Comparison of Two Different CEC Determination Methods Regarding the Soil Properties

Zeljka ZGORELEC[1] (✉)
Branka GRAHOVAC[2]
Aleksandra PERCIN[1]
Vlatka JURKOVIC[2]
Lola GANDJAEVA[3]
Nada MAUROVIĆ[1]

Summary

Cation Exchange Capacity (CEC) is a parameter which reveals extent of the soil surface sites that can potentially retain cations by electrostatic forces. Different soil types vary in CEC values, which in turn depend on many factors (soil pH, texture, organic matter content, etc.). CEC is a good indicator of soil quality and fertility. CEC can be measured using different methods and it is difficult to recommend a universal one. The most commonly used methods include exchange of cations with a specific solution of known salt concentrations that are not present in the soil, followed by analytical detection of these cations by standard techniques. The aim of this study was to determine and compare the CEC and the amount of exchangeable cations measured on the same samples (n = 50) of soil with different characteristics, using two common methods (one with $BaCl_2$ and the other with CH_3COONH_4 solution), and to determine their dependence on soil pH, content of organic matter and clay content. Correlation between the values of CEC measured with two different methods was very high (r=0.83). Still, significant difference between the two methods (F test, $p \leq 0.05$) was noted. Transformation of the CEC values achieved by one method into the estimated values of the other method is possible. Very high correlation was observed between CEC (CEC_{BaCl_2} and $CEC_{CH_3COONH_4}$) and OM content in soil (r=0.78 and r=0.80), high correlation with soil pH (r=0.58 and r=0.52), and very weak or no correlation with clay content (r=0.12 and r=-0.04). Also, soil salt content influenced measured values of CEC (in CH_3COONH_4) and sum of exchangeable cations (in $BaCl_2$).

Key words

barium chloride, ammonium acetate, soil pH, soil texture, soil organic matter

[1] University of Zagreb Faculty of Agriculture, Svetošimunska 25, 10 000 Zagreb, Croatia
[2] Croatian Center for Agriculture, Food and Rural Affairs, Svetošimunska 25, 10 000 Zagreb, Croatia
[3] ERASMUS student, Urgench State University, Khamid Alimjan 14, 220100 Urgench, Uzbekistan

✉ Corresponding author: zzgorelec@agr.hr

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Introduction

Exchange of ions is a significant process in the soil, which involves adsorption, desorption and substitution of cations and anions from soil solution to a positive or negatively charged soil particles surface. Cation Exchange Capacity (CEC) is a measure of how many cations can be retained by electrostatic (Coulomb) forces on soil particle surfaces (Foth, 1990). Effective CEC is the sum of all permanent and variable negative surface charges in a soil that is balanced by exchangeable cations at the soils native pH (Scheffer and Schachtschabel, 2015). Different soil types vary in CEC, which depends on many soil factors such as pH, texture, clay and organic matter content (Foth, 1990; Škorić, 1991) and values of effective CEC can ranged widely, with extreme values of < 1 $cmol^+kg^{-1}$ (e.g. pure sands) to > 200 $cmol^+kg^{-1}$ (e.g. strongly humified peats) (Scheffer and Schachtschabel, 2015). Usually, normal soil CEC range is from 3 $cmol^+kg^{-1}$ (in sandy soils with low OM content) up to 25 $cmol^+kg^{-1}$ (in soils with high clay and OM content) (Ross, 1995).

CEC is a good indicator of soil quality and fertility; recommendations in agriculture and ameliorative techniques in real life regarding the fertilization or calcification very depend on soil CEC. Cation exchange in soil solution depends on: (1) cation selectivity, or the charge (valence) and size (hydrated radius) of the cation, (2) charge equivalence – charge for charge principle, (3) reversibility - balance between ions in soil solution and on soil adsorption complex, (4) complementary cations and (5) anion influence on balance in soil solution (Brady and Weil, 2010).

CEC can be measured using different methods and it is difficult to recommend a universal one. Since 1850, when Thomson discovered cation exchange phenomenon in soil after whom Way developed methodology in 1952 and Kelly in 1948 first developed method for quantitative CEC measurement (NH_4Cl extraction), numerous methods through history were investigated and developed by different scientist (SSSA, 1996). So, today different methods can be used to determine CEC, and they can give different results for the same soil (Brady and Weil, 2010). The most commonly used methods include exchange of cations with a specific solution of known salt concentrations that are not present in the soil ($BaCl_2$, CH_3COONH_4, $[Co(NH_3)_6]Cl_3$, $AgSC(NH_2)_2$) and analytical detection of these cations by standard techniques. Due to various methods of measuring CEC, it is important to know the purpose of data usage (ISO 11260, 1994; Ross, 1995; Ciesielski et al., 1997; Bergaya et al., 2006; ISO 23470, 2007; Tomašić, 2011; Tomašić et al., 2013). All mentioned methods have advantages and disadvantages. The errors in measurements can occur due to high content of $CaCO_3$ or gypsum ($CaSO_4 \times 2H_2O$) in soil, or K^+ and NH_4^+ adsorption in interlayer space in vermiculite and mica, or because of adsorption of three-valent cations like Al^{3+} and Fe^{3+} on soil particulate surface. In the literature, it can be found a lot of methods (different reagents) that can be used for minimization or elimination of interferences (SSSA, 1996; Tomašić, 2011).The aim of this study was to measure and compare the CEC values and the amount of exchangeable cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) on the same soil samples (n = 50; with different physical and chemical characteristics) using two different methods ($BaCl_2$ extract solution - HRN ISO 11260:2004 and CH_3COONH_4 extract solution - agitation method, NF X 31-108:2002) and to determine its dependence on soil reaction, content of organic matter and clay content.

