Impact of reclamation practices on the content and qualitative composition of exchangeable base cations of the solonetz soil

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Abstract

This paper shows the impact of long-term reclamation practices on the content and qualitative composition of exchangeable base cations of the solonetz soil. Based on the results of field visits and laboratory analyses, chemical and agrotechnical reclamation practices (phosphogypsum application 25 t ha^{-1} or 50 t ha^{-1}, drainage pipes distance 20 m, trenching 50 cm, fertilization, soil tillage and cropping) have been applied to the solonetz soil. Analyses of cation exchange capacity (CEC) have shown that calcium (Ca^{+2}) and sodium (Na$^+$) cations prevailed over magnesium (Mg^{+2}) and potassium (K$^+$) cations in the soil exchange complex in all variants and all depths. Comparisons among variants and soil layers have shown that the contents of individual exchangeable base cations varied significantly (P $\leq$ 0.05). The highest changes in exchangeable calcium content were achieved to the depth of 30 cm, in both treated variants, and these changes were still higher in the variant with 50 t ha^{-1} of phosphogypsum. The content of exchangeable Na$^+$ decreased by 43 % to 71% in variant I and by 23% to 64% in variant II in comparison with the control variant. The application of the reclamation practices caused changes in the composition and proportions of cations in the layers of the solonetz soil to the depth of 50 cm. When compared with CEC in the control variant, the exchangeable sodium percentage (ESP) in the treated variants decreased by 6% to 15% after fifteen years.

Keywords: reclamation; exchangeable cations; phosphogypsum; solonetz soil.
Abbreviations: cation-exchange capacity (CEC); exchangeable sodium percentage (ESP); sodium adsorption ratio (SAR); gypsum requirements (GR); exchangeable Na (Na$_{exch}$); equivalent weight (Eqwt)

Introduction

Solonetz soils cover large areas around the world. In Europe only, they cover more than 20 million ha. There are about 80.000 ha of solonetz soil in Vojvodina - a region in the south of the Pannonian basin, in the north of the Republic of Serbia. It is characterized by unfavorable physical and chemical features, caused by high contents of clay and sodium in the Bt,na horizon (Belić et al., 2006). Sodium causes a strong alkaline reaction and peptization of colloids, which are primary causes of extremely unfavorable chemical, physical, and water and air properties of solonetz soils. For those reasons, this soil type is typically used as a natural pasture. The objective of applying reclamation measures to solonetz soils is to change their cation content, which is achieved by decreasing the sodium level and increasing the calcium cation level (Ca^{2+}), which leads to the coagulation of soil colloids (Kruzhilin and Kazakova, 2011). Improvement of solonetz properties, achieved by application of complex reclamation practices, has been achieved in a variety of different climatic conditions. The time needed to reclaim soils such as solonetz depends on climatic conditions, reclamation practices applied, and the predefined extent of improvement. In order to attain best possible effects in the shortest period of time and maintaining economic viability, it is necessary to choose reclamation practices based on the specific nature of the soil type in question and the climatic conditions of the given area. Based on the above theoretical postulates and the results of solonetz reclamation projects previously conducted in this region, the following reclamation practices were determined to be necessary: chemical reclamation - phosphogypsum application, physical reclamation - loosening the compact Bt,na horizon, excess sodium removal - setting up a combination of underground pipes and surface drainage canals, agrotechnical reclamation - fertilization with mineral and organic fertilizers, biological reclamation - selecting and growing appropriate field crops (Petrović et al., 2010). The use of chemical reclamation dates back to German naturalist Meyer (cit. Lozanovska, 1987). He noticed positive effects of gypsum on sodic soils and recommended its application. The chemical reaction created by the input of gypsum in soil was explained by Hilgard (1906): Na$_2$CO$_3$ + CaSO$_4$ $\leftharpoonup \rightharpoonup$ Na$_2$SO$_4$ + CaCO$_3$. Hilgard was cited in numerous papers, because his theoretical and practical instructions have been accepted in many countries (Miljković, 1963). The research results of Gedroiz (1917) served as the scientific basis for solonetz reclamation in the former USSR. Numerous studies showed that solonetz reclamation by gypsum application was highly effective, bringing significant increases in the productivity of the

cultivated plants (Pak, 1975; Abrol and Gupta, 1988; Bahceci, 2009; Makoi, 1995; Agar, 2011; Lyubimova, 2011; Voropaeva et al., 2011). Phosphogypsum is a byproduct in the process of phosphoric acid production. Depending on the origin of phosphates, phosphogypsum contains around 1-1.25% P_2O_5, 0.25-1.0% F, 2-3% SiO_2, 0.05-0.4% Al_2O_3, 0.1-0.2% Fe_2O_3, 0.01-0.2% Na_2O, and 0.01-0.07% organic matter. Phosphogypsum provides good results in reclaiming highly alkaline soils. Phosphogypsum application leads to the forming of sodium sulphate (Na_2SO_4), which is leached from the soil profile. The application of phosphogypsum increases the content of Ca^{2+} and decreases the alkaline reaction, thus improving the content and stability of structural aggregates, water and air properties, thermal and nutrient status, and the effective fertility of solonetz soils (Amstrong and Tanton, 1992; Gharaibeh et al., 2009). In the years following phosphogypsum application, increased amounts of organic and mineral fertilizers are combined with conventional cultivation practices. During that period, crops tolerant to a high alkaline reaction (wheat, barley, sunflower, sorghum, castor bean) are grown. After soil quality improvement has been achieved, other crops may be grown on the reclaimed solonetz soil as well (Dimitrijević et al., 2011). The aim of this paper was to determine the changes in the content and qualitative composition of exchangeable base cations in the adsorptive complex of a solonetz soil after fifteen years of application of reclamation practices.

Results and Discussion

Content of exchangeable Ca^{2+}

Compared with the control variant, the content of exchangeable Ca^{2+} increased in the treated variants, in all soil layers to the depth of 50 cm (Table 1). In the control variant, the content of Ca^{2+} varied from 1.85 cmol kg^{-1} in the surface layer (0 - 10 cm) to 4.31 cmol kg^{-1} in the layer from 40 to 50 cm, with a trend of increase with depth. In variant I, the content of Ca^{2+} varied from 8.47 to 9.35 cmol kg^{-1} and in variant II from 10.27 to 14.22 cmol kg^{-1}. In contrast to the control, with the which the content of Ca^{2+} decreased with depth in variants I and II. Largest changes in the content of exchangeable Ca^{2+} were achieved to the depth of 30 cm in both treated variants, and better results were obtained in the variant with 50 t ha^{-1} of phosphogypsum.

