

Quantification of Exchangeable Cations Using Soil Water Retention Curve

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Abstract: The amount of exchangeable cation (EC) and cation types play important roles in fundamental soil behavior such as mechanical, hydraulic, chemical transport, and soil water retention (SWR). A methodology is proposed for the EC quantification of individual exchangeable cations using the SWR curve (SWRC) in matric potential < -100 MPa. The methodology is based on a SWRC model for homoionic soils that links soil water content to the cation exchange capacity (CEC) and the type of the exchangeable cations by considering the explicit effect of cation hydration on soil water content. Using the principle of local thermodynamic equilibrium, the authors extend the SWRC model to include soils with multiple cation species, leading to the quantification of exchangeable cations in soils. A suite of natural and artificially mixed homoionic soils are used to examine the validity of the methodology. The results reveal that the predicted exchangeable cations agree with those obtained by an independent experimental method, all within $\pm 15\%$ difference in CEC, indicating the potential applicability of the methodology in quantifying exchangeable cations in soils. DOI: 10.1061/(ASCE)GT.1943-5606.0001732. © 2017 American Society of Civil Engineers.

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Introduction

The cation exchange capacity (CEC) of a soil is a measure of the quantity of negatively charged sites on all soil surfaces retaining exchangeable positively charged ions [e.g., sodium (Na^+), potassium (K^+), calcium (Ca^{++}), and magnesium (Mg^{++})] (e.g., Dohrmann and Kaufhold 2009; Ross and Ketterings 2011). The amount of exchangeable cations (EC) in the soil plays an important role in water sorption, Atterberg limits, hydraulic conductivity, solubility and the transport of contaminants, shear strength, swelling and shrinkage, flocculation and deflocculation, consolidation and compaction, and the fertility of the soil (e.g., Grim 1962, 1968; van Olphen 1977; Shainberg and Lety 1984; Gaston and Selim 1990; Lal and Shukla 2004; Dontsova et al. 2004; Mitchell and Soga 2005; Astera 2014; Khorshidi and Lu 2016b; Khorshidi 2015).

The quantification of individual ECs in soil using chemical methods has been a focus of attention for soil science researchers for several decades. The chemical methods available to analyze exchangeable cations in soils involve the complete replacement of all exchangeable cations with an index cation through multiple extraction processes to achieve cation saturation, after which an accurate analysis of the extraction solution is obtained by different techniques.

The most commonly used technique to analyze the extraction solution is atomic absorption spectroscopy (AAS) (Sumner and Miller 1996). Other commonly available techniques include inductively coupled plasma emission spectroscopy (ICPES), flame emission spectroscopy, high-performance liquid chromatography

(HPLC), and ICP-mass spectrometry (ICP-MS) (e.g., Grim 1968; Watson and Isaac 1990; Sumner and Miller 1996). Titrimetric procedures and colorimetric methods were used before the development of AAS and ICP. The details about all these techniques can be found in Sumner and Miller (1996).

Errors can be introduced through the quantification of ECs using chemical methods during two stages: (1) the preparation of the solution to be analyzed through the replacement and extraction processes, and (2) the usage of the technique to analyze the exchangeable cation concentrations in the solution. These errors include chemical interferences, ionization interferences, matrix interferences, emission interferences, spectral interferences, and background absorption (e.g., David 1960; Skoog et al. 2006). Indeed, the chemical methods are time consuming and labor intensive.

The primary objective of this study is to investigate the potential application of the soil water retention curve (SWRC) in the quantification of individual ECs. The SWRC is the energy–equilibrium relationship between the matric potential and the corresponding retained water in the soil (e.g., van Genuchten 1980; Lu and Khorshidi 2015). First, the relationship between the matric potential and type of exchangeable cations in the homoionic soils is delineated. Local thermodynamic equilibrium is then used to determine the relationship between the matric potential and the amounts and types of different exchangeable cations in soils with multiple cation species. Using this relationship, the measured SWRC of the soil at matric potentials < -100 MPa, and the CEC of the soil, a new methodology for the determination of the amount of ECs in soils is developed. This methodology is validated by different natural bulk soils and artificially mixed homoionic soils.