Material and Methods

Soil

In total 50 soil samples were collected in Croatia during 2015 and 2016. Eleven samples were collected from arable cultivated land (CL), 11 from grassland (GL) and 28 from forest land (FL). Soil samples were collected from different depth layers. Fifteen were collected from surface soil layer (0-10 cm), four from 0-20 cm, 14 from 10-20 cm and 17 from 20-30 cm. The samples were air dried, milled, sieved through a 2 mm sieve and homogenized before analysis according to ISO 11464:2006. Soil reaction (pH), texture, organic matter (OM), carbonate content and hydrolytic acidity (HA) were determined according to protocols given in the Table 1. The range values of studied soil characteristics are shown in Table 1.

Thirty studied samples had acid (pH_{H_2O} < 6.5), 11 alkaline (pH_{H_2O} > 7.5) and 9 neutral pH reactions. Twenty one were clayey (> 30 % clay), 29 were humic (OM > 3 %) and 13 were classified as carbonate (> 10 % $CaCO_3$).

In two different laboratories: (1) Faculty of Agriculture and (2) Agency for Agricultural Land, two different methods for determination of CEC and the amount of exchangeable cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) were used: (1) The barium chloride extracts method - HRN ISO 11260:2004 and (2) The ammonium acetate extracts method - agitation method, NF X 31-108:2002).

The barium chloride extracts method

This method was standardized in 1994 under the reference ISO 11260 - Soil quality - Determination of effective cation exchange capacity and base saturation level using barium chloride solution. In Croatia it was adapted 2004 (HRN).

A test portion of 2.5 g[1] of soil was firstly saturated with respect to barium. The same soil portion is treated with 30 mL 0.1 $molL^{-1}$ $BaCl_2$ solution and shaken for 1 hour. The solid and liquid phases were separated by centrifugation. This operation was repeated three times. In supernatant exchangeable ions (potassium, sodium, magnesium and calcium) were measured. Soil cake was equilibrated with 30 mL 0.0025 $molL^{-1}$ $BaCl_2$ by shaking overnight. The solid and liquid phases were separated by centrifugation. The supernatant liquid was decanted and soil cake mass was weighed. On soil cake 30 mL 0.02 $molL^{-1}$ $MgSO_4$ was added, and mixture was shaken overnight and later on centrifuged. Supernatant liquid was decanted through filter paper and CEC (excess Mg^{2+}) was measured in the solution. All the barium present in the solution as well as adsorbed was precipitated in the form of highly insoluble $BaSO_4$ and, consequently the sites with exchangeable ions (Na, K, Ca, Mg, but also: Fe, Mn, Al, and H) were readily occupied by Mg^{2+}. The residual content of this (excess magnesium) and subtracted from the initial content (blank) were determined by FAAS or ICP-AES. To prevent the formation of refractory compounds of magnesium with phosphate, aluminum, etc. in the flame, an acidified lanthanum solution had been added and Mg was than determined. The difference gives the CEC value ($cmol^+kg^{-1}$).

[1] If measured CEC is > 40 $cmol^+kg^{-1}$ or soil has high clay content (> 30 %), an analysis with smaller amount of soil (1.50 g) need to be repeated

Table 1. Main characteristics of the soils used in the study

All soils (n=50)	pH_{H_2O}	pH_{CaCl_2}	$CaCO_3$, %	OM, %
Protocol	ISO 10390:2005		ISO 10693:1995	ISO 14235:1998
Range (min-max)	3.86 – 8.13	3.10 – 7.63	< 0.01 – 38.6	< 0.1 - 14.8
All soils (n=50)	clay (< 2 µm), %		silt (2-63 µm), %	sand (63 -2000 µm), %
Protocol	ISO 11277:2009			
Range (min-max)	7.6 - 78.3		19.1 – 76.2	1.6 – 59.2
All soils (n=50)	Hydrolytic acidity (HA), $cmol^+kg^{-1}$			
Protocol	Škorić, 1982			
Range (min-max)	3.8 - 22.0			

The ammonium acetate extracts method

In this study we followed the 2002 French standard AFNOR NF X 31-108.

A test portion of 10 g of soil was saturated with respect to ammonium ion. The same soil portion is treated with 50 mL of 1 $molL^{-1}$ CH_3COONH_4 buffered solution (pH=7) overnight. The solid and liquid phases were separated by centrifugation. This operation was repeated three times. In this solution exchangeable ions (potassium, sodium, magnesium and calcium) were determined by AAS or ICP-OES. CEC ($cmol^+kg^{-1}$) and calculated as sum of equivalent content of all four exchangeable ion. Soil hydrolytic acidity (HA) was determined for the same soil sample ($cmol^+kg^{-1}$). Equivalent content of each exchangeable cation as HA are calculated as ratio of measured mass ratio ($mg100g^{-1}$) divided by atomic mass of the (+) ion.

