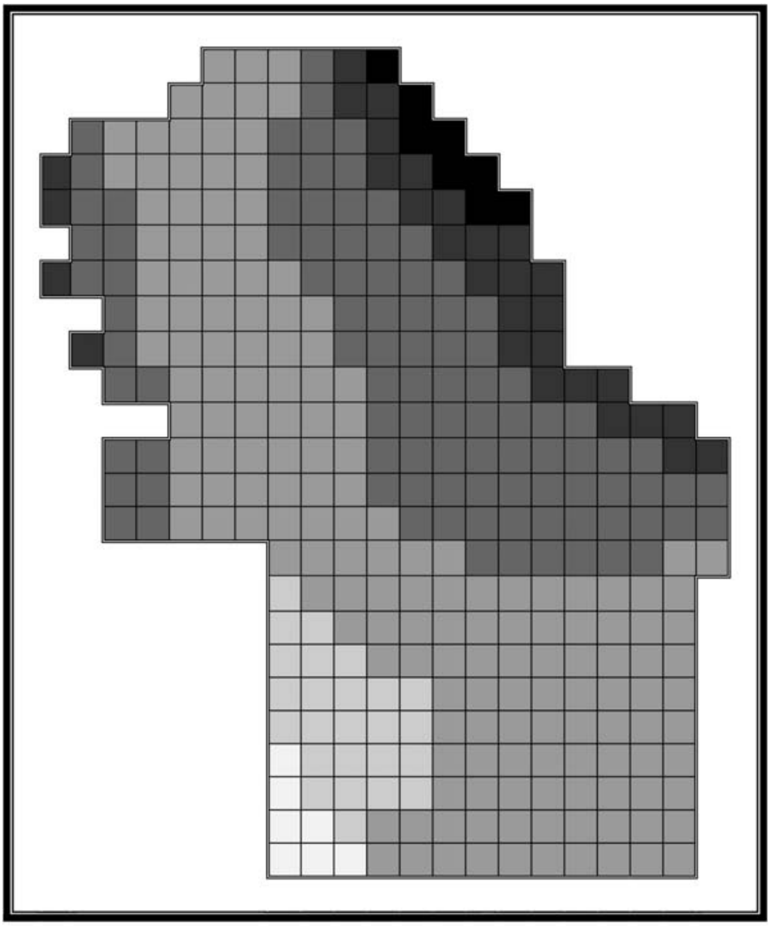


Available Ca (mg/100g)	93-230	230-375	375-1575	1575-1913	1913-2000

Figure 1. – Content and spatial distribution of available calcium in the investigated soils from Serbia

smaller variations between than within the soil types. In general, magnesium total content varies in wide range limits between 0.20 to 1.26%. Its total content averages are quite low (0.35—0.48%) in the following soil types: vertisol, luvisol, dystric cambisol, pseudogley and eutric cambisol. These are more weathered and more acid soils, with progressive transformation of mica and illite to clay minerals with subsequent leaching of magnesium as well as other base elements.

The average content of available magnesium in soils investigated is 41 mg/100 g, with interval from 10 to 93 mg/100 g, as could be seen from the



Available Mg (mg/100g)	< 20	20 - 40	40 - 65	65 - 80	> 80

Figure 2. – Content and spatial distribution of available magnesium in the investigated soils from Serbia

map presented in Figure 2. The average contents of available magnesium show good correlation with its total content as could be seen for vertisol, pseudogley and luvisol from the Table 1. In general, all investigated soils are on average quite well supplied with available magnesium for plant nutrition, with only two soil types (pseudogley and ranker) approaching the upper limits of magnesium deficit (10 mg/100 g) in soils.