Relationship between the Matric Potential and Cation Hydration

At high matric suctions, three hydration mechanisms are responsible for the attraction of water on or within soil particles: particle surface, interlayer surface, and exchangeable cations (e.g., Lu and

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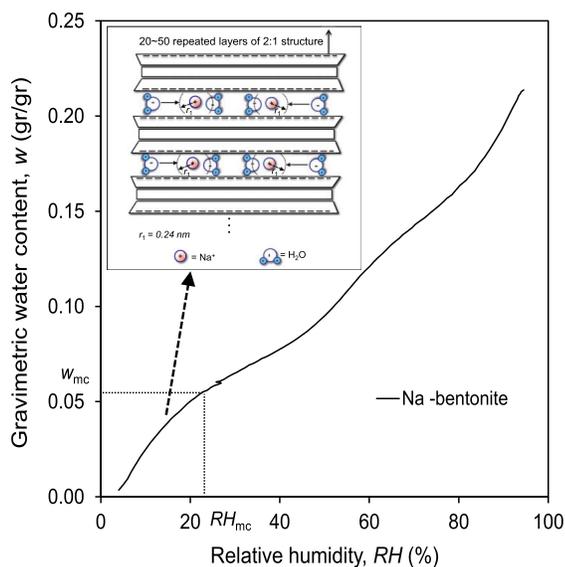


Fig. 1. Water sorption on soil due to cation hydration mechanism at very low water content up to monolayer cation hydration water content (w_{mc}) in Na^+ -bentonite

Likos 2004; Mitchell and Soga 2005; Lu and Khorshidi 2015). Several studies have illustrated that cation hydration is the dominant hydration mechanism at very low water contents (e.g., Quirk 1955; Hu et al. 1995; Prost et al. 1998; Laird 1999; Sposito 2008; Woodruff and Revil 2011; Revil and Lu 2013; Khorshidi and Lu 2016a). At higher water contents, interlayer and particle surface hydration mechanisms play the dominant role in retaining water on or within soil particles (e.g., Tuller and Or 2005; Frydman and Baker 2009; Khorshidi et al. 2016d). It is important to recognize that water sorption on soil in the hydration regime is independent of density and pore size distribution (e.g., Lu and Khorshidi 2015).

Over the range of very low water contents, exchangeable cations are hydrated similarly to hydrated cations in aqueous solutions (e.g., Quirk 1955; Chang et al. 1998; Sposito 2008; Khorshidi et al. 2016a). Therefore, in a homoionic soil with a water content of less than the monolayer cation hydration water content (w_{mc}), all water molecules are located in the first hydration shell of the cations with a certain distance r_{1i} from the cations (cation–oxygen distance). Fig. 1 illustrates the SWRC of Na^+ -exchanged bentonite at high suction values and the arrangement of water molecules around exchangeable cations in the range of relative humidity (RH) values at which cation hydration is the dominant hydration mechanism. The gravimetric water content w of homoionic soils at this condition can be obtained by

$$w = \frac{w_w N_i EC_i}{V_{c_i}} \quad (1)$$

where w_w = molar mass of water; N_i = number of water molecules hydrating the exchangeable cation type i ; V_{c_i} = cation i valence; and EC_i = amount of exchangeable cations i , which is equal to CEC for homoionic soils. As stated in Khorshidi and Lu (2016a), the N_i value reaches the cation i hydration number I_i at monolayer cation hydration, at which the soil water content is w_{mc} . The values of I_i and r_{1i} for each type of exchangeable cation are listed in Table 1.

To correlate the matric potential to the cation hydration through the amount and type of exchangeable cations, Khorshidi et al. (2016a) derived a theoretical SWRC model to quantify the matric potential and its retained water using the concept of thermodynamics and the Gibbs free energy equation. Different soils ranging from expansive to nonexpansive were used in this study. All water sorption mechanisms such as surface tension, van der Waals force field, and cation–water molecule interaction on or within the soil particles were accounted for in developing the equation. After simplifying the equation, for a homoionic soil with a water content of less than w_{mc} , the relationship between the matric potential ψ (Pa) and exchangeable cation i was derived as follows (Khorshidi et al. 2016a):

$$\psi = -2.97 \times 10^{-10} \frac{V_{c_i}}{\kappa_i r_{1i}^2} \quad (2)$$

In this equation, the κ_i parameter, which is directly related to the N_i in soil, is a factor to consider the effect of electrical work and cation–water interaction on matric potential. The relationship between κ_i and N_i , as depicted in Fig. 2, is

$$\kappa_i = 0.06N_i^2 + 3.77N_i + 9.30 \quad (3)$$

For more details about the derivation of this SWRC model, the reader is referred to Khorshidi et al. (2016a).