Soil HA was determined using 40 g soil portion and 100 mL 1 $molL^{-1}$ CH_3COONa. After one hour shaking, 50 mL of aliquot was taken for volumetric (titrimetric) determination using 0.1 M NaOH (Škorić, 1982). Soil hydrolytic acidity (HA) is sum of active (free H^+ in soil solution) and exchangeable (H^+ and Al^{3+} bounded to soil adsorption complex) acidity. Soil HA exists and could be determined only in acid soils according to Škorić, 1982 (pH_{KCl} < 6.5) and Vukadinović and Lončarić, 1998 (pH_{CaCl_2} < 6) due to hydrolytic salts can be substitute with acid cations in adsorption complex. Soil HA in this research was measured in soil samples with pH_{CaCl_2} < 5.5.

CEC measurement, data analysis and quality control

The values of CEC (Mg^{2+} $cmol^+kg^{-1}$) and exchangeable cations (Na^+, K^+, Ca^{2+} and Mg^{2+} $cmol^+kg^{-1}$) were measured ($BaCl_2$ method) or calculated (CH_3COONH_4 method) from concentrations detected in extract [mgL^{-1}] after they were analyzed on AAS (Varian AA240FS, 2004) in Agricultural Land Agency Laboratory and on AAS (Perkin Elemer 3110, 1996) and ICP-OES (Varian, Vista MPX Axial, 2004) at University of Zagreb Faculty of Agriculture Laboratories according to the calibration curves created from known cation concentrations (standards).

Statistical data analysis was performed for the whole range of 50 soil samples and two reference soil samples. The functional dependences of pH, clay and OM content to CEC were provided for a whole range of analyzed samples and were determined by the linear regression method. Statistical determination of significance of differences between means of studied parameters was done by F test (Microsoft Excel, 2010). The correlations of studied parameters were calculated and interpreted on the basis of correlation coefficient values according to Roemer-Orphal scale (Vasilj, 2000).

Quality control of CEC_{BaCl_2} and exchangeable ion measurements were included in the study. Descriptive statistical analysis was conducted in order to calculate the measurement accuracy and precision, including: arithmetic mean, standard deviation, relative standard deviation (RSD) and absolute error. Accuracy of measurement was controlled by a reference samples ISE 864 and 879, WEPAL - Wageningen Evaluating Programs for Analytical Laboratories. Precision of measurement was controlled by repeating measurements of the same sample in three replications and were calculated as relative standard deviation (RSD). Accuracy and precision were satisfactory, absolute error for CEC_{BaCl_2} measurement ranged up to 9% and precision (RSD) of reference and real samples varied up to maximal 8%.

Result and Discussion

Sum of exchangeable cations and CEC measured in 50 soil samples, using two different methods are shown in Fig. 1. Soil pH, OM content and clay content are very important factor in CEC determination and interpretation. Usually, CEC is almost equal to the sum of exchangeable K, Na, Ca and Mg, but in soils with very low pH, CEC could be much higher than sum of exchangeable K, Na, Ca and Mg, which can be explained by high presence of Al, Mn, Fe and H ions. In this study maximal difference between CEC_{BaCl_2} (5.49 $cmol^+kg^{-1}$) and sum of exchangeable cations (1.43 $cmol^+kg^{-1}$) was observed in sample No. 36 with 4.72 $cmol^+kg^{-1}$ (pH_{CaCl_2}=3.1; OM=8% and clay=26.54%).

Maximal difference (of even 40.36 $cmol^+kg^{-1}$) between measured sum of exchangeable cations (72.15 $cmol^+kg^{-1}$) and CEC_{BaCl_2} (31.79 $cmol^+kg^{-1}$) was observed in sample No. 30

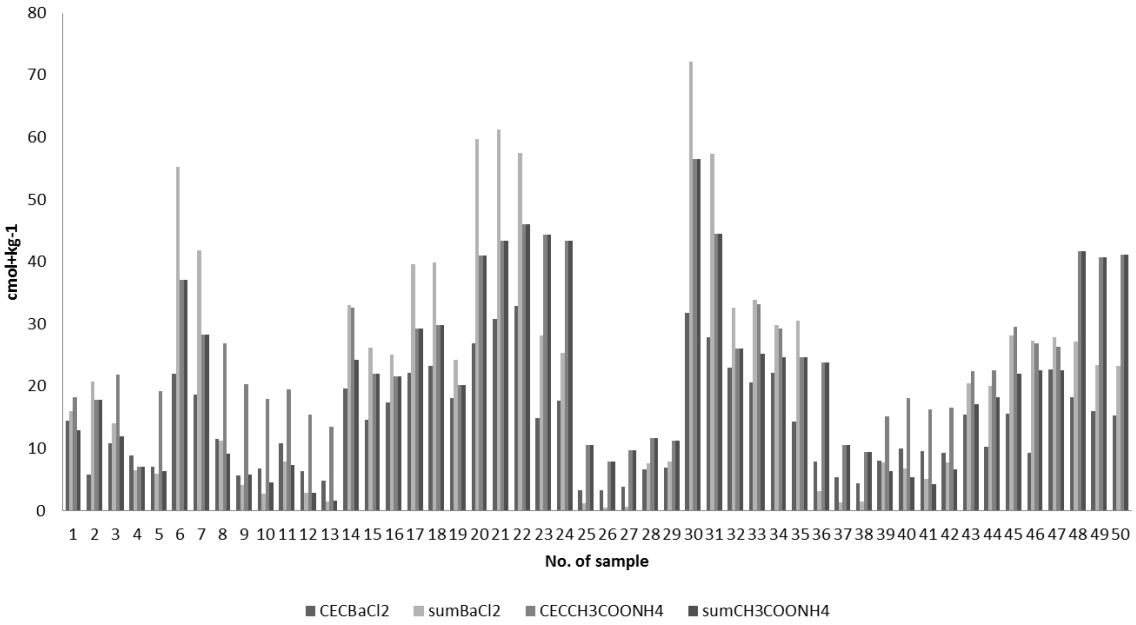


Figure 1. Comparison of CEC and the sum of exchangeable cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) measured on the same soil samples (n = 50) using two different methods ($BaCl_2$ and CH_3COONH_4)