Content of exchangeable Mg^{2+}

Magnesium (Mg^{2+}) content was less abundant than Ca^{2+} content in all variants and examined layers (Table 2). The application of phosphogypsum increased the content of exchangeable Mg^{2+} in both treated variants, with a tendency of Mg^{2+} increase with depth in both variants too.

Content of exchangeable Na^+

The distribution of exchangeable sodium (Table 3) in the examined layers was similar to that of the exchangeable magnesium. The contents of exchangeable sodium, however, were significantly higher in all examined layers than the contents of magnesium. In the control variant, the content of Na^+ varied from 4.62 cmol kg^{-1} in the surface layer (0 - 10 cm) to 13.79 cmol kg^{-1} in the layer from 40 to 50 cm. When compared to the Na^+ content in the control variant, the content of exchangeable Na^+ decreased by 43% to 71% in variant I, and by 23% to 64% in variant II.

Content of exchangeable K^+

Highest contents of exchangeable K^+, from 2.88 to 3.30 cmol kg^{-1}, were found in variant II, followed by variant I, from 2.08 to 2.45 cmol kg^{-1} (Table 4). The contents of exchangeable potassium in the control variant were lower than those in the treated variants. The control variant contained only 0.38 cmol kg^{-1}of exchangeable K^+ in the surface layer (from 0 to 10 cm), while the highest content of exchangeable K^+, 0.83 cmol kg^{-1}, was in the layer 20 to 30 cm. The distribution of exchangeable K^+ along soil profile was fairly uniform in the treated variants.

Sum of base cations

The sums of base cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) in variants I and II were increased from 9% to 57% in comparison with the control variant (Table 5). The highest sums of base cations were found in variant II (from 19.40 cmol kg^{-1} to 26.23 cmol kg^{-1} of soil). In the control variant, the sums of base cations ranged from 7.55 to 20.23 cmol kg^{-1} of soil and they were significantly lower than the values in variants I and II. According to the distribution per soil layers, the sums of base cations increase with depth, almost invariably in all variants.

Soil pH

The values of soil pH (in 1M KCl) differed in the examined variants and soil layers (Table 6). The soil reaction varied from slightly acid, over neutral, to alkaline. The surface layers of all examined variants had lower pH values than the deeper layers. According to Thun's (1955) classification, the surface layer (0 - 10 cm) in the control variant had a slightly acid to neutral reaction (pH 6.5). The soil reaction increased with depth, with all the deeper layers becoming alkaline. Compared with the control variant, the pH value decreased in almost all layers of the treated variants. In variant I, the layers from 0 to 20 cm were neutral (pH 6.68-6.88) and from 20 to 50 cm alkaline (pH 7.36-7.91). In variant II, the lowest pH value (pH 5.41) was in the surface layer, the highest (pH 7.13) in the layer from 40 to 50 cm.

ESP

Compared with the values of CEC, the exchangeable sodium percentage was below 15% in almost all layers of the treated variants, except in the layer 40 to 50 cm in variant I and variant II (23.88% and 18.72%, respectively). The reclamation measures decreased the values of ESP from 6.02% to 15.55 % in all analyzed layers (Table 7).
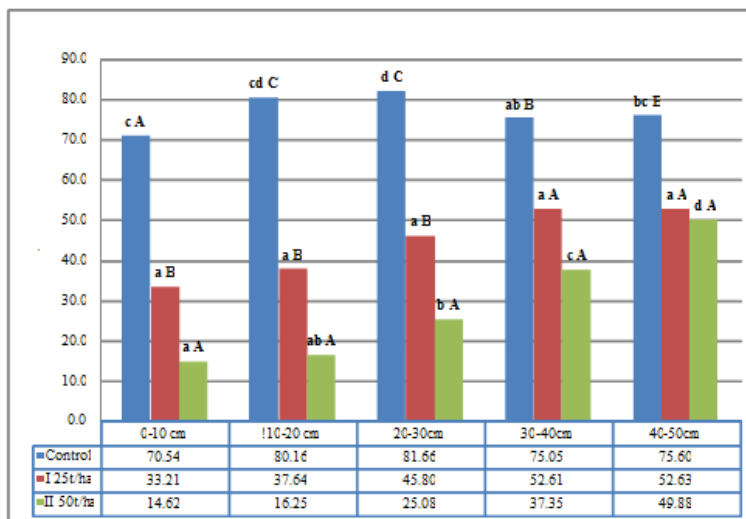
Cation exchange

A primary goal of solonetz reclamation is to decrease the exchangeable sodium percentage below 15% of CEC (WRB, 2006; Agar 2011; Voropaeva et al., 2011). Soil cation content is variable due to specific properties of soil colloids, which are typically negatively charged and have the ability to adsorb and desorb cations. The energy of adsorption depends on the charge of individual cations and the thickness of the layers of water molecules. Hydrophilic Na^+ ions have lower adsorption energy than K^+ ions. When in soil, ions are placed in the following order according to their adsorption energy: $Ca^{2+} > Mg^{2+} > K^+ > Na^+$. It is characteristic for cations that, beside the adsorption in the diffuse and adsorptive layer, they

Table 1. The values of exchangeable calcium (Ca^{2+}) in the treated variants and the control.

Depth (cm)	Ca^{2+} (cmol kg^{-1})					Ca (%)	
	Control	Variant I	Variant II	Difference I	Difference II	Difference I	Difference II
0-10	1.85 aA	8.85 aB	13.34 bcC	+7.00	+11.49	+478	+721
10-20	1.91 aA	9.21 aB	14.22 cC	+7.30	+12.31	+482	+745
20-30	2.40 aA	9.35 aB	12.97 abcB	+6.95	+10.57	+390	+540
30-40	4.21 bA	9.34 aB	11.25 abB	+5.13	+7.04	+222	+267
40-50	4.31 bA	8.47 aB	10.27 aB	+4.16	+5.96	+197	+238

Control - natural pasture, variant I - PG 25 t ha^{-1} + soil loosening down to 50 cm of depth, drain spacing of 20 m, variant II - PG 50 t ha^{-1} + soil loosening down to 50 cm of depth, drain spacing of 20 m. Means in the same column followed by different small letters are significantly different at P ≤ 0.05 using Fisher's LSD test. Means in the same row followed by different capital letters are significantly different at P ≤ 0.05 using Fisher's LSD test.

