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Cation Exchange Capacity of Dominant Soil Types in the Republic of Croatia

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ABSTRACT

The study was conducted on 18 locations and 11 dominant soil types in the Republic of Croatia including their evolution-genetic horizons. In total, 51 soil samples were examined. Analysis of soil was done by saturating patterns using barium chloride solution in three replications. Descriptive statistics of the analyzed data was conducted. Basic statistical parameters were calculated, and functional dependence between the base saturation (V%) of analyzed soil samples and their pH was observed. The correlation coefficient (r) between base saturation (V%) and pH for all examined soils was r=0.79 (n=51; very strong correlation). For acid soils it was r=0.82 (n=17; very strong correlation), for neutral soils r=0.75 (n=8; very strong correlation), and finally for alkaline soils r=0.15 (n=26; very weak correlation). Cation exchange capacity values ranged from 2.39 cmol^{+}*kg^{-1} to 33.8 cmol^{+}*kg^{-1} depending on soil type, pH, organic content and other soil parameters. The content of exchangeable cations in the sum of basic cations ranged from: Ca^{2+} (16% - 94%), Mg^{2+} (2% - 41%), K^{+} (1% - 68%) and Na^{+} (<0.01%) also depending on soil type, depth, location and other physical and chemical soil parameters.

Keywords: basic cations, base saturation, correlation, pH

INTRODUCTION

Cation exchange capacity (CEC) is a parameter of soil which represents the capability of soil to attract, retain and hold exchangeable cations (K^{+}, Na^{+}, Ca^{2+}, Mg^{2+}, Al^{3+}, etc.). Many soil parameters influence the soil exchangeable capacity especially soil pH, soil texture, and organic matter content up to a certain extent. Soil pH is an important soil parameter which is positively correlated with CEC (Foth, 1990), thereby high pH values increase numbers of negative charges on the colloids and CEC. High content of organic matter and clay conduces to the higher CEC values because both have a large number of negative charges on their surface which attract and hold cations. Negative charges of soil particles are the result of isomorphic substitutions in phyllosilicate structures, non-compensated bonds at the edges of reticular plans, or dissociation of functional organic groups (Pansu and Gautheyrou, 2006). Wang et al. (2005) observed a positive correlation between soil

CEC and soil organic C and soil clay content in calcareous soils. Cation exchange reactions in soils occur mainly near the surface of clay and humus particles, called micelles (Foth, 1990). Cations from the soil surface can be quite easily exchangeable with the cations from the solution. Acording to Škorić (1991) exchangeable sites on the soil colloids can be permanent (stable) or pH dependant (variable), mostly depending on pH, clay and organic matter content. Clay particles can possess both permanent and variable charge depending on clay type, while the soil organic matter can possess only variable charge.

Various methods have been proposed for measuring CEC and exchangeable cations. The most frequently used methods are based on soil cation exchange with solution of known concentrations of salts which contain cations that are not present in soil, and cation detection with standard techniques such as atomic absorption, spectophotometry or titration (Bergaya et al., 2006). In this study the determination of CEC was conducted using a compulsive exchange procedure with barium chloride ($BaCl_2$). This method is adopted and accepted as the international standard. Also, it is a highly repeatable, precise, direct method for measuring soil CEC (Ross, 1995).

The main goal of this paper was to determine the cation exchange capacity, as well as the content of exchangeable base cations (Ca^{2+}, Mg^{2+}, N^+ and K^+) of most represented soils of the Republic of Croatia (11 dominant soil types) and to determine the dependence of soil pH on soil base saturation for all examined soils.

MATERIALS AND METHODS

Research locations and soil sampling

Sampling was conducted at 18 locations on 11 dominant types of soil by their evolution-genetic horizons. The samples are presenting the types of soil that are most common in the Republic of Croatia (Husnjak et al., 2005). The same soil types were used in previous study by Čapka et al., 2009 which included the following locations and soil types: in the vicinity of Zalesina (Podzol[1] – Haplic Podzols[2]); Fužine (Calcocambisol[1] – Calcic Cambisols[2]); Delnice (Rendzina, leached[1] – Rendzic Leptosols[2]); Vodnjan (Calcocambisol[1] - Calcic Cambisols[2]); Tinjan near Poreč (TerraRossa[1] –Rhodic Cambisols[2]); Ripenda near Plomin (Rendzina, brownish[1] - Rendzic Leptosols[2]); Stružec near Popovača (Pseudogley[1] – Stagnic Gleysols[2]); Gospić - Veliki Žitnik (Brown dystric[1]- Dystric Cambisols[2]); Kneževo in Baranja (Chernozem[1] - Kastenozems[2]); Bilje near Osijek (Semigley, calcareous[1] – Gleyic Fluvisols[2]); Ivanovec near Osijek (hydromorphous Black soil, calcareous[1] – Humic Gleysols[2]); Đakovo (Brown eutric[1] – Eutric Cambisols[2]); Županja (Epigley non-calcareous[1]- Gleysols[2]); Zagreb, in floodplain of the Sava River, near the Cvjetno settlement – (Alluvial soil[1] - Calcaric Fluvisols[2]) and in surroundings of the gas wells Molve 10 (Semigley, non-calcareous[1] - Gleyic Fluvisols[2]); Molve 11 (Epigley[1] - Gleysols[2]), Molve 12 (Eugley, ami gley, vertic[1] – Haplic Gleysols[2]) and Molve 14 (Sirozem-regosol[1] –Haplic Regosols[2]). Sampling, transport and preservation of samples were conducted in compliance with the basic standards of measurement.