(pH_{CaCl_2}=7.2, OM=14.1%, clay=24.2% and $CaCO_3$ = 33.4%). This high difference could be explained by high content of organic matter but much more by high ambient carbonate conditions (exchangeable Ca in this sample was 57 $cmol^+kg^{-1}$). Explanation is also confirmed by Soil Science Society of America (SSSA, 1996) that claims that the accurate determination of exchangeable cations in saline and calcareous soils is clearly compromised because of problem of quantitatively separating soluble or sparingly soluble cations from exchangeable cations during the extraction procedure by any method. As result in such cases, CEC cannot be estimated by summing exchangeable cations and often not by simple saturation techniques. So, just in no saline soils the sum of cations in leachate can give the CEC. Other studies (Tomašić et al., 2013) also observed difference between CEC and sum of exchangeable cations measured using BaCl2 method on 51 dominant soil types in Croatia. The highest difference (12.8 $cmol^+kg^{-1}$) between CEC_{BaCl_2} (18.5 $cmol^+kg^1$) and sum of exchangeable cations (31.3 $cmol^+kg^{-1}$) was observed in sample collected from surface soil layer 0-11 cm, (pH_{CaCl_2}=5.2, pH_{KCl}=4.6, clay=32.4%, OM=8.05%). On the other hand, the highest difference (15.8 $cmol^+kg^{-1}$) between sum of exchangeable cations (49.6 $cmol^+kg^{-1}$) and CEC_{BaCl_2} (33.8 $cmol^+kg^{-1}$) was observed in sample collected at 0-5 cm (pH_{CaCl_2}=6.3, pH_{KCl}=6.2). Very high correlation (r=0.87) between sum of exchangeable cations (y) and CEC (x) was revealed by Tomašić et al. (2013) (y=0.5636*x+5.5936), as in this study where complete correlation (r=0.94) between sum of exchangeable cations (y) and CEC (x) was observed (y=2.1948*x+9.0506) (Fig. 2, Table 2).

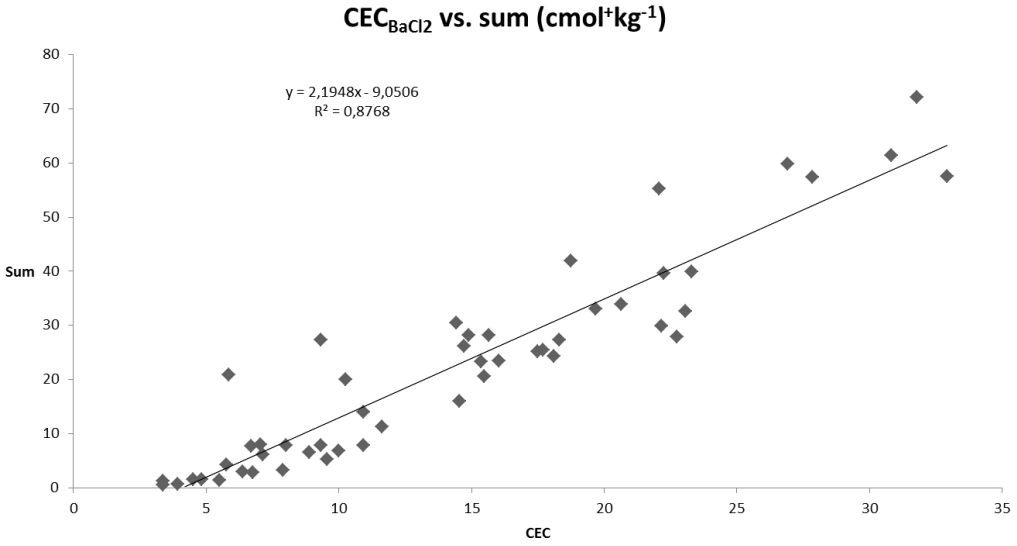


Figure 2. Functional dependence of CEC and sum of exchangeable cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) measured on the same soil samples (n = 50) using $BaCl_2$ method

Table 2. Correlation matrix of studied parameters

	CEC_{BaCl_2}	sum_{BaCl_2}	$CEC_{CH_3COONH_4}$	pH_{H_2O}	clay	OM
CEC_{BaCl_2}	1.00					
sum_{BaCl_2}	**0.94***	1.00				
$CEC_{CH_3COONH_4}$	**0.83***	0.84	1.00			
pH_{H_2O}	**0.78***	0.81	**0.80***	1.00		
clay	**0.12***	0.06	**-0.04***	0.06	1.00	
OM	**0.58***	0.65	**0.52***	0.36	-0.27	1.00

* Significant at 0.05 probability level (F test, p≤0.05)

In method with ammonium acetate, $CEC_{CH_3COONH_4}$ was calculated as sum of exchangeable cations (K^+, Na^+, Ca^{2+}, Mg^{2+}), so no difference between them can even exist in neutral and alkaline soils. For acid soils determined hydrolytic acidity (HA) was also added to $CEC_{CH_3COONH_4}$.