Fig 1. Percentages of Mg^{2+} and Na$^+$ compared with the sum of base cations.

can be bonded in the interlaminar space of clay minerals with the 2:1 grid structure, and they are excluded from cation exchange. For example, this is the case with ions of K$^+$ (ion radius 0.13 nm), which enter the hexagonal apertures in tetrahedrons. Only the three-layered minerals, for example smectites, have the ability of bonding cations. Cations enter the interlaminar space when it is expanded (Vozbuckaja, 1968) and they bond with both negative oxygen surfaces.

Sum of exchangeable cations

Examining a solonetz soil under irrigated alfalfa, Szabolcs (1971) found that the sum of exchangeable cations in the surface layer (0 - 20 cm) increased from 28.0 cmol kg^{-1} to 31.94 cmol kg^{-1}. Typical steppe solonetz soils in various regions of Russia were found to be similar in the sum of exchangeable cations (Ca^{2+}, Mg^{2+}, Na$^+$ and K$^+$). The sum of exchangeable cations in the surface horizon is typically very low and it varies from 5 to 10 cmol kg^{-1}. This value increases with depth and in the Bt,na horizon it varies from 10 to 20 cmol kg^{-1}. In the C-horizon, the value decreases back to the level of 5 to 10 cmol kg^{-1} (Pak, 1975). The increased sums of exchangeable cations in the Bt,na horizon are connected with high contents of clay fraction and exchangeable sodium and a high alkaline reaction. Mozheiko (1966) reported that the sum of exchangeable cations in a solonetz soil was increased by reclamation measures from 22.4 to 30.38 cmol kg^{-1} in the surface horizon and from 20.06 to 23.93 cmol kg^{-1} in deeper horizons.
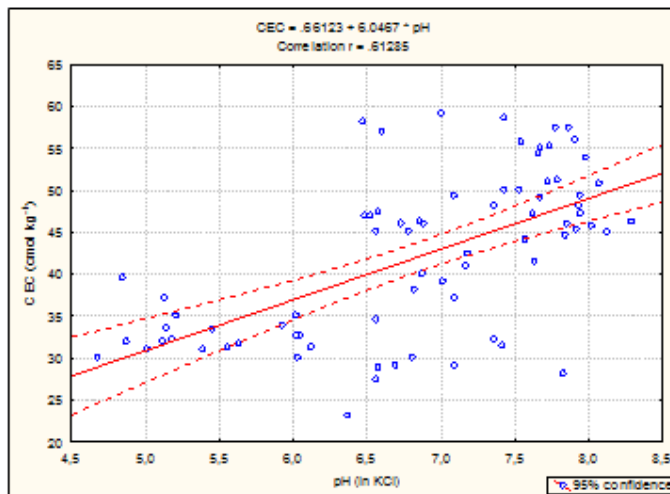
Contents and relationships between exchangeable cations

The results presented in Tables 1 to 7 show that the applied reclamation measures changed the quantitative and qualitative composition of exchangeable cations. Compared with the control variant, the content of exchangeable calcium was increased in all treated variants. Highest contents of exchangeable calcium were found in the soil layers in variant II (50 t ha^{-1} PG). Oborin (1958) wrote that, 12 years after gypsum application to solonetz soils, the content of exchangeable sodium was decreased from 38.5% to 16.4% in the illuvial Bt,na horizon while the content of calcium was increased. Šlevkova (1991) reported that, ten years after phosphogypsum application to solonetz soils, the content of exchangeable calcium was increased from 32.8-41.6% to 72.8-77.6%, and the content of exchangeable sodium was decreased from 9.7-19.8%, to 3.9-4.6%. A single application of the complete rate of phosphogypsum (32 t ha^{-1}, the optimum rate for the top 20 cm layer) considerably decreased the sodium content (from 18.8 meq100g^{-1} of soil in the control variant to 12.7 meq100g^{-1} of soil by the end of the first year after reclamation, and to 2.2, 2.7, and 2.9 meq100g^{-1} of soil in the fourth, seventh, and twentieth year after reclamation, respectively (Voropaeva et al., 2011). Changes in the relations among exchangeable cations significantly improved the chemical, physical and production characteristics of solonetz soils (Sahin et al., 2003, Kruzhilin and Kazakova, 2011). A study of the content of exchangeable cations in typical solonetz soils in various regions of Russia

Table 2. The values of exchangeable magnesium (Mg $^{2+}$) in the treated variants and the control.

| Depth (cm) | Mg^{2+}(cmol kg^{-1}) | | | | | Mg (%) | |
	Control	Variant I	Variant II	Difference I	Difference II	Difference I	Difference II
0-10	0.71 aA	1.42 aA	0.87 aA	+0.71	+0.16	+200	+123
10-20	1.01 abA	2.14 abA	1.14 aA	+1.13	+0.13	+212	+113
20-30	1.90 cA	3.53 cA	2.30 bA	+1.63	+0.40	+186	+121
30-40	1.67 cA	4.05 cB	3.51 cB	+2.38	+1.84	+243	+210
40-50	1.47 bcA	3.17 bcB	4.26 cC	+1.70	+2.79	+216	+290

Control - natural pasture, variant I - PG 25 t ha^{-1} + soil loosening down to 50 cm of depth, drain spacing of 20 m, variant II - PG 50 t ha^{-1} + soil loosening down to 50 cm of depth drain, spacing of 20 m. Means in the same column followed by different small letters are significantly different at P ≤ 0.05 using Fisher's LSD test. Means in the same row followed by different capital letters are significantly different at P ≤ 0.05 using Fisher's LSD test.