Since the Ca/Mg and K/Mg ratios are limiting factor for available magnesium in plant nutrition, its averages, standard deviation and ranges are presented in the Table 3. With respect to plant nutrition Ca/Mg ratio has beneficial

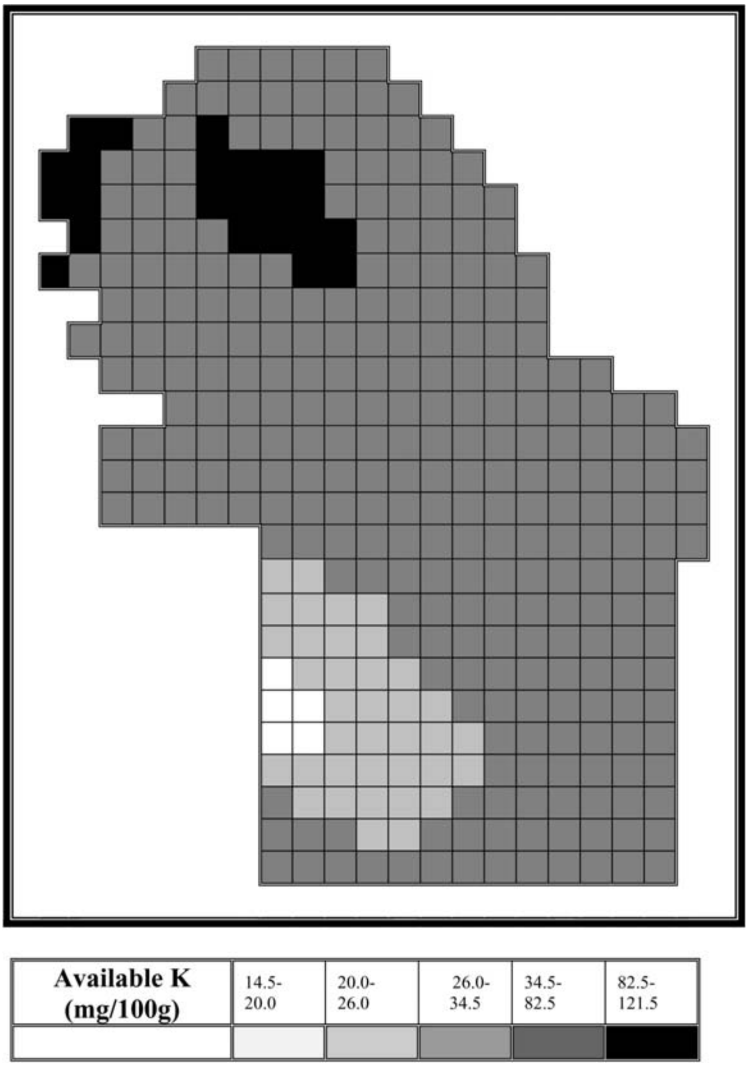


Figure 3. – Content and spatial distribution of available potassium in the investigated soils from Serbia

effects in the range from 1:1 to 5:1. Ratios lower than 5:1 are detected in about 10% of soils investigated, whilst the bulk of soils have shown the ratio between 5:1 and 20:1. The average value for all soils is 15.4:1. Lower Ca/Mg ratio values are limited to some areas in Sumadija and Pomoravlje, whilst the higher values could be associated to far northern areas of Backa, where total content of magnesium is connected to high contents of magnesium bearing minerals (dolomite and chlorite) in soils. On average, even our acid soils have shown Ca/Mg ratio higher then 5:1, whilst chernozem has shown 22:1 and ranker, regosol and rendzina have even 29.9:1. Maximum values were detected