In Fig. 3a functional dependence of CEC measured on the same soil samples (n = 50) using two different methods is shown. Correlation between methods was very high (r=0.83, Table 2); still significant difference between methods was observed (F test, $p \leq 0.05$). Difference in the methodology between $BaCl_2$ and CH_3COONH_4 is connected with the pH of extract solution and soil. CEC_{BaCl_2} is a measure of soil CEC at "field" pH (effective CEC), while $CEC_{CH_3COONH_4}$ is a measure of soil CEC buffered at pH=7, in which condition it gives highly inflated values for CEC (could be accurate for neutral and alkaline but not for acid soils). In this study higher range for measured $CEC_{CH_3COONH_4}$ (7.1-56.6 $cmol^+kg^{-1}$) was observed in comparison to CEC_{BaCl_2} (3.4-32.9 $cmol^+kg^1$). On other hand, higher range of measured sum of exchangeable cations (0.6-72.1 $cmol^+kg^{-1}$) was observed in $BaCl_2$ in comparison to CH_3COONH_4 (7.1-56.6 $cmol^+kg^1$) method. Borge (1997) in her study also compared two methods (using extracant solutions buffered at pH=7 and unbuffered) and observed the same as we did, that CEC measured in buffered solution was higher than in unbuffered, while sum of exchangeable cations was lower in buffered one.

Transformation of data achieved by one method to estimated values of the other method is possible (Fig. 3a; $y=CEC_{CH_3COONH_4}$; $x=CEC_{BaCl_2}$; y=1.2426*x+7.5254; r^2= 0.689). The highest difference (29.5 $cmol^+kg^1$) between $CEC_{CH_3COONH_4}$ and CEC_{BaCl_2} was observed on sample No. 23 (pH_{H_2O}=7.8, OM=2.9%, clay=29% and $CaCO_3$ = 34.1%) (Figure 3b). Beside it, five more samples No. 24 (pH_{H_2O}=7.8, OM=2.0%, clay=28% and $CaCO_3$ = 24.1%), 30 (pH_{H_2O}=7.6, OM=14.1%, clay=24% and $CaCO_3$=33.4%) and 48-50 (pH_{H_2O}=7.9-8.1, OM=up to 4.7%, clay=26-28% and $CaCO_3$ = 25.3-27.0%) had CEC difference > 23 $cmol^+kg^1$) (Fig. 3(b)). According to ISO 11260 (1994) advantage of barium chloride extracts method for soil CEC determination is that CEC is determined at the natural pH of the soil and at low total ionic strength. But, the presence of any soluble salts present in the soil may give values for the sum of exchangeable cations that are higher than the actual CEC amounts. The $BaCl_2$ method can suffer from interference of Ca as calcite ($CaCO_3$) or gypsum ($CaSO_4 \times 2H_2O$) in the sample. Overestimation of the $CEC_{CH_3COONH_4}$ values in some soil samples as result of summing the exchangeable cations was also observed and could be explained due to buffering and/or high OM and $CaCO_3$ content.