Fig 2. Relationship between pH in KCl and cation exchange capacity (CEC).

showed that calcium and magnesium had highest contents regardless of the bioclimatic characteristics of the region, characteristics of the native substrate and soil texture. This feature was characteristic for all solonetz soils subject to the steppe climate. According to the results of this study, the sum of exchangeable Na$^+$ and Mg^{2+} was over 50% of the sum of base cations in all soil layers of the control variant (Fig 1). In the treated variants, the shares of Na$^+$ and Mg^{2+} decreased in all examined layers due to the increased contents of exchangeable Ca^{2+} and K$^+$, especially in variant II. If the sum of exchangeable sodium and magnesium is higher than 50% of the sum of exchangeable base cations, the features of solonetz soils are less favorable. In the soils with a low level of sodium and a high level of magnesium, gypsum placement lessens the risk of formation of toxic Mg-humates (Pak, 1975). High magnesium level in solonetz soils is a consequence of a change in the structure of montmorillonites. Al^{3+} changes from tetrahedron to octahedron position, substituting Mg$^+$. This weakens the stability of mineral structure and increases the chances of its disintegration and the release of the Mg$^+$ ion. The above mechanism is considered to be a possible explanation for a high level of magnesium in solonetz soils from the crystallochemical point (Pak, 1975). In our study, increased contents of exchangeable Mg^{2+} in the treated variants resulted from changes in the mineralogical composition of the treated soil, as confirmed by positive correlations between the content of exchangeable Mg^{2+} on one side and smectite and vermiculite on the other, r = 0.82 and r =0.76, respectively. Based on a study of the composition of clay fractions, Čižikova (1973) concluded

that Na$_2$CO$_3$ influences disintegration of mixed-layer phyllosilicates. Under the influence of Na$_2$CO$_3$ and NaHCO$_3$ the mixed-layer mica-montmorillonite becomes highly dispersed. Also, it partially decomposes and due to the substitution in the structure of Mg^{2+}- and Al^{3+}-containing minerals (Kellerman, 1972). Based on laboratory studies, he concluded that chloride salts and sodium or magnesium sulphates decompose aluminosillicates more effectively than carbonates. High contents of NaCl and Na$_2$SO$_4$ in the solution significantly increase CaCO$_3$ solubility. CaCO$_3$ solubility is also affected by increased contents of CO$_2$ in the soil air that had formed as a result of biochemical processes. Ca^{2+} released from CaCO$_3$ may have a reclamation role: CaCO$_3$ + H$_2$O→ Ca^{2+} + 2OH$^-$ + CO$_2$, although the solubility of CaCO$_3$ is very low (0.00014 moles L^{-1}) when compared with CaSO$_4$*2H$_2$O (0.0154 moles L^{-1}) (Seelig, 1991). According to Sigmond (1933), 16 t ha^{-1} of CaCO$_3$ applied to the non-calcareous solonetz soil in Hungary decreased the content of exchangeable sodium from 34 to 6 cmol kg^{-1} after three years. In our study, the increased content of exchangeable K$^+$ in the treated variants resulted from the application of mineral and organic fertilizers and changes in the mineralogical composition. It is believed that a share of K$^+$ ions is bound inside the interlaminar space of the illite lattice, and it is less responsive to ionic exchange. The small size of the interlaminar space of illite (0.35 nm) slows down the entry of water molecules (0.27 nm) and cations which may substitute K$^+$ ions in the lattice. With time, however, under the influence of water and the present cations (H$^+$, Ca^{2+} and Mg^{2+}), the chemical content of illite changes, via the

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Table 3. The values of exchangeable sodium (Na^+) in the treated variants and the control.

Depth (cm)	Na^+ (cmol kg^{-1})					Na (%)	
	Control	Variant I	Variant II	Difference I	Difference II	Difference I	Difference II
0-10	4.62 aB	3.30 aB	1.94 aA	-1.32	-2.68	-71	-42
10-20	9.66 bC	4.12 aB	2.20 aA	-5.54	-7.46	-43	-23
20-30	12.55 cC	5.60 abB	2.92 abA	-6.95	-9.63	-45	-23
30-40	13.19 cC	8.26 bB	4.80 bA	-4.93	-8.39	-63	-36
40-50	13.79 cB	8.34 bA	8.81 cA	-5.45	-4.98	-60	-64

Control - natural pasture, variant I - PG 25 t ha^{-1} + soil loosening down to 50 cm of depth, drain spacing of 20 m, variant II - PG 50 t ha^{-1} + soil loosening down to 50 cm of depth, drain spacing of 20 m. Means in the same column followed by different small letters are significantly different at P ≤ 0.05 using Fisher's LSD test. Means in the same row followed by different capital letters are significantly different at P ≤ 0.05 using Fisher's LSD test.
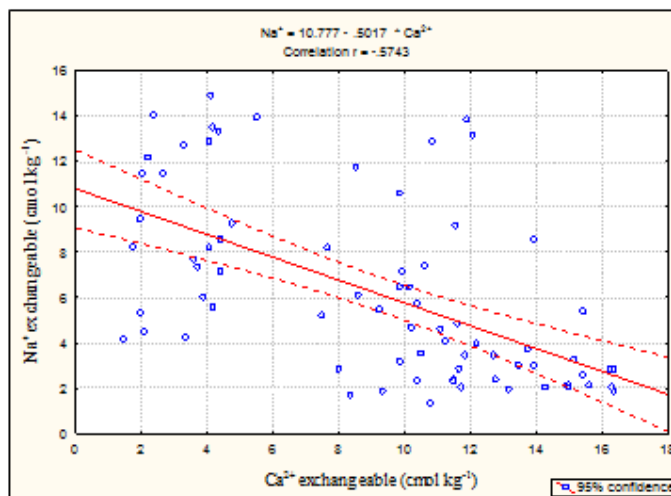
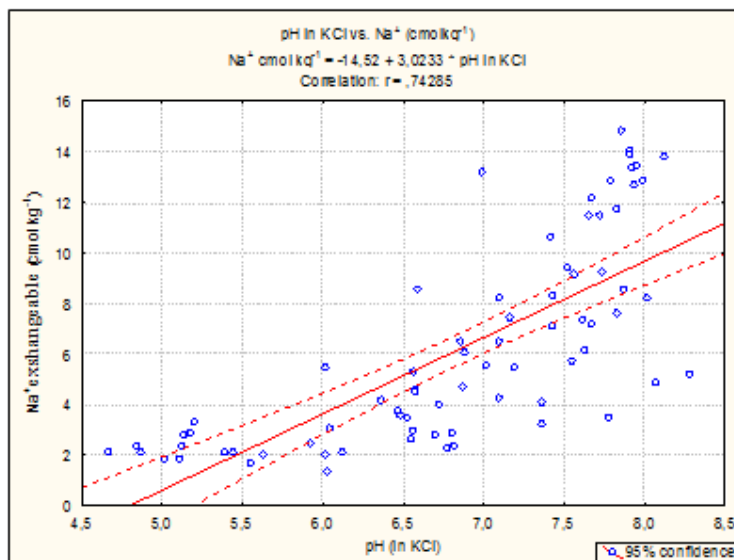**Fig 3.** Relationship between exchangeable Ca^{2+} and Na^+.