[1] Croatian classification according to Škorić, 1985.

[2] Classification according to World reference base for soil resources, 2006.

Sample preparation and analysis

Preparation (drying/grinding/sieving/homogenization) of soil samples for chemical analysis followed the protocol of HRN ISO 11464:2004. Analysis of CEC values was conducted in compliance with the protocol HRN ISO 11260:2004. Procedure implies to weigh 2.50 g of air dried soil, which was before pretreated, sieved ($\leq$ 2 mm), than saturated with respect to barium by treating the soil three times with 0.1 mol*L^{-1} $BaCl_2$ solution (30 mL and 1 h shaked – 3× - supernatant liquid is used for determination of exchangeable cations). Thereafter, the soil was equilibrated with a 0.01 mol*L^{-1} $BaCl_2$ solution (30 mL on soil cake and shaked overnight). Subsequently, a known excess of 0.02 mol*L^{-1} $MgSO_4$ was added (30 mL to the soil cake and shaked overnight). All the barium present, in solution as well as adsorbed was precipitated in the form of highly insoluble $BaSO_4$ and, consequently, the sites with exchangeable ions are readily occupied by magnesium. The excess magnesium was determined by flame atomic absorption spectrometry - FAAS. In supernatant liquid 0.1 mol*L^{-1} $BaCl_2$ extract of the soil concentrations of sodium, potassium, calcium and magnesium were determined also by FAAS. A cesium solution is added to the test solutions to eliminate ionization interference for Na^+ and K^+ determination while lanthanum was added to prevent formation of refractory compounds Ca^{2+} and Mg^{2+} with phosphate, aluminium, etc. in the flame for Ca^{2+} and Mg^{2+} determination. Investigated samples were analyzed on atomic absorption spectrometer (AAS - Parkin Elmer AAnalyst 400, 2003).

Cation exchange capacity (Mg^{2+}) was detected at 285.2 nm, while ions: Ca^{2+} at 422.7 nm; Mg^{2+} at 285.2 nm; K^+ at 766.0 nm; and Na^+ at 589.0 nm. Calibration was done according to guidelines in the protocol and correlation coefficient for CEC (Mg^{2+}) was 0.998, Ca^{2+} 0.999, Mg^{2+} 0.998, K^+ 0.949 and Na^+ 0.944.

Quality control

Quality control of measurement was included in the study. Statistical analysis was conducted in order to calculate the accuracy and precision of given data, including: arithmetic mean, standard deviation and relative standard deviation (RSD).

Accuracy of measurement was controlled by a reference sample ISE 882, Wepal, Wageningen program in which the Analytical Laboratory for General Agronomy participates (International Soil-Analytical Exchange) in order to assess laboratory quality. True values were controlled using the ISE material (CEC 23.9 $cmol^+$*kg^{-1}; Ca^{2+} 6.13 $cmol^+$*kg^{-1}; Mg^{2+} 12.8 $cmol^+$*kg^{-1}; K^+ 1.07 $cmol^+$*kg^{-1}; Na^+ 3.21 $cmol^+$*kg^{-1}) and average accuracy ranged between 23-165% depending on parameters.

Precision of measurement was controlled through three replications (A, B, C), and is shown through relative standard deviation (RSD). Relative standard deviation of the reference sample varied up to 10%.

Soil reaction (pH)

Soil reaction is determined based on concentrations of hydrogen (H^+) or hydroxyl (OH^-) ions. There are numerous interpretation criteria in the literature about soil acidity, neutrality and alkalinity measured in different media (KCl, H_2O, $CaCl_2$) and in different ratios (1:2,5, 1:5, 1:20,..). In this study it was interpreted according to

Geochemical Atlas of Europe pH scale measured in 0,01 M $CaCl_2$ w/v (1:5) (HRN ISO 10390:2005), and it can be acid (<5.5), neutral (5.5-6.2) or alkaline (>6.2). The soil reaction ranged from 3.27 to 7.90 units for all analyzed samples (Čapka et al. 2009).

Data analysis

Statistical data analysis was performed for the whole range of samples including 51 samples and one reference sample ISE 882. The values of CEC ($cmol^{+}*kg^{-1}$) and exchangeable cations (Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} $cmol^{+}*kg^{-1}$) were calculated from concentration in extract in [$mg*L^{-1}$] of analyzed samples on AAS according to the calibration curve created from known cations concentrations.

The functional dependence of pH and base saturation (V%) was provided for a whole range of samples and separately for the three groups of samples according to their acidity: alkaline, neutral and acid. The functional dependence of pH and base saturation of analyzed samples was determined by the method of linear regression $y=ax+b$. The correlations of given parameters were calculated and interpreted on the basis of correlation coefficient values according to Roemer-Orphal scale (Vasilj, 2000).