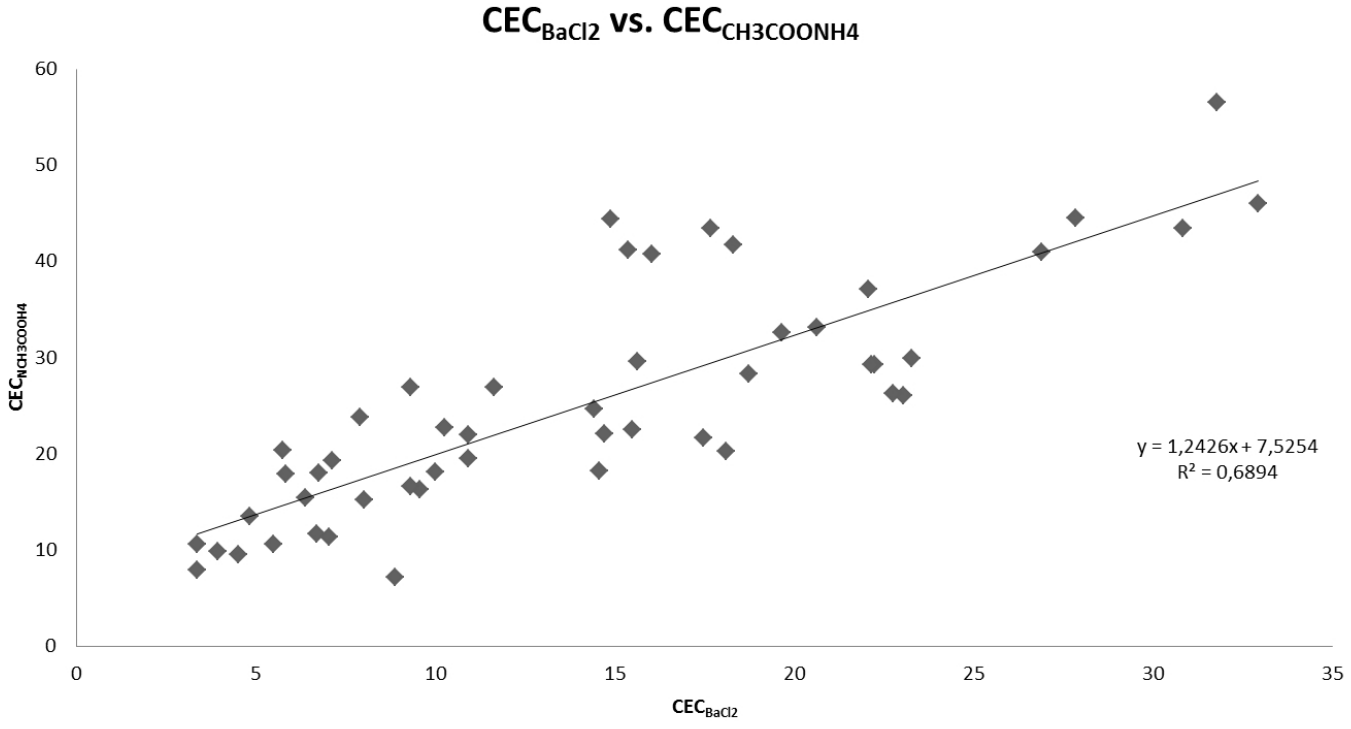
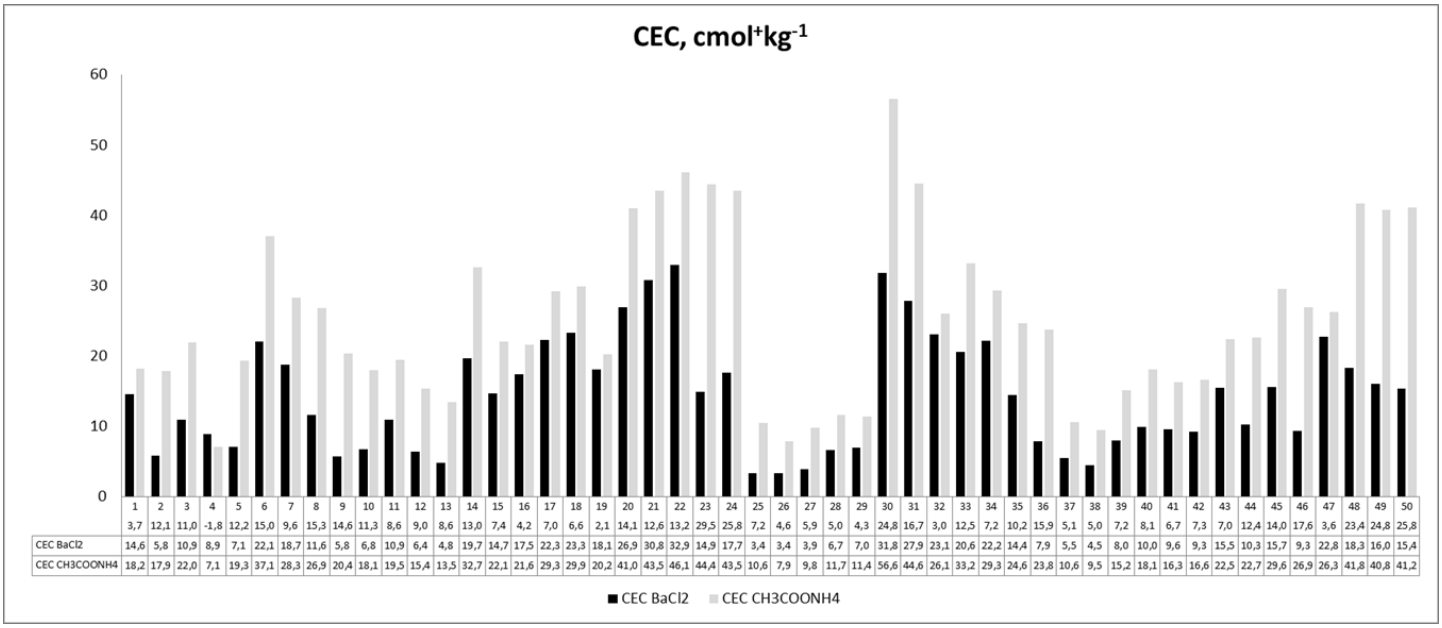


Figure 3 (a). Functional dependence of CEC measured on the same soil samples (n = 50) using two different methods



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
	3,7	12,1	11,0	-1,8	12,2	15,0	9,6	15,3	14,6	11,3	8,6	9,0	8,6	13,0	7,4	4,2	7,0	6,6	2,1	14,1	12,6	13,2	29,5	25,8	7,2	4,6	5,9	5,0	4,3	24,8	16,7	3,0	12,5	7,2	10,2	15,9	5,1	5,0	7,2	8,1	6,7	7,3	7,0	12,4	14,0	17,6	3,6	23,4	24,8	25,8
CEC BaCl2	14,6	5,8	10,9	8,9	7,1	22,1	18,7	11,6	5,8	6,8	10,9	6,4	4,8	19,7	14,7	17,5	22,3	23,3	18,1	26,9	30,8	32,9	14,9	17,7	3,4	3,4	3,9	6,7	7,0	31,8	27,9	23,1	20,6	22,2	14,4	7,9	5,5	4,5	8,0	10,0	9,6	9,3	15,5	10,3	15,7	9,3	22,8	18,3	16,0	15,4
CEC CH3COONH4	18,2	17,9	22,0	7,1	19,3	37,1	28,3	26,9	20,4	18,1	19,5	15,4	13,5	32,7	22,1	21,6	29,3	29,9	20,2	41,0	43,5	46,1	44,4	43,5	10,6	7,9	9,8	11,7	11,4	56,6	44,6	26,1	33,2	29,3	24,6	23,8	10,6	9,5	15,2	18,1	16,3	16,6	22,5	22,7	29,6	26,9	26,3	41,8	40,8	41,2