expanded illite, to montmorillonite or vermiculite. Potassium is present in soil in several forms. It may be present in soil solution or in minerals, or it may be adsorbed or bound. Low levels of potassium in soil solution and significantly high levels of adsorbed and bound potassium can be explained by the fact that K^+ ions have higher binding capacity that the other cations (Jakovljević and Pantović, 1991; Al-Zubaidi and Bashour, 2008; Najafi and Abtahi, 2012). In the alkaline environment caused by a high level of exchangeable Na^+, calcium and magnesium form less soluble compounds, which tend to decrease the solubility of phosphogypsum. The previous statement is further confirmed by a high negative correlation between the content of exchangeable sodium on one side and the contents of calcium and magnesium in soil solution on the other (r = -0.66 and r = -0.60, respectively). Krupskij et al. (1983) found high correlations between exchangeable calcium and calcium content in soil solution in both, the surface horizon (r = 0.83), and in the illuvial horizon (r = 0.88) of solonetz soils. A high positive correlation (r = 0.68) between the exchangeable Ca^{2+} and Ca^{2+} in soil solution was also found in our study. Based on this correlation, it could be concluded that calcium is more strongly adsorbed in the divalent form, which has a thin layer of water molecules and which decreases the zeta potential of colloid particles. Unlike calcium, sodium is more readily desorbed from the surface of colloid particles to the diffuse layer, as confirmed by a low correlation between the content of exchangeable Na^+ and Na^+ in the soil solution (r = 0.18). As desorbed sodium ions pass into the diffuse layer, the zeta potential of colloid particles increases, and they begin to repulse each other. At the same time, the thickness of the water layer around sodium ions and colloid particles increases. The increased zeta potential and the thicker water layer lead to peptization of colloids (Atinut et al., 2004). Apart from cations in the surface layer of colloid particles, the colloid potential is also affected by electrolytes in the soil solution. For example, if, due to poor drainage, the soil has a high content of exchangeable sodium and there is a high content of sodium ions in the soil solution, it lowers the rate of dissociation and the zeta potential decreases (Ilyas et al., 1997). This may explain the low correlation between the content of exchangeable sodium and the content of sodium in water solution. Similarly to sodium, magnesium, but only if present in a high content, can also cause the peptization of colloids. In the case of reclamation of solonetz soils, the drainage practice serves to remove the desorbed sodium from soil profile. If there is no sufficient water supply, the substitution of exchangeable sodium ions by calcium ions is not complete, calcium from the adsorptive complex is partially desorbed into the soil solution, and sodium from the solution becomes adsorbed into the adsorptive complex (Rižova, 1975). The balance between exchangeable cations and cations in soil solution is shown by SAR. The SAR values determined in this study were in a high positive correlation with the content of exchangeable sodium (r = 0.70). Several authors (Jakovljević and Pantović, 1991; Živković, 1991; Miljković, 1996) claimed that, in the alkaline soil, adsorption of base cations increased because the content of acidoid was increased during the previous desorption of H^+ ions from mineral and organic colloids. In the alkaline soil, cations from soil solution substitute not only H^+ ions from all COOH groups, but also H^+ ions from OH$^-$ groups in

Table 4. The values of exchangeable potassium (K^+) in the treated variants and the control.

| Depth (cm) | K^+ (cmol kg^{-1}) | | | | | K (%) | |
	Control	Variant I	Variant II	Difference I	Difference II	Difference I	Difference II
0-10	0.38 aA	2.45 aAB	3.24 aB	+2.07	+2.86	+645	+853
10-20	0.71 abA	2.28 aA	3.30 aA	+1.57	+2.59	+321	+465
20-30	0.83 bA	2.34 aA	2.93 aA	+1.51	+2.10	+282	+353
30-40	0.73 abA	2.40 aA	2.88 aA	+1.67	+2.15	+329	+395
40-50	0.65 abA	2.08 aA	2.89 aA	+1.43	+2.24	+320	+445

Control - natural pasture, variant I - PG 25 t ha^{-1} + soil loosening down to 50 cm of depth, drain spacing of 20 m, variant II - PG 50 t ha^{-1} + soil loosening down to 50 cm of depth, drain spacing of 20 m. Means in the same column followed by different small letters are significantly different at P $\leq$ 0.05 using Fisher's LSD test. Means in the same row followed by different capital letters are significantly different at P $\leq$ 0.05 using Fisher's LSD test.

Fig 4. Relationship between pH (in KCl) and exchangeable Na$^+$.

humic acids as well as those from OH$^-$ groups in clay minerals. The value of CEC depends on the mechanical and mineralogical content, quantity and quality of cations and anions, content and quality of organic matter, chemical reaction, physical, water/air and other properties of the soil (Belić, 2005). According to Bresler et al. (1982), in arid regions, the active soil surface depends primarily on the contents of minerals (smectites and/or vermiculites) and organic colloids (organic matter), pH value, and the content and quality of salts in soil solution. The same author claimed that the value of CEC increased significantly with the rise in pH value, which was also confirmed in our study (r = 0.61). Curtin and Rostad (1997) also determined a high dependence between pH and CEC (r = 0.86).

Materials and methods

Phosphogypsum is a byproduct in the process of phosphoric acid production by a so-called wet procedure, when natural phosphates are treated with sulfuric acid. It is commonly stored in dump areas close to the factories of phosphoric acid, which frequently present ecological problems. Depending on the origin of phosphates, phosphogypsum contains around 1-1.25% P_2O_5, 0.25-1.0% F, 2-3% SiO_2, 0.05-0.4% Al_2O_3, 0.1-0.2% Fe_2O_3, 0.01-0.2% Na_2O, and 0.01-0.07% organic matter. Due to favorable chemical and mineralogical contents and the acid chemical reaction (pH 2.8-3.0), phosphogypsum provides good results in reclaiming highly alkaline soils.

Gypsum requirement is estimated on the basis of the status of the cation exchange complex in the soil, cation exchange efficiency and the initial and final ESP, i.e., using the formula described in USSL Staff (1954) as follows:

$$GR = Na_{exch} \times \frac{E_{qwt}\,gypsum}{E_{qwt}\,Na} \times mg\ Na\ mmol^{-1}\ kg^{-1}\ soil$$

where, GR is gypsum requirement (g kg^{-1}); Na exch is exchangeable Na (mmol kg^{-1} soil); Eqwt is Equivalent weight.