RESULTS AND DISCUSSION

Results of mean values of basic exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}), the sum of cations, CEC and their relative standard deviation (RSD), base saturation (V%) and pH for all investigated soil horizons are shown in Table 1. Analysis of Na^{+} was also included but its amount was below the instrument detection limit in all analyzed samples, where limit of detection (LOD) was <4 mg/L.

Table 1. Mean values of basic cations (Ca^{2+}, Mg^{2+} and K^{+}), sum of cations, CEC, base saturation (V%) and pH

Mark	Location	Horizon, depth (cm)	Ca^{2+}	RSD (n=3)	Mg^{2+}	RSD (n=3)	K^{+}	RSD (n=3)	Sum of cations	RSD (n=3)	CEC	RSD (n=3)	V%	$pH_{CaCl2\ (1:5)}$
1	Zalesina	A (0-12)	2.71	± 22	1.38	± 2	0.73	± 63	4.82	± 14	16.8	± 25	29	3.27
2		E (12-50)	0.34	± 51	0.18	± 61	0.45	± 16	0.97	± 20	10.9	± 35	9	3.35
3		Bh (20-50)	0.09	± 138	0.09	± 88	0.37	± 69	0.55	± 45	7.90	± 50	7	3.92
4	Fužine	Aoh (0-5)	44.5	± 17	3.66	± 9	1.53	± 57	49.6	± 15	33.8	± 36	147	6.31
5		(B)v (5-30)	31.8	± 17	1.46	± 7	0.43	± 58	33.7	± 16	21.9	± 58	154	6.48
6	Delnice	A (0-5)	28.9	± 15	3.09	± 2	1.38	± 51	33.4	± 15	23.3	± 49	143	6.16
7		C (5-30)	6.51	± 49	4.26	± 2	0.41	± 71	11.2	± 26	11.6	± 58	97	5.85
8	Vodnjan	A (0-7)	28.7	± 15	1.34	± 5	1.55	± 50	31.6	± 16	18.0	± 52	175	6.96
9		Brz (7-32)	23.8	± 14	0.99	± 12	1.10	± 52	25.9	± 15	20.0	± 53	129	7.02
10	Tinjan	A (0-40)	11.6	± 16	1.75	± 9	0.51	± 60	13.9	± 14	13.3	± 60	104	5.62
11		I-C (40-120)	12.3	± 8	1.55	± 10	0.51	± 45	14.4	± 8	14.6	± 58	98	5.86
12	Ripenda	Ap (0-22)	30.5	± 17	0.73	± 17	2.04	± 46	33.3	± 18	20.3	± 58	164	7.16
13		C (22-60)	29.0	± 15	0.56	± 20	1.28	± 56	30.8	± 17	22.7	± 48	136	7.44
14	Stružec	P (0-30)	6.70	± 5	1.53	± 7	0.38	± 52	8.61	± 4	10.5	± 64	82	6.56
15		E/Bt (30-58)	2.99	± 16	1.27	± 9	0.18	± 63	4.44	± 14	4.40	± 88	101	5.29
16		Btg (58-80)	4.26	± 17	3.29	± 4	0.46	± 46	8.01	± 10	7.53	± 58	106	4.87
17	Veliki Žitnik	A/P (0-22)	0.70	± 37	0.11	± 91	0.82	± 18	1.63	± 14	4.93	± 77	33	4.24
18		A/B (22-55)	0.13	± 153	0.05	± 87	0.36	± 21	0.54	± 29	2.39	± 146	23	4.30
19		C (55-90)	2.10	± 20	0.36	± 19	0.93	± 19	3.39	± 12	4.95	± 71	68	4.17
20	Kneževo	Amo (0-30)	20.2	± 3	3.19	± 6	2.96	± 16	26.4	± 3	18.1	± 47	146	6.69
21		AC (30-45)	20.5	± 18	2.96	± 11	1.70	± 18	25.2	± 15	20.2	± 51	124	6.97
22		C (50-80)	20.2	± 8	2.95	± 8	1.28	± 20	24.4	± 6	21.5	± 39	114	7.25
23	Bilje	A (0-30)	12.9	± 16	1.47	± 10	1.55	± 24	15.9	± 11	13.9	± 26	115	7.36
24		C (30-50)	15.4	± 13	1.53	± 19	1.36	± 21	18.3	± 9	13.8	± 32	133	7.47
25		G (50-70)	18.1	± 8	2.02	± 13	0.97	± 29	21.1	± 6	17.3	± 10	122	7.49
26	Ivanovec	Aa (0-30)	13.0	± 10	6.46	± 6	1.87	± 21	21.3	± 5	19.7	± 8	108	7.24
27		Amo (30-50)	13.8	± 10	5.61	± 5	1.14	± 32	20.6	± 7	16.7	± 13	123	7.69
28		Gso (50-70)	17.5	± 12	5.57	± 5	0.69	± 33	23.8	± 8	11.5	± 13	207	7.90
29	Đakovo	A (0-25)	10.6	± 7	2.05	± 11	0.89	± 34	13.5	± 3	13.8	± 8	98	7.38
30		(B)v (25-45)	8.96	± 5	2.30	± 8	0.76	± 34	12.0	± 3	14.3	± 11	84	6.87
31		C (45-70)	10.3	± 9	2.85	± 10	0.89	± 28	14.0	± 5	14.5	± 5	97	6.72
32	Županja	A (0-25)	12.1	± 9	3.15	± 13	1.39	± 35	16.6	± 5	17.3	±11	96	5.63
33		Gso/r (25-50)	14.4	± 9	3.77	± 15	1.03	± 27	19.2	± 6	16.2	± 33	119	6.00
34		Gr/so (50-70)	19.5	± 19	4.18	± 12	0.80	± 39	24.5	± 14	18.2	± 26	134	7.19