Figure 3 (b). Measured CEC ($BaCl_2$ and CH_3COONH_4) values and the differences between methods

In Fig. 4 average ratios (n=50) of basic cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) in (a) CEC_{BaCl_2} and (b) $CEC_{CH_3COONH_4}$ is shown. Ratio of studied exchangeable ions measured in $BaCl_2$ were Na:K:Mg:Ca = 3:5:20:72 and in NH_4Ac Na:K:Mg:Ca=0.3:2:13:51. According to Tomašić et al. (2013) range and ratios of optimal saturation with enumerate basic cations in soils were Na:K:Mg:Ca = (0-5):(2-7):(15-20):(65-75) and according to Scheffer and Schachtschabel (2015) were Na:K:Mg:Ca = (< 2):(2-5):(5-15):(> 80).

In Fig. 5 CEC (CEC_{BaCl_2} and $CEC_{CH_3COONH_4}$) functional dependence with (a) pH_{H_2O}, (b) OM and (c) clay content were shown and mathematically expressed (linear model) with equations (y=ax+b). Very high correlation was observed between CEC (CEC_{BaCl_2} and $CEC_{CH_3COONH_4}$) and OM content in soil, with observed coefficient of correlation r=0.78 and r=0.80, respectively (Table 2).

High correlation was observed between CEC (CEC_{BaCl_2} and $CEC_{CH_3COONH_4}$) and soil pH_{H_2O} with revealed coefficients of correlation r=0.58 and r=0.52, respectively. Very weak and no correlation was observed between CEC (CEC_{BaCl_2} and $CEC_{CH_3COONH_4}$) and soil clay content with observed coefficients of correlation r=0.12 and r=-0.04, respectively (Table 2).

Skinner et al. (2001) investigated appropriateness of three different methods for forest soils (acid), and observed that method with buffered CH_3COONH_4 (pH=7) had artificially high CEC, especially in soils with high OM content and low pH, while method with $MgCl_2$ had no changes regarding the OM and pH. Furthermore, Jaremko and Kalembasa (2014) compared four different methods for CEC determination and concluded that $BaCl_2$ and $[Co(NH_3)_6]Cl_3$ can be considered as equivalent methods because values measured as index cations were very comparable. Kappen and CH_3COONa methods overestimate the CEC results. Buffered CH_3COONa causes increase of numbers of negatively charged sites and particularly those bonded to organic matter. Kappen method shows overestimation for acid soils, soils rich in OM and very calcelourous soils. Nevertheless, it is possible

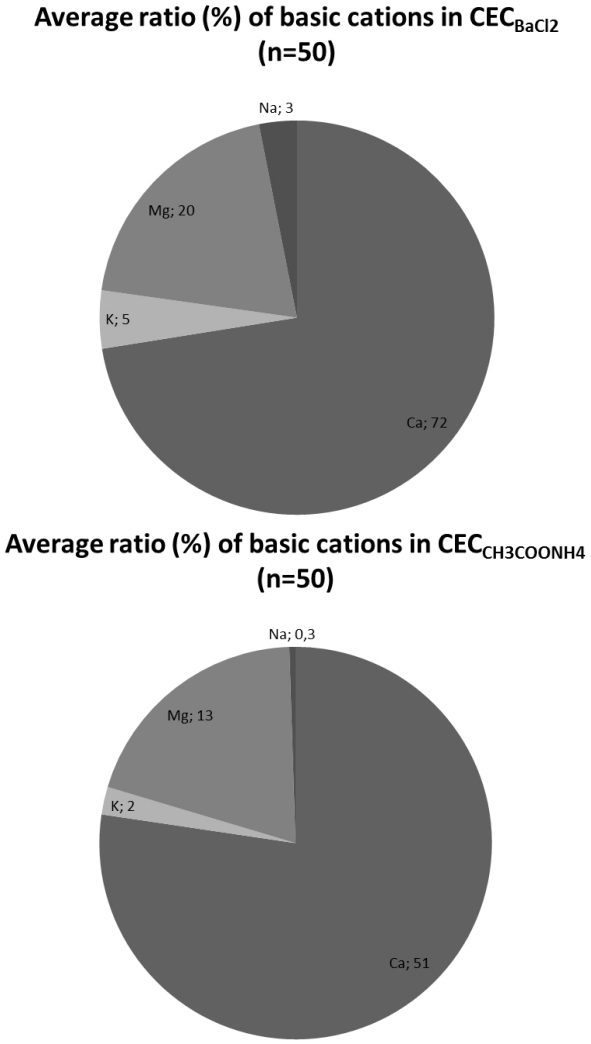


Figure 4. Average ratios (n=50) of basic cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) in (a) CEC_{BaCl_2} and (b) $CEC_{CH_3COONH_4}$