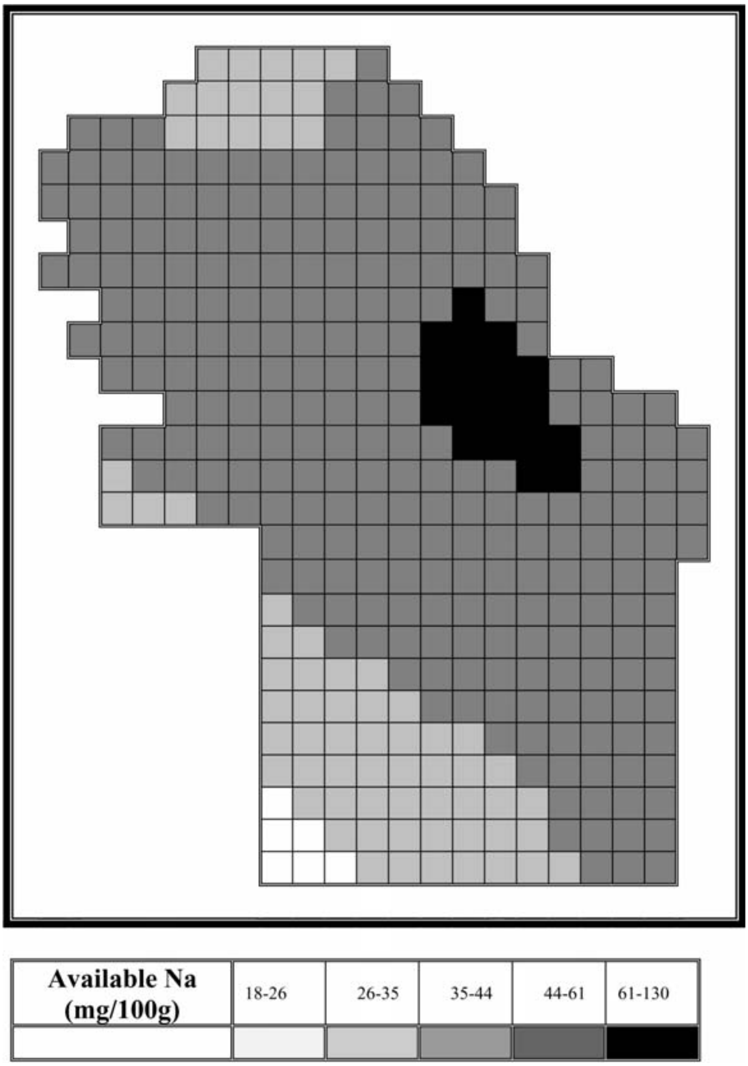


Figure 4. – Content and spatial distribution of available sodium in the investigated soils from Serbia

mostly about 30:1, with some extreme values of 50.4:1 in eutric cambisol and 78.8:1 in rendzina developed on marly limestone. With regards to the afore mentioned, it imply that our soils have slightly higher Ca/Mg ratio, which could affect some sensitive plants to magnesium deficits in their nutrition. Because of this it would be necessary to continue with such, but detailed investigation in future.

Another important factor in magnesium plant nutrition is the K/Mg ratio. The obtained results presented in the Table 3., have shown that the rations for the bulk of samples and soil types are below 1:1, which is adequate/agreeable for the most arable and vegetable crops. Only in more acid soils the K/Mg ratios are over 2:1, which could lead to reduced uptake of magnesium in some plants.

Table 3 — Ca/Mg and K/Mg ratios in the soils investigated (mean, standard deviation and interval)

Soil type and number of samples	Ca/Mg	K/Mg
	m.e./100 g	
Fluvisol (n = 8)	12.3±9.2 3.9—28.9	0.3±0.1 0.2—0.5
Eutric cambisol (n = 14)	11.1±12.0 3.3—50.4	0.6±0.2 0.3—1.0
Pseudogley (n = 5)	6.0±2.0 4.8—9.5	0.6±0.4 0.4—1.4
Semigley (n = 20)	15.8±7.1 5.6—30.8	0.6±0.2 0.3—1.2
Humogley and eugley (n = 12)	11.2±7.8 2.5—31.5	0.7±0.5 1.2—1.9
Regosol, Ranker, Rendzina (n = 6)	29.9±28.7 5.3—78.8	0.7±0.2 0.4—0.9
Chernozem (n = 20)	22.1±8.7 5.6—36.6	0.7±0.3 0.3—1.5
Vertisol, Luvisol, Distric cambisol (n = 10)	6.8±2.9 4.0—17.3	0.8±0.3 0.4—1.2
Halomorphic soils (n = 5)	17.1±9.2 7.2—30.0	1.2±0.3 0.9—2.5
All soils (n = 100)	15.4±12.4 2.5—78.8	1.5±0.8 0.1—2.5

The average total content of potassium in soils investigated is slightly higher (1.76%) then the average (1.36%) for the world soils. The results presented in the Table 1., have shown only slight variation (1.68—1.98%) in the average values of total potassium content for soils investigated. This could be only explained with an even and uniform distribution of potassium bearing minerals (orthoclase, micas and illite) in the soils. However, these variations between investigated soil types could be quite significant, within wider limits (0.84—2.85%) or even within the same soil type e.g. fluvisol (0.86—2.30%).