Eqs. (1) and (2) have been derived for homoionic soils. In natural soils with multiple cation species, each type of exchangeable cation in the soil has its particular V_{c_i} , I_i , and r_{1i} values. In addition, the CEC of soil is the summation of the exchangeable cation values. Thus, the local thermodynamic equilibrium, in conjunction with Eqs. (2) and (3), should be used to describe the SWRC at high suction values (soil water sorption isotherm).

Local Thermodynamic Equilibrium in Soil

Thermodynamics equilibrium governs the multiphase transfer in porous media (e.g., Hassanizadeh and Gray 1979, 1980; Sposito and Chu 1981, 1982). In an equilibrated soil system consisting of multiple cation species, as shown in Fig. 3, the local thermodynamic equilibrium should be reached over the entire system. To reach the equilibrium, the matric potential in the entire soil sample over all different exchangeable cations should be the same. This dictates the number of water molecules around each type of

Table 1. Average Hydration Number and Hydration Shell Distance for Individual Cations

Cation type	Cation valence, z	Cation hydration number, I^a (± 1)	Cation-water molecule distance, r_{1i} (nm)	Reference
Li^+	1	5	0.195	Chang et al. (1998) and Mähler and Persson (2012)
Na^+	1	4	0.240	Chang et al. (1998) and Mähler and Persson (2012)
K^+	1	3	0.275	Chang et al. (1998) and Mähler and Persson (2012)
Mg^{++}	2	6	0.212	Bernal-Uruchurtu and Ortega-Blake (1995)
Ca^{++}	2	6	0.240	Bernal-Uruchurtu and Ortega-Blake (1995)

^aFrom Israelachvili (2011).

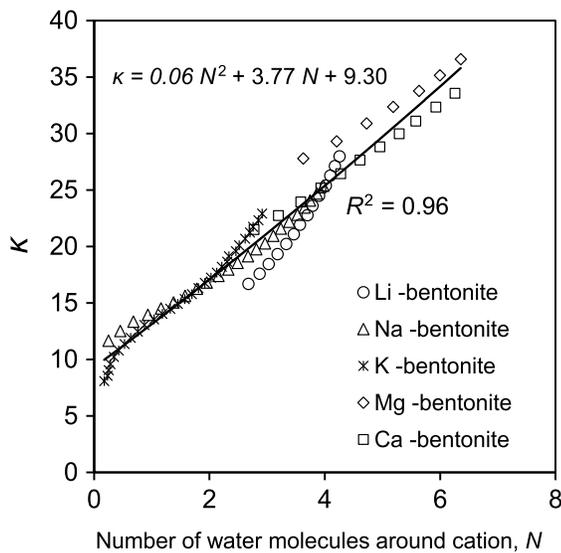


Fig. 2. Relationship between parameter κ and number of water molecules around each cation (N) for five homoionic cation-exchanged bentonites (adapted from Khorshidi et al. 2016a, © ASCE)

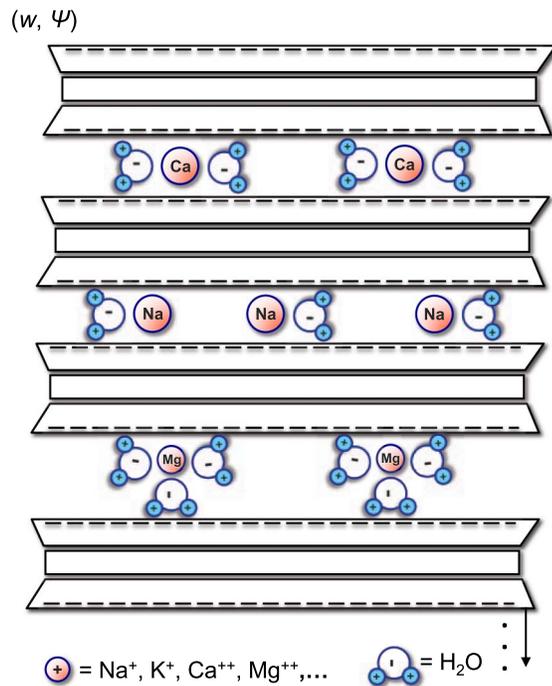


Fig. 3. Local thermodynamic equilibrium in a soil with multiple cation species

exchangeable cation over very low matric potentials where cation hydration only occurs. At any ψ value, individual exchangeable cations have different numbers of water molecules in their hydration shells based on their charge-dipole (cation-water molecule) interactions, as illustrated in Fig. 3. The N_i value for each type of exchangeable cation at any given ψ value can be obtained by using Eqs. (2) and (3). The combination of these equations is shown in Fig. 4, illustrating the relationship between ψ and N_i for each type of exchangeable cation. Based on this figure, for instance, in a soil containing the exchangeable cations of K^+ , Na^+ , Ca^{++} , and Mg^{++} , the values of N_K , N_{Na} , N_{Ca} , and N_{Mg} at the