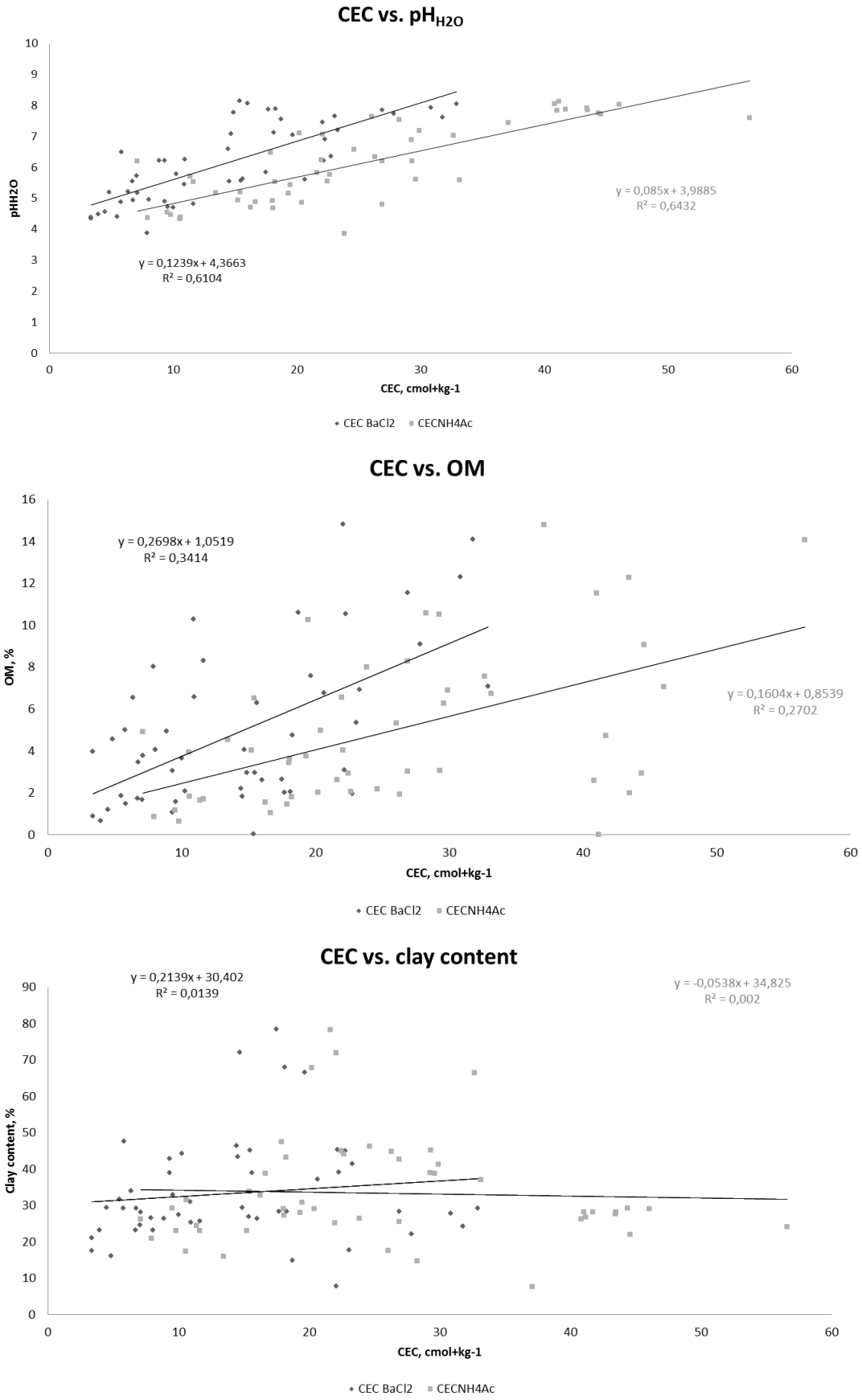


Figure 5. Functional dependence of CEC and (a) pH_{H_2O}, (b) and OM (c) clay content measured on the same soil samples (n = 50) using two different methods

to correct method errors (Kappen and CH_3COONa) for a given soil sample by regression equation considering pH of soil, clay and organic carbon content.

Conclusion

Two studied methods used different extract solutions $BaCl_2$ and CH_3COONH_4 (pH=7), first one is unbuffered and measures effective CEC (at natural soil pH conditions) and second one is buffered at pH=7.

Obtained values of CEC_{BaCl_2} were more corresponded to the actual sorption capacity of soils than $CEC_{CH_3COONH_4}$. Still, a pH 7 buffered ammonium acetate solution is widely used method, but its use for some acid and/or salty and/or high OM content soils has been questioned, due to it may result in an overestimation of CEC in soils with pH dependent charges due to increases in pH dependent charges (buffering).

Accuracy and precision of values measured with reference materials and real samples were satisfied for CEC_{BaCl_2}, still, overestimation of sum of exchangeable cations in some samples (high in salt content) were observed. This could be explained by the dissolution of larger amount of salt from soil solution during successive extractions. Thus, CEC_{BaCl_2} value is more relevant than sum of exchangeable cations.

Transformation of data achieved by one method to estimated values of the other method for investigated data set is possible ($y=CEC_{CH_3COONH_4}$; $x=CEC_{BaCl_2}$; $y=1.2426*x+7.5254$; $r^2 = 0.689$).

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