The average content of available potassium is 41 mg/100 g, and according to the map in the Figure 3. the most of soils comprise of over 20 mg/100 g of available potassium, which could purport that our soils are quite well supplied with this important plant nutrient. It is necessary to emphasize that the range limits for available potassium are quite wide, between 14 and 122 mg/100 g. The highest values and the averages are observed in halomorphic soils, eugleys, humogleys and smigleys. Only a limited number of samples have shown values below 20 mg/100 g, which could be considered as moderate contents in supply of this important plant nutrient.

Our soils have shown slightly higher averages (0.85%) of total sodium than the average world soils (0.6%). Its behavior is similar to that of plagioclase and has shown similar average values of soils investigated, but the variations within the soil types are quite significant and range between 0.34 to 1.58%.

The average content of available sodium is 40mg/100 g, with uniform and slight variations between the soil types, which are between 32 and 51 mg/100 g. However, these variations within the samples are in much wider interval between 18 and 130 mg/100 g. Maximum content of available sodium is determined in fluvisols, which could be an effect of high concentration of soluble salts. Content of available sodium in soils investigated is almost the same as for potassium and magnesium, so it could be concluded that our soils are well supplied with available sodium, but its limits are not determined, since there is no published data for this element, which is considered as an no-essential in plant nutrition.

CONCLUSIONS

The comprehensive investigation of soils from Vojvodina, Sumadija and Northern Pomoravlje, of our main arable regions, has showed a wide range of base alkali metals concentrations. Based on the results the following conclusions could be presented:

Total contents of all investigated alkali metals in our soils and their variations between and within various soil types are in close correlation with concentrations of primary and secondary minerals and their rate of weathering in soils.

The averages of total content of Ca, Mg and K in our soils are slightly higher than their averages in world soils, whilst sodium content is similar to the world average.

Taking in account average values of available K, Ca Mg and Na, our soils could be considered as well supplied for the plant nutrition. Only a limited number of samples has shown lower values and are considered as deficient in base alkali metals.

However, in the case of deficit of available magnesium in soils with high ratios of Ca/Mg and K/Mg, it could be a limiting factor in available magnesium uptake and utilisation by plants, particularly to the sensitive plants with higher demand for magnesium as well as favourable ratios of available cations such as: Ca, K, Na, and H.

This paper has shown a need for the wider investigation of chemistry and mineralogy of soils in Serbia, which are considered in general as well supplied with base alkali metals.

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СНАБДЕВЕНОСТ ВАЖНИЈИХ ТИПОВА ЗЕМЉИШТА СРБИЈЕ ОСНОВНИМ АЛКАЛНИМ ЕЛЕМЕНТИМА (Ca, Mg, K и Na)

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Резиме

У овом раду је испитивано 100 репрезентативних узорака 14 типова земљишта Србије (Војводина, Шумадија и Северно Поморавље) у погледу укупног и приступачног садржаја основних алкалних метала (Ca, Mg, K и Na). Такође је приказан и просечан минералошки састав испитиваних земљишта. Нађени су следећи средњи укупни садржаји испитиваних елемената: Ca — 2,25%; K — 1,77%; Na — 0,85% и Mg — 0,61%. Укупни садржаји испитиваних алкалних метала у нашим земљиштима и њихова варирања између и унутар земљишних типова у уској су вези са заступљеношћу одређених примарних и секундарних минерала и њиховом отпорношћу на распадање. Према средњим вредностима за приступачне садржаје највише има калцијума (947 mg/100 g), а средњи садржаји за остале базе (Mg, K и Na) су врло слични и крећу се око 40 mg/100 g. Добијени резултати показују да су испитивана земљишта добро и средње обезбеђена K, Ca и Mg и да се не могу очекивати њихови дефицити за исхрану биљака, осим за неке културе у случају магнезијума, због понекад сувише повишених односа Ca/Mg и K/Mg.