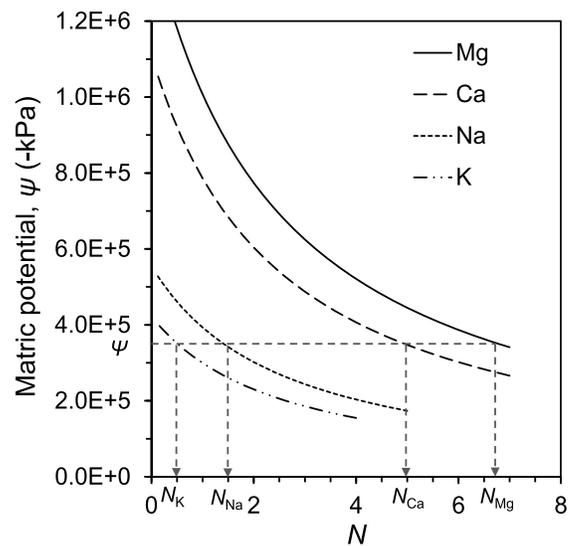


Fig. 4. Number of water molecules around each type of exchangeable cations (N_i) at extremely low matric potential

matric potential of $-350,000$ kPa are 0.50, 1.50, 5.00, and 6.75, respectively.

The gravimetric water content of the soil at any matric potential can be determined using the superposition principle. Knowing N_i values for each cation type at any given ψ value from Eqs. (2) and (3) or Fig. 4, the gravimetric water content of the soil can be obtained by

$$w = w_w \sum_i \frac{N_i EC_i}{V_{c_i}} \quad (4)$$

Eq. (4) implies that in a soil with multiple cation species, the SWRC at very low matric potentials can be predicted if the exchangeable cation values of the soil are known. Reversibly, the exchangeable cation values can be determined using Eqs. (2)–(4) by having the measured soil's CEC and SWRC at extremely high suction values. The methodology to quantify ECs in the soil is described in the next section.

Quantification of Exchangeable Cations in Soil

Soils contain a variety of different exchangeable cations; however, the key cations associated with the CEC are K^+ , Na^+ , Ca^{++} , and Mg^{++} (e.g., Warncke and Brown 1982; Thomas 1982; Rayment and Higginson 1992; Sumner and Miller 1996; ASTM 2010; Ross and Ketterings 2011). These cations, which are essential for soil fertility and are the main focus of soil science and soil characterizations, are generally referred to as the base cations (e.g., Warncke and Brown 1982; Rayment and Higginson 1992; Sumner and Miller 1996). When the soil pH value is greater than 6, which is the case for most soils, summing the exchangeable cation values of the base cations provides a reasonable estimation of the CEC (Grove et al. 1982; Warncke and Brown 1982; Thomas 1982; Ellis and Foth 1996; Sumner and Miller 1996; ASTM 2010; Ross and Ketterings 2011). Therefore

$$CEC = \sum_{i=K^+, Na^+, Ca^{++}, Mg^{++}} EC_i \quad (5)$$

However, as soils become more acidic, these base cations are replaced by H^+ and Al^{+++} ; the summation method will produce

Table 2. Geotechnical Engineering Properties of the Tested Soils

Soil	Mineralogy	Clay (%)	LL (%)	PL (%)	PI (%)	USCS classification	Origin
Georgia kaolinite	K	35	44	26	18	CL	Georgia
Wyoming montmorillonite	Discrete S, trace Qtz.	100	485	353	132	CH	Wyoming
Denver bentonite	Discrete S, trace K, Qtz., K-Feld	90	118	45	73	CH	Colorado
Denver claystone	Mixed layer I/S, trace K, Qtz., gypsum	55	44	23	21	CL	Colorado
Bonny silt	N/A	14	25	21	4	ML	Colorado
BALT silt	N/A	14	26	19	7	CL-ML	California
Hopi silt	N/A	3	26	19	7	SC-SM	Arizona
Missouri clay	N/A	N/A	N/A	N/A	N/A	N/A	Missouri

Note: I = illite; K = kaolinite; K-Feld = K-feldspar.; Qtz. = quartz; S = smectite; USCS = unified soil classification system.

a CEC with values that are higher than the real CEC values of the soils in the field (Sumner and Miller 1996; McKenzie et al. 2004). The focus of this study is only on the base cations. Thus, only soils with a $pH > 6$, where Eq. (5) is valid, are considered.