When phosphogypsum containing $CaSO_4*2H_2O$-dihydrate is applied, calcium ions are adsorbed and they replace sodium ions in the adsorptive complex, thus forming sodium sulphate (Na_2SO_4), an easily soluble salt which is then leached from the soil profile through drainage pipes. After the application of gypsum or phosphogypsum, the content of Ca^{2+} increases, the alkaline reaction decreases, improving the content and stability of structural aggregates, water and air properties, thermal and nutrient status, and the effective fertility of solonetz soils (Amstrong and Tanton, 1992; Gharaibeh et al., 2009). In the first years of ameliorations, the surface layer of solonetz soil is disked in order to achieve good incorporation of phosphogypsum, its mixing with the soil and the formation of a mealy layer for sowing. Ploughing would extract Bt, na horizon on the surface, and therefore it is not applied. Apart

Table 5. The sums of base cations in the treated variants and the control.

Depth (cm)	Sum of base cations (cmol kg⁻¹)					Sums of base cations (%)	
	Control	Variant I	Variant II	Difference I	Difference II	Difference I	Difference II
0-10	7.55 aA	16.02 aB	19.40 aB	+8.47	+11.85	+212	+257
10-20	13.29 bA	17.75 abAB	20.86 aB	+4.46	+7.57	+134	+157
20-30	17.68 cA	20.83 abcA	21.12 aA	+3.15	+3.44	+118	+119
30-40	19.81 cdA	24.05 dA	22.44 abA	+4.24	+2.63	+121	+113
40-50	20.23 dA	22.05 cdA	26.23 bA	+1.82	+6.00	+109	+130

Control - natural pasture, variant I - PG 25 t ha⁻¹ + soil loosening down to 50 cm of depth, drain spacing of 20 m, variant II - PG 50 t ha⁻¹ + soil loosening down to 50 cm of depth, drain spacing of 20 m. Means in the same column followed by different small letters are significantly different at P ≤ 0.05 using Fisher's LSD test. Means in the same row followed by different capital letters are significantly different at P ≤ 0.05 using Fisher's LSD test.

Table 6. Soil pH in the treated variants and the control.

Depth (cm)	pH in KCl					pH in KCl (%)	
	Control	Variant I	Variant II	Difference I	Difference II	Difference I	Difference II
0-10	6.51 aB	6.68 aB	5.41 aA	+0.17	-1.1	+103	-83
10-20	7.45 bB	6.88 abB	5.43 aA	-0.57	-2.02	-92	-73
20-30	7.75 bcB	7.36 bcB	5.93 abA	-0.39	-1.82	-95	-77
30-40	7.89 cB	7.64 cB	6.43 bcA	-0.25	-1.46	-97	-81
40-50	7.91 cB	7.91 cB	7.13 cA	0.00	-0.78	+100	-90

Control - natural pasture, variant I - PG 25 t ha⁻¹ + soil loosening down to 50 cm of depth, drain spacing of 20 m, variant II - PG 50 t ha⁻¹ + soil loosening down to 50 cm of depth, drain spacing of 20 m. Means in the same column followed by different small letters are significantly different at P ≤ 0.05 using Fisher's LSD test. Means in the same row followed by different capital letters are significantly different at P ≤ 0.05 using Fisher's LSD test.

from the regular agrotechnical measures, ameliorative amounts of organic and mineralogical fertilizers are inserted, and in the first years crops which can handle alkali reaction (wheat, barley, sunflower, sorghum, ricinus) are grown, and after improving the features of solonetz soils, other crops as well (Dimitrijević et al., 2011).

Site location and sampling

The study of the effect of reclamation practices on the content and qualitative composition of exchangeable base cations of the solonetz soil was conducted at Kumane experimental field (N - 45° 31' 20", E - 20° 11' 43", 75 m asl, area 2 ha) in Serbian Province of Vojvodina, established on a solonetz soil. A total of 75 soil samples were collected from all treated variants, from 0-10, 10-20, 20-30, 30-40 and 40-50 cm soil layers. The analyzed soil belongs to the order of halomorphic soil, the class - solonetz soils (Aoh/E-Bt,na-C), the type - solonetz soils, the subtype - typical, the variety - non-saline, the form - medium deep (Škorić et al., 1985).

Soil treatment

During the amelioration of solonetz, complex physical-chemical processes occur, such as: dissolution of phosphogypsum, adsorption, desorption, substitution, retention of ions, forming and leaching of the products of chemical reactions. Amounts of rainfall and air temperatures have a high impact on the course and intensity of these processes. The impact of the applied reclamation practices on the adsorption complex of the solonetz soil was studied in conditions of natural rainfall, without irrigation. As the ground water table was below 2 m, the rainfall (Table 8) was the only source of water to the studied soil. Complex chemical and cultural reclamation measures were applied within the following variants: control variant - natural pasture, variant I - drainage pipes 20 m apart + 25 t ha⁻¹ PG + trenching to 50 cm, variant II - drainage pipes 20 m apart +

50 t ha⁻¹ PG + trenching to 50 cm. The mineralogical analysis of the phosphogypsum applied showed that its composition was: gypsum ($CaSO_4 \cdot 2H_2O$) - 80-95%; calcium hydrophosphate ($CaHPO_4 \cdot 2H_2O$) - 10-15%; apatites, illites, smectites, quartz, feldspars, and gaotaiite - 3%; and other trace minerals - 1% (Rajković et al., 1995, Belić, 1999).

Laboratory analyses

Soil texture was determined by the pipette method. Samples were prepared for analysis using sodium pyrophosphate according to Thun (1955). Soil pH was measured in a soil suspension with potassium chloride (1M KCl) 1:2.5, potentiometrically in an InoLab pH meter (Chapman and Pratt, 1961). Samples were saturated with deionized water and used for preparation of soil paste. The paste was vacuum filtered in order to obtain a saturated water extract for analyses of Ca^{2+}, Mg^{2+}, Na^+ and K^+ contents. Ca^{2+} and Mg^{2+} contents were determined by atomic adsorption spectrophotometry; Na^+ and K^+ contents were determined by atomic emission spectrophotometry. An atomic absorption spectrophotometer Varian 600. The mineral composition of phosphogypsum and soil was determined using an X-ray powder diffractometer (XRPD) (Chung, 1975; JCPDS, 2009). Sodium adsorption ratio was calculated as follows:

$$SAR = \frac{Na}{\sqrt{Ca + Mg / 2}}$$

Cation exchange capacity was determined by extraction with 1M NaOAc solution of sodium acetate (pH 8.2) and 1M NH4OAc solution of ammonium acetate (pH 7.0). Na^+ content in the extract was then measured by an Evans flame photometer. Total cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were extracted with a neutral solution of 1M NH₄OAc and determined by atomic absorption and emission

Table 7. Exchangeable sodium percentages (ESP) in the treated variants and the control.