Table 1. continuation

Mark	Location	Horizon, depth (cm)	Ca^{2+}	RSD (n=3)	Mg^{2+}	RSD (n=3)	K^{+}	RSD (n=3)	Sum of cations	RSD (n=3)	CEC	RSD	V%	$pH_{CaCl2\ (1:5)}$
35	Molve 14/40	P (0-20)	4.51	± 9	1.28	± 25	0.35	± 55	6.14	± 5	7.42	± 18	83	4.85
36		P/C (20-40)	4.95	± 10	1.20	± 24	0.25	± 59	6.40	± 4	7.52	± 18	85	4.89
37		C (>40)	3.89	± 16	1.05	± 29	0.15	± 69	5.09	± 11	6.92	± 40	73	5.07
38	Molve 10	A (0-12)	6.71	± 14	2.22	± 3	0.64	± 50	9.57	± 9	11.8	± 22	81	5.00
39		Gso (12-28)	6.00	± 7	1.61	± 14	0.32	± 58	7.93	± 5	10.9	± 36	73	5.00
40		Gso/r (28-63)	3.03	± 40	1.17	± 20	0.16	± 76	4.36	± 27	6.14	± 33	71	4.86
41	Molve 11	A (0-11)	13.2	± 21	4.66	± 8	0.67	± 49	18.5	± 14	31.3	± 56	59	5.20
42		Gso (11-32)	11.9	± 38	3.93	± 8	0.45	± 65	16.3	± 27	13.5	± 53	120	5.03
43		Gso/r (32-67)	13.2	± 26	4.04	± 9	0.47	± 62	17.7	± 19	14.9	± 63	119	5.55
44		Gr/so (67-110)	16.6	± 22	5.11	± 10	0.65	± 58	22.4	± 17	17.5	± 42	127	5.95
45	Molve 12	Aa (0-13)	24.9	± 24	5.65	± 9	1.12	± 54	31.7	± 17	32.3	± 4	98	5.65
46		Gr_1 (13-47)	29.1	± 38	7.33	± 7	0.96	± 44	37.4	± 30	30.1	± 18	124	6.01
47		Gso (47-71)	28.0	± 10	7.74	± 6	0.97	± 60	36.7	± 8	26.7	± 39	137	6.38
48		Gr_2 (71-94)	15.1	± 9	4.58	± 4	1.06	± 47	20.7	± 8	20.4	± 13	102	6.52
49	Zagreb, Cvjetno settlement	A/I (0-20)	13.0	± 8	1.35	± 19	0.64	± 64	15.0	± 5	11.5	± 14	131	7.02
50		II (20-40)	13.1	± 3	1.03	± 29	0.29	± 78	14.4	± 2	11.8	± 9	122	7.19
51		III (40-60)	16.4	± 12	1.42	± 19	0.28	± 52	18.1	± 11	14.1	± 17	128	7.26
ISE 882			4.73	± 10	9.62	± 3	2.84	± 2	21.6	± 1	16.3	± 10	132	

EXCHANGEABLE CATIONS

Soil exchangeable Ca^{2+}

The highest value of exchangeable Ca^{2+} was recorded at the location Fužine in surface Aoh horizon (44.5 $cmol^{+}*kg^{-1}$). At the locations of Fužine (Bv horizon), Delnice (A horizon), Vodnjan (A horizon), Ripenda and Molve 12 (Gr_1 and Gso horizons), higher values of exchangeable Ca^{2+} were recorded than in all other investigated locations, and values ranged from 28.0 $cmol^{+}*kg^{-1}$ up to the above mentioned 44.5 $cmol^{+}*kg^{-1}$ depending on the depth (horizon). At these locations higher pH values were also observed, ranging from 6.01 to 7.44. Moreira and Fageria (2009) reported that the pH in Amazonas soils had a significant positive relationship with Ca^{2+} which means that the increasing soil pH improved Ca^{2+} content.