The ultimate goal of the methodology for the quantification of ECs in soil using the SWRC is to determine the EC_K , EC_{Na} , EC_{Mg} , and EC_{Ca} values (four unknowns). According to Eq. (4), to find these values, the N_i value for each type of exchangeable cation at any given (w , ψ) value on the measured soil water sorption isotherm should first be obtained. Substituting Eq. (2) into Eq. (3) and solving Eq. (3) gives N_i as

$$N_i = -29.7 + \frac{5}{317} \sqrt{-1.9 \times 10^{-5} \frac{V_{c_i}}{\psi r_{i_1}^2} + 2956700} \quad (6)$$

Substituting Eq. (6) into Eq. (4) gives the final relationship between w and ψ , with exchangeable cation values as unknowns

$$w = w_w \sum_i \frac{EC_i}{V_{c_i}} \left(-29.7 + \frac{5}{317} \sqrt{-1.9 \times 10^{-5} \frac{V_{c_i}}{\psi r_{i_1}^2} + 2,956,700} \right) \quad (7)$$

These equations are valid only for the range of matric potentials where the N_i value of each individual exchangeable cation is less than the corresponding I_i value. This criterion can be met at the range of matric potentials between $-320,000$ and $-370,000$ kPa. According to Fig. 4, the former value constrains the N_{Mg} to be less than 7.5; the latter value constrains the N_K to be greater than 0.35. Eq. (2) fits the experimental results of the K^+ cation very well in the range of $N_K > 0.35$, based on Fig. 2.

Overall, the four exchangeable cation values of the soil can be determined as fitting parameters having the CEC and SWRC of the soil at very low matric potentials. The theoretical SWRC model in Eq. (7) should be fitted to the measured isotherm in the range of $-370,000 \text{ kPa} < \psi < -320,000 \text{ kPa}$ ($\approx 6.75\% < RH < 9.75\%$) using a least-squares regression to optimize the corresponding fitting parameters. Simultaneously, Eq. (5), for the CEC of the soil, should be satisfied.

Materials and Methods

The soils used in this study for the validation of the new methodology were both artificially mixed cation-exchanged soils and natural bulk soils. The corresponding geotechnical engineering properties of these soils are listed in Table 2. For the cation-exchanged soils, three bulk natural silty and clayey soils ranging from expansive to nonexpansive were used and treated: Wyoming bentonite (NaS) (Lu and Khorshidi 2015), Bonny silt (Bs)

(McCartney and Rosenberg 2011), and Georgia kaolinite (GaK) (Lu and Khorshidi 2015). To have control over the types of exchangeable cations, these soils were treated with 1.0 M of NaCl and KCl, 0.1 M of $CaCl_2$, and $MgCl_2$ to produce the homoionic Na^+ , K^+ , Ca^{++} , and Mg^{++} saturated soils. Furthermore, these mono-cation soils were artificially mixed together with predetermined mass percentages to produce six soils with a known exchangeable cations composition. The soils are denoted by their respective mass percentage content. For example, a 40% mass percentage of “40% Na^+ -Bs / 60% K^+ -Bs” is composed of Na^+ -exchanged -Bs. Two to four different types of exchangeable cations are present in these artificially mixed soils, as shown in Table 3.

Five natural bulk soils, ranging from expansive to nonexpansive collected from different parts of the United States, were also used in this study. An atomic absorption spectrometer was used to measure the ECs of the NH_4OAc extract of these soils. AAS is a spectro-analytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state.

The CECs of the studied soils were measured using the ammonium displacement method standardized in ASTM D7503 (ASTM 2010); the CEC values are listed in Table 3 (data from Akin 2014). Although there might be a small difference between the CECs of cation-exchanged soil and the bulk natural soil, it is assumed that the CEC of the cation-exchanged soil is the same as that of the bulk natural soil. Recently, Khorshidi and Lu (2017) proposed a methodology for a CEC measurement using a soil water sorption isotherm that can also be used for the CEC measurement of soils instead of the ammonium displacement method.