Depth (cm)	ESP%				
	Control	Variant I	Variant II	Difference I	Difference II
0-10	17.56 aC	9.53 aB	6.22 aA	-8.03	-11.34
10-20	19.22 abC	10.21 aB	6.79 aA	-9.01	-12.43
20-30	22.75 bcB	10.64 aA	7.20 aA	-12.11	-15.55
30-40	26.66 cdB	14.99 abA	11.92 aA	-11.67	-14.74
40-50	29.90 dA	23.88 bA	18.72 bA	-6.02-	-11.18

Control - natural pasture, variant I - PG 25 t ha^{-1} + soil loosening down to 50 cm of depth, drain spacing of 20 m, variant II - PG 50 t ha^{-1} + soil loosening down to 50 cm of depth, drain spacing of 20 m. Means in the same column followed by different small letters are significantly different at P $\leq$ 0.05 using Fisher's LSD test. Means in the same row followed by different capital letters are significantly different at P $\leq$ 0.05 using Fisher's LSD test.

Table 8. Mean annual rainfall, air temperatures and water deficit in the examined location in the period 1964-2010.

Mean annual rainfall (mm)	Mean annual air temperature (°C)	Mean ETo (mm)	Mean ETa (mm)	Mean annual water deficit (mm)
569	11.0	713	511	202

ETo – reference evapotranspiration, ETa – actual evapotranspiration.

spectrophotometry using an atomic absorption spectro-photometer Varian 600.

Contents of exchangeable cations (C_{exch}) (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were calculated separately for each cation using the following equation:

$$C_{exch} = C_t - C_{we}$$

where C_t is total cation content and C_{we} is the cation content in water extract. Exchangeable Na percentage was estimated by direct determination of exchangeable Na^+ and CEC and calculated as follows:

$$ESP = \frac{Na^+_{exch}}{CEC} \times 100$$

where ESP is the exchangeable sodium percentage and CEC is the cation exchange capacity (Richards, 1954; Thomas, 1982). To determine rainfall deficit and excess in individual months, we made a soil water balance sheet. The reference evapotranspiration (ETo) was calculated by Thorntwaite's method (Thorntwaite et al., 1955). Pejić et al. (2011) claimed that the above method is acceptable for calculating ETo in the climatic conditions of Vojvodina.

Statistical analysis

The collected data were analyzed statistically using the one-way ANOVA. The analysis was performed using Statistica (2007) StatSoft Inc., Tulsa, OK, USA. Where the f-value was significant, Fisher's least significant difference was used to compare treatment means at P $\leq$ 0.05.

Conclusion

Following conclusions were drawn on the content and qualitative composition of exchangeable base cations of the solonetz soil subjected to reclamation practices for 15 years. The content and qualitative composition of the cations changed under the effect of the reclamation measures applied. The content of exchangeable calcium was significantly increased and that of sodium was decreased. The sum of base cations in the treated soil was increased. The exchangeable sodium percentage decreased below 15% in almost all layers of the treated variants. When compared with the sum of base cations, the sum of magnesium and sodium was below 50% in the treated soil variants. The applied reclamation measures decreased the pH value in all treated variants.

References

Abrol IP, Gupta KR (1988) Recent Advances in the Chemistry of Alkali Soils. In: Adam M (ed) Proceedings of the International Symposium on Solonetz Soils, Problems Properties Utilization, Osijek, 1988

Agar Aİ (2011) Reclamation of saline and sodic soil by using divided doses of phosphogypsum in cultivated condition. Afr J Agric Res. 6:4243-4252

Al-Zubaidi A, Yanni S, Bashour I (2008) Potassium status in some Lebanese soils. Leban Sci J. 9:81-97

Amstrong ASB, Tanton TWT (1992) Gypsum applications to aggregated saline-sodic clay topsoils. Eur J Soil Sci. 43:249-260

Atinut S, Olivier G, Somsri A, Fabienne F, Daniel T, Pascal B (2004) Critical Coagulation Concentration of Paddy Soil Clays in Sodium–Ferrous Iron Electrolyte. Soil Sci Soc Am J. 68:789-794

Bahceci I (2009) Determination of salt leaching and gypsum requirements with field tests of saline – sodic soils in central Turkey. Irrig Drain. 58:332–345

Belić M (1999) Effect of meliorative practices on the adsorptive complex in the solonetz soil. Doctoral thesis. University of Novi Sad, Faculty of Agriculture, Novi Sad

Belić M (2005) Effect of meliorative practices mechanical composition and adsorptive complex of the solonetz soil. Contemp agric. 54:47-51

Belić M, Nešić Lj, Dimitrijević M, Petrović S, Pejić B (2006) The influence of water-physical properties changes of solonetz on the yield and yield components of wheat after phosphogypsum application. Agricultural Engineers and Technicians Society of Serbia, Belgrade

Bresler E, Mc Neal LB, Carter LD (1982) Saline and Sodic Soils, Principles, Dynamics, Modeling. Springer-Verlang, Berlin, Heidelberg, New York

Chapman HD, Pratt PF (1961) Methods of Analysis for Soils, Plants and Waters. University of California, Agr Sci, Berkeley

Chung FH (1975) Quantitative interpretation of X-ray diffraction patterns of mixtures. III. Simultaneous determination of a set of reference intensities. J Appl Cryst. 8:17-19

Curtin D, Rostad HPW (1997) Cation exchange and buffer potential of Saskatchewan soils estimated from texture, organic matter and pH. Can J Soil Sci. 77:621-626

Čižikova NP (1973) Izmenenie mineralogičeskogo sostava černozemov tipičnih pri oroшeni. Eurasian Soil Sci. 2:65-81

Dimitrijević M, Petrović S, Belić M, Banjac B, Vukosavljev M, Mladenov N, Hristov N (2011) The influence of solonetz soil limited growth conditions on bread wheat yield. J Agr Sci Tech. 5:194-201

Gedroiz KK (1917) Saline soils and thei improvement. Zhur Opytn Agron. 18:122-140