The lowest value of exchangeable Ca^{2+} was recorded at the location Zalesina in the deepest Bh horizon (0.09 $cmol^{+}*kg^{-1}$). At the locations of Zalesina and Veliki Žitnik, lower values of exchangeable Ca^{2+} were recorded than in all other investigated locations, and values ranged from the above mentioned 0.9 $cmol^{+}*kg^{-1}$ up to 2.71 $cmol^{+}*kg^{-1}$ depending on the depth (horizon). Possible reasons for low values could be that the parent material on which soil has developed is poor in bases (Škorić, 1986), and the low pH values in these soil types, where pH ranged from 3.27 to 4.30.

Soil exchangeable Mg^{2+}

The highest value of exchangeable Mg^{2+} was recorded at the location of Molve 12 in deeper Gso horizon (7.74 $cmol^{+}*kg^{-1}$). At Delnice (C horizon), Ivanovec, Županja (Gr/so horizon), Molve 12 and Molve 11 locations, the recorded values of exchangeable Mg^{2+} were higher than in other investigated locations, and values ranged from 3.93 $cmol^{+}*kg^{-1}$ up to the above mentioned 7.74 $cmol^{+}*kg^{-1}$ depending on the depth (horizon).

The lowest value of exchangeable Mg^{2+} was recorded at the location of Veliki Žitnik in A/B horizon (0.05 $cmol^{+}*kg^{-1}$). At Veliki Žitnik, Ripenda and Zalesina locations (E and Bh horizons), the recorded values of exchangeable Mg^{2+} were lower than in any other investigated locations, and values ranged from the above mentioned 0.05 $cmol^{+}*kg^{-1}$ up to 0.73 $cmol^{+}*kg^{-1}$ depending on the depth (horizon).

Soil exchangeable K^{+}

The highest value of exchangeable K^{+} was recorded at the location of Kneževo in upper Amo horizon (2.96 $cmol^{+}*kg^{-1}$), and the lowest value was recorded at the location Molve 14/40 in the deepest C horizon (0.15 $cmol^{+}*kg^{-1}$).

Sum of exchangeable cations in soli

Sum of exchangeable cations is the sum of bases (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) capable of exchange. The values of the sum of exchangeable cations for each repeated series (A, B, C) of analyzed soils are shown in Figure 1.

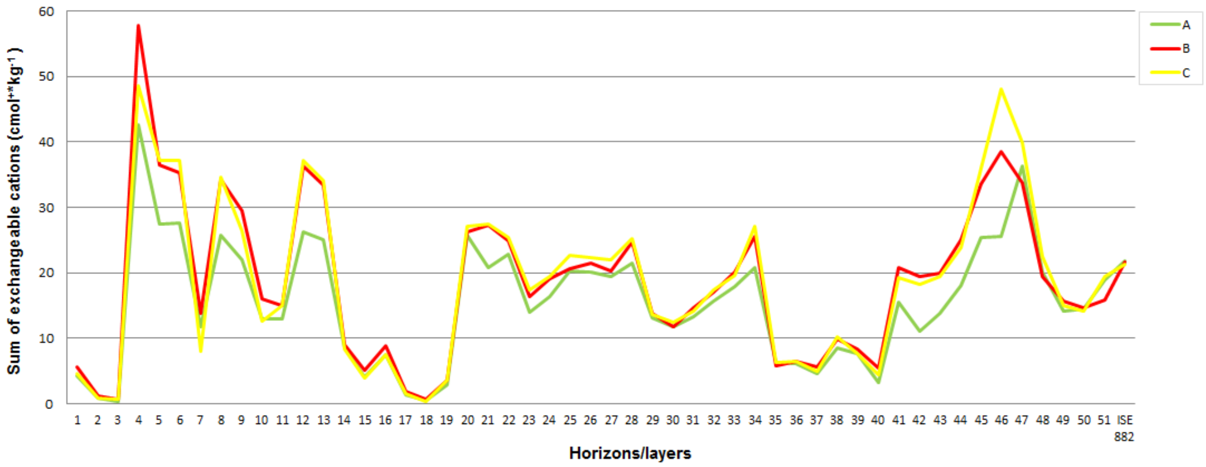

Figure1. Relationship between sums of base cations for each replication (A, B, C)

The highest value of the sum of exchangeable cations was recorded at the location Fužine in upper Aoh horizon (49.6 cmol^{+}*kg^{-1}). At the locations of Fužine ((B)v horizon), Delnice (A horizon), Vodnjan (A horizon), Ripenda, and Molve 12 (Aa, Gr$_1$, Gso horizons), higher values of the sum of exchangeable cations were recorded than in any other investigated locations, and values ranged from 30.8 cmol^{+}*kg^{-1} up to the above mentioned 49.6 cmol^{+}*kg^{-1} depending on the depth (horizon).

The lowest value was recorded at the location of Veliki Žitnik in A/B horizon (0.54 cmol^{+}*kg^{-1}). At Zalesina, Veliki Žitnik, Stružec (E/Bt horizon) and Molve 10 (Gso/r horizon) locations, lower values of sum were recorded than in any other investigated locations, and values ranged from the above mentioned 0.54 to 6.40 cmol^{+}*kg^{-1}.

According to Martinović (2000), the sum of exchangeable cations ranged from 3.9 to 38.5 cmol^{+}*kg^{-1} on 17 different locations in Croatia. Also, he noted that the amount of cations in adsorption complex and the amount of each exchangeable cation vary depending on bioclimate.

Soil CEC

Cation exchange capacity of soil is a total sum of exchangeable cations that it can adsorb at a specific pH. The differences (Δ) between CEC and the sum of exchangeable cations are presented in Figures 2a and 2b, which shows that the absolute maximum observed difference Δ was 15.9.

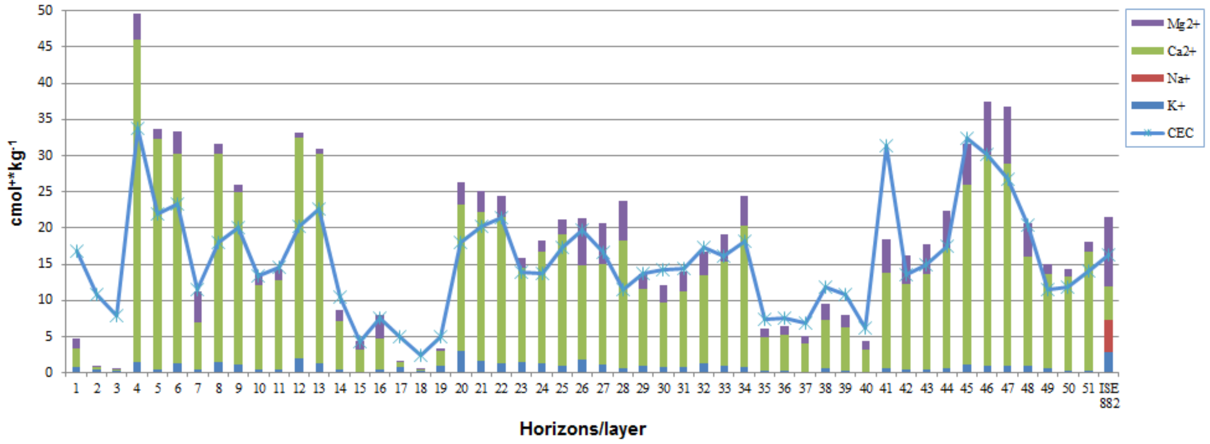

Figure 2a. Difference between sum of exchangeable cations and CEC

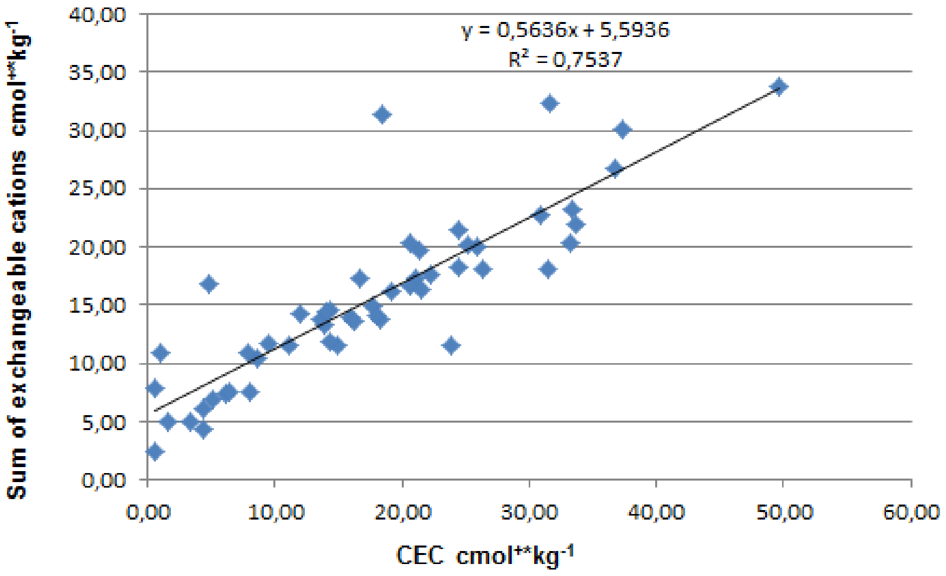

Figure 2b. Correlation between sum of exchangeable cations and CEC

The highest value of CEC was recorded at the location of Fužine in surface Aoh horizon (33.8 cmol$^+$*kg^{-1}). At the locations of Fužine, Ripenda, Delnice (A horizon), Vodnjan (Brz horizon), Kneževo (A and AC horizons), Molve 11 (A horizon) and Molve 12 higher values of CEC were recorded than in any other investigated locations, and values ranged from 20.0 cmol$^+$*kg^{-1} to the above mentioned 33.8 cmol$^+$*kg^{-1}.

The lowest value of CEC was recorded at the location of Veliki Žitnik in A/B horizon (2.39 cmol$^+$*kg^{-1}). At Stružec (E/Bt and Btg horizons), Veliki Žitnik, Molve 14/40 and Molve 10 (Gso/r horizon) locations, the recorded values of CEC were lower than in any other investigated locations, and they ranged from the above mentioned 2.39 cmol$^+$*kg^{-1} up to 7.53 cmol$^+$*kg^{-1}.