Gharaibeh MA, Eltaif NI, Shunnar OF (2009) Leaching and reclamation of calcareous saline-sodic soil by moderately saline and moderate-SAR water using gypsum and calcium chloride. J Plant Nutr Soil Sci. 172:713-719

Hilgard EW (1906) Soils, their formation, properties, composition, and relations to climate and plant growth in the humid and arid regions. The Macmillan company, New York and London

Ilyas M, Qureshi RH, Qadir MA (1997) Chemical changes in a saline-sodic soil after gypsum application and cropping. Soil Technol. 10:169-274

Jakovljević M, Pantović M (1991) Soil and water chemistry. Scientific Book, Belgrade

JCPDS - Joint Committee on Powder Diffraction Standards (2009)

Kellerman VV (1972) Vlijanije solej Na i Mg na izmenenie svetlo-kaštanovih i černozemnih počv. Vsb. Melioracija Soloncov M. 82-105

Krupskij NK, Čausova LA, Aleksandrova AM (1983) Urovni aktivnosti jonov natrija i kalcija i ih sootnošenij v malonatrievih soloncovih počvah. Eurasian Soil Sci. 9:33-41

Kruzhilin IP, Kazakova LA (2011) Combined Amelioration of Soils of Solonetz Complexes in the Lower Volga Region. Russ Agric Sci. 37:55–57

Lozanovska, IN (1987) K istorii gipsovani počv. Pochvovedenie 2. Moskva.

Lyubimova NI (2011) Soil Reclamation Studies of Salt Affected and Solonetzic Soils in Ukraine. Eurasian Soil Sci. 44:939-939

Makoi JHJR (1995) Effectiveness of gypsum application in reclaiming a saline soil. MSc Thesis. Ghent University, Faculty of Agricultural and Applied Biological Sciences, International Centre for Eremology, Ghent, Belgium

Miljković N (1963) Characteristics of saline and alkali soils in Vojvodina. Savez vodnih zajednica NRS, Novi Sad

Miljković N (1996) Fundaments of Pedology. University of Novi Sad, Faculty of Sciences, Institute for Geography, Novi Sad

Mozheiko AM (1966) Dynamics of exchangeable cations in solonetz soil of the middle Prednie-per region (Soviet Union) under the effect of permanent agricultural utilization. Trudy kharkov. Sel-khoz inst. 49:109-127

Najafi MG, Abtahi A (2012) Factors affecting potassium fixation in calcareous soils of southern Iran. Arch Acker Pfl Boden. 58:335-352

Oborin AI (1958) O melioracii i osboenii soloncov v uslovja neorošaemogo zemledelija černozemnoj zoni Zapadnoj Sibiri. V kn. Voprosi melioracii soloncov. M.-L., Izd-vo AN SSSR, 239-278

Pak PK (1975) Solonci SSSR i puti ih povišenija plodorodija. Kolos, Moskva

Pejić B, Rajić M, Bošnjak Dj, Mačkić K, Jaćimović G, Jug D, Stričević R (2011) Application of reference evapotranspiration in calculation water use of maize evapotranspiration in climatic conditions of Vojvodina. Ann Sci Pap. 35:32-46.

Petrović S, Dimitrijević M, Belić M, Banjac B, Bošković J, Zečević V, Pejić B (2010) The variation of yield components in wheat (Triticum aestivum L.) in response to stressful growing conditions of alkaline soil. Genetika 42:545-555

Rajković BM, Hadžić V, Molnar I (1995) The waste phosphogypsum from chemical industry – term, application, perspective. University of Novi Sad, Faculty of Agriculture, Institute of Field and Vegetable Crops, Novi Sad

Richards AL (1954) Diagnosis and Improvement of Saline and Alkali Soils. USDA Handb. 60, U.S. Gov. Print. Office, Washington, DC

Rižova VL, Gorbunov IN (1975) Desorbcia natria, kalia, kalicia i magnia iz solonca pri vzaimodeystvi ego s vodoj i gipsom. Nauč tr Počv in-ta im V. V. Dokučaeva 65-76

Sahin U, Oztas T, Anapali O (2003) Effects of consecutive applications of gypsum in equal, increasing, and decreasing quantities on soil hydraulic conductivity of a saline-sodic soil. J Plant Nutr Soil Sci. 166:621-624

Seelig BD, Richardson JL (1991) Salinity and sodicity in North Dakota soils. North Dakota State Univ. Extension Service Bulletin 57

Sigmond AA (1933) The Alkali Soils in Hungary and Their Reclamation. Soil Sci. 18:379-381

Statistica (2007) StatSoft Inc., Tulsa, OK, USA

Szabolcs I (1971) European Solonetz Soils and Their Reclamation. Akadémiai Kiadó, Budapest

Škorić A, Filipovski G, Ćirić M (1985) Classification of Yugoslav soils. Academy of Sciences and Arts of Bosnia and Herzegovina, Book LXXVIII

Šlevkova ME (1991) Posledejstvie melioraci i orošenija na svojstva staropahotnih počv soloncovogo kompleksa Nižnego Povolžja. Nauč tr Počv in-ta im V. V. Dokučaeva 101-107

Thomas GW (1982) Exchangeable Cations: Methods of Soil Analysis Part 2. In: Page AL, Miller RH, Keeney DR (eds) Chemical and Microbiological Properties, 2nd edn., Agronomy Monograph 9, ASA and SSSA, Madison, WI

Thornthwaite CW, Mather JR (1955) The water budget and its use in irrigation. In: Water, Yearbook of Agriculture. US Department of Agriculture, Washington, DC

Thun R, Hermann R, Knickmann, F (1955) Die Untersuchung von Böden. Band I, Methodenbuches des Verbandes Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten. 3. Aufl., Neumann Verlag, Radebeul und Berlin

USSL Staff (1954) Diagnosis and Improvement of Saline and Alkali Soil, Agriculture Handbook 60. Richards, LA

Voropaeva ZI, Trotsenko IA, Parfenov AI (2011) Changes in the Properties of a Crusty Solonetz, with Soda Salinization after Single and Repeated Amelioration with Phosphogypsum. Eurasian Soil Sci. 44:314–325

Vozbuckaja HE (1968). Chimija počv. Izd-vo "Višaja škola", Moskva

WRB (2006) A Framework for International Classification, Correlation and Communication. Food and Agriculture Organization of the United Nations, Rome

Živković M (1991) Soil science. Scientific book, Belgrade