Soil texture is one of the parameters that have great influence on CEC values, therefore, the possible reasons for low CEC values at Molve 14/40 location could be the unfavorable texture of soil where a higher content of sand particles is recorded (through horizons: P=60.7%; C=64.1%)[3] and a lower content of clay particles (through horizons: P=3.3%; C=9.9%)[3], as well as low pH values (in P horizon 4.85 and 5.07 in C horizon).

According to Wang et al. (2005) positive correlations existed between the soil CEC and soil organic content C (R^2=0.34) and soil clay content (R^2=0.59), but a negative correlation was observed between the soil CEC and soil sand content (R^2=0.43) in the calcareous soils with a wide range of CaCO3.

In comparison to Molve 14/40 location, at Molve 12 location the recorded CEC values were higher as well as the content of clay particles (through horizons: Aa=35.4%; Gr_1=40.6%; Gso=56.4%; Gr_2=52.1%)[3], which leads to the known fact that clay has an important impact on CEC values.

According to Oorts et al. (2003) clay and fine silt fractions were responsible for 76 to 90% of the soil CEC at pH 5.8. The CEC values for the clay fractions varied between 15 and 20 $cmol^{+}* kg^{-1}$ at pH 3 and from 24 to 32 $cmol^{+}* kg^{-1}$ at pH 7.

[3] Soil texture data was taken from the “Report on results for permanent soil monitoring in the surroundings of the gas wells Molve” (Bašić et al., 2011)

Base saturation (V%)

Base saturation is the percentage of CEC that is saturated with base exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+), V%=∑sum of base exchangeable cations/CEC*100. The soil is retained when exchangeable cations saturate all available sites on soil absorption complex, which results in a 100% saturation. Under such conditions there are no acid cations, such as H^+, Al^{3+}, which is according to Duchaufour (1998) characteristic of soils with high calcium level. Base saturation higher than 100% indicates the presence of soluble salts or lime, and free cations which are not attached to the soil complex. In unsaturated soils acid cations occupy a significant part of the complex. Base saturation greatly varies based on the soil type and its horizons, depending on the content of organic matter, humus and pH.

The lowest percentage (V%) was calculated for the location of Zalesina in Bh horizon only 7%. The highest percentage (V%) was calculated for the location of Ivanovec near Osijek in Gso horizon, 207%.

Correlation between pH and base saturation (V%)

The linear regression analysis was applied to establish a correlation between base saturation and pH of the analyzed soils. The relationship between base saturation and pH was observed and graphically presented for all investigated samples (n=51) (Figure 3), but also according to acidity determined in $CaCl_2$ suspension, for the acid soils (n=17) (Figure 4), neutral soils (n=8) (Figure 5) and alkaline soils (n=26) (Figure 6).

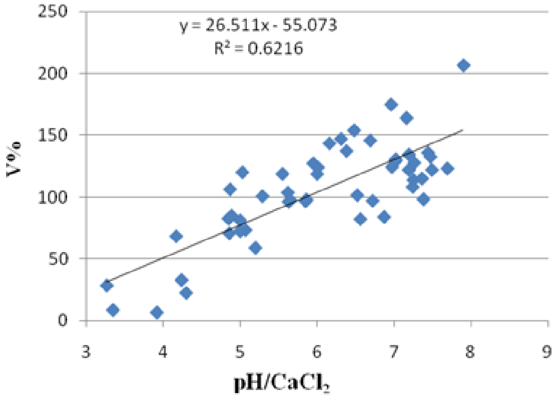

Figure 3. Functional dependece of pH and base saturation (V%) of all analysed samples (n=51)

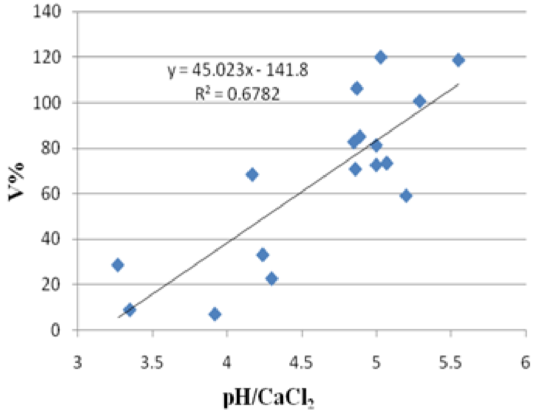

Figure 4. Functional dependece of pH and base saturation (V%) for the acid soils (n=17)

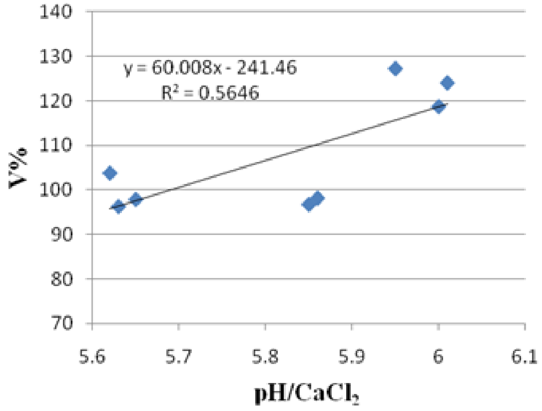

Figure 5. Functional dependece of pH and base saturation (V%) for the neutral soils (n=8)

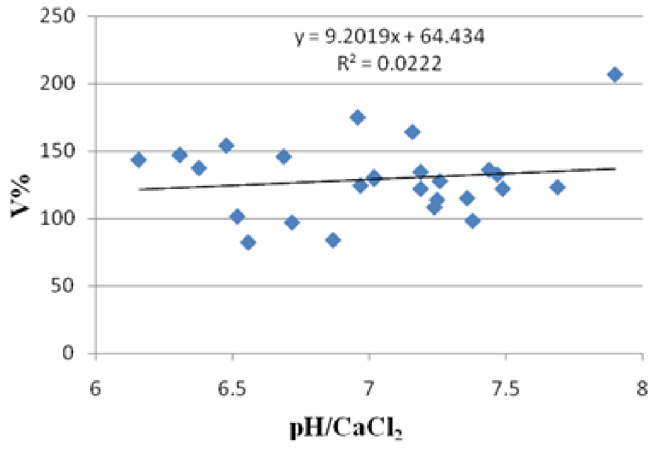

Figure 6. Functional dependece of pH and base saturation (V%) for the alkaline soils (n=26)

One of the goals of this examination was to establish a functional connection between pH and base saturation for all samples and separately for acid, neutral and alkaline samples. The functional connections are shown in Table 2.

Table 2. The correlation coefficient and functional dependence for all measurements

Soil distribution	Horizons number (n)	Observed correlation	Linear regression	Correlation coefficient	Intensity of correlation
The whole range	51	$pH/CaCl_2$ – V (%)	y = 26,511x - 55,073	r=0.79	Very strong
Acid soils	17	$pH/CaCl_2$ – V (%)	y = 45,023x - 141,8	r=0.82	Very strong
Neutral soils	8	$pH/CaCl_2$ – V (%)	y = 60,008x - 241,46	r=0.75	Very strong
Alkaline soils	26	$pH/CaCl_2$ – V (%)	y = 9,2019x + 64,434	r=0.15	Very weak

The correlation coefficient between base saturation (V%) and pH for all soils was r=0.79 (very strong correlation). For acid soils it was r=0.82 (very strong correlation), for neutral soils r=0.75 (very strong correlation), and finally for alkaline soils r=0.15 (very weak correlation).

According to Berry and Wilding (1971), the correlation coefficient between base saturation and pH measured in water and KCl ranged from r=0.596 to r=0.928 in acid soils of Ohio state. A stronger correlation was detected between base saturation and pH measured in water than in KCl. Also, stronger correlation was determined between Ap horizon (r=0.838 to 0.928) and pH measured in water, than in B horizon (r=0.668 to 0.801) and pH measured in water.

Moreira and Fageria (2009) reported that Amazonas soils pH <5.4 (96.5% of investigated soils) had a significant positive relationship between base saturation and pH, with a correlation coefficient r=0.49.

In relation to our study, negative correlations between soil pH and cation exchange capacity (CEC) or base saturation were detected in acid forest soils of the northeastern USA (Johnson, 2002), where one of the possible reasons for negative correlation was partly related to the acidity of organic matter.

CONCLUSION

According to the obtained results, we can state that the values of CEC and base exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) significantly vary depending on soil type and their horizons which can be seen in the obtained values of CEC and each base cation. Cation exchange capacity is under the influence of numerous chemical and physical parameters of soil which, with climate and relief, influence its values. In addition, in order to obtain a stronger connection, further investigation would be needed to determine texture and content of organic carbon.

It is notable that sodium concentrations were below the instrument detection limit in all samples. Analysis of sodium was conducted under the norm HRN ISO 11260 (2004), where provided concentrations for sodium ions in solution were 0-20 mg*L^{-1}. According to our investigations it is suggested to reduce the range of concentrations on 0-10 mg*L^{-1} or even wider (0-5mg*L^{-1}) for Na^+ because of low concentrations of sodium ions in the soil solution.

At some locations it is observed that the values of CEC are notably higher in relation to the sum of base exchangeable cations, for example at the location Zalesina where CEC ranged through horizons: A=16,8 $cmol^+$*kg^{-1}; E=10,9 $cmol^+$*kg^{-1}; Bh=7,90 $cmol^+$*kg^{-1} and the sum of cations through horizons was: A=4,82 $cmol^+$*kg^{-1}; E=0,97 $cmol^+$*kg^{-1}; Bh=0,55 $cmol^+$*kg^{-1}, indicating the possibility of the presence of H^+ and Al^{3+} ions and other cations in the soil. However, the opposite situations were also recorded where the values of CEC are lower than the values of the sum of base exchangeable cations, which points to the possibility of the presence of soluble salts or lime, and free cations which are not attached to the soil complex.

In this investigation a very strong correlation has been recorded between base saturation and pH for all examined soils. But, different correlations were recorded depending on the soil acidity, which indicates that the pH had a different impact on soil depending on acidity.

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