An approximate 1.5 grams of air-dried soil samples passed through the #40 sieve were used for water sorption measurements. Water desorption isotherms of the tested soils were measured using a Vapor Sorption Analyzer (VSA; Decagon Devices, Pullman, Washington) at 25°C in the range of $3\% < RH < 95\%$, even though a water desorption measurement in the range of $6.75\% < RH < 9.75\%$ is enough for the purposes of this study. The VSA is an automated device working based on the concurrent dynamic measurement of the RH and w of the soil during both the adsorption (wetting) and desorption (drying) cycles.

Validation of the Proposed Methodology

The water desorption isotherms of three artificially mixed soils containing various types of exchangeable cations are represented in Fig. 5. Considering the CEC of these soils listed in Table 3, the effect of types of exchangeable cations on soil water content, particularly at low RH values, can be deduced from this figure. Specifically, “20% Na^+ -GaK / 50% Ca^{++} -Bs / 15% K^+ -GaK / 15% Mg^{++} -Bs” and “50% Na^+ -Bs / 50% Ca^{++} -GaK” have very close CEC values,

Table 3. Comparison between the EC Values Obtained by Experiment and Those Obtained from SWRC for All Tested Soils

Soil	CEC (meq/100 g)	EC _i (meq/100 g)							
		K ⁺		Na ⁺		Ca ⁺⁺		Mg ⁺⁺	
		Experimental	Predicted	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
K ⁺ -bentonite	77.0	77.0	77.0	0.0	0.0	0.0	0.0	0.0	0.0
Na ⁺ -bentonite	77.0	0.0	7.4	77.0	69.6	0.0	0.0	0.0	0.0
Ca ⁺⁺ -bentonite	77.0	0.0	0.0	0.0	0.7	77.0	69.5	0.0	6.8
Mg ⁺⁺ -bentonite	77.0	0.0	1.1	0.0	0.8	0.0	1.4	77.0	73.7
K ⁺ -Bs	21.0	21.0	18.3	0.0	0.0	0.0	2.1	0.0	0.6
Na ⁺ -Bs	21.0	0.0	1.1	21.0	18.6	0.0	1.3	0.0	0.0
Ca ⁺⁺ -Bs	21.0	0.0	0.3	0.0	0.0	21.0	20.7	0.0	0.0
Mg ⁺⁺ -Bs	21.0	0.0	1.1	0.0	0.8	0.0	1.7	21.0	17.4
K ⁺ -GaK	9.0	9.0	8.4	0.0	0.0	0.0	0.3	0.0	0.3
Na ⁺ -GaK	9.0	0.0	1.0	9.0	8.0	0.0	0.0	0.0	0.0
Ca ⁺⁺ -GaK	9.0	0.0	1.1	0.0	0.0	9.0	7.9	0.0	0.0
Mg ⁺⁺ -GaK	9.0	0.0	0.0	0.0	0.0	0.0	0.0	9.0	9.0
Na ⁺ -NaS	70.6	0.0	4.6	70.6	66.0	0.0	0.0	0.0	0.0
40% Na ⁺ -Bs/60% K ⁺ -Bs	21.0	12.6	10.3	8.4	7.6	0.0	1.1	0.0	2.0
50% Na ⁺ -Bs/50% Ca ⁺⁺ -GaK	15.0	0.0	0.0	10.5	13.0	4.5	2.0	0.0	0.0
30% Na ⁺ -Bs/30% Ca ⁺⁺ -GaK/ 40% K ⁺ -Bs	17.2	8.3	8.1	6.2	4.2	2.7	4.0	0.0	0.7
44% Na ⁺ -NaS/12% K ⁺ -GaK/ 44% Mg ⁺⁺ -Bs	41.4	1.1	0.0	31.1	36.1	0.0	0.0	9.2	5.3
20% Na ⁺ -GaK/50% Ca ⁺⁺ -Bs/ 15% K ⁺ -GaK/15% Mg ⁺⁺ -Bs	16.8	1.4	3.4	1.8	2.9	10.5	10.5	3.2	0.0
Denver bentonite	106.0	0.6	0.0	1.5	0.9	75.1	83.5	28.9	21.5
Denver claystone	30.0	0.6	0.0	0.8	0.0	17.1	15.5	11.5	14.5
BALT silt	8.7	1.1	0.7	0.5	0.7	5.1	4.6	2.0	2.7
Hopi silt	17.0	0.1	1.0	0.8	2.1	15.2	13.9	0.9	0.0
Missouri clay	11.0	0.4	0.0	0.6	0.0	7.5	7.5	2.5	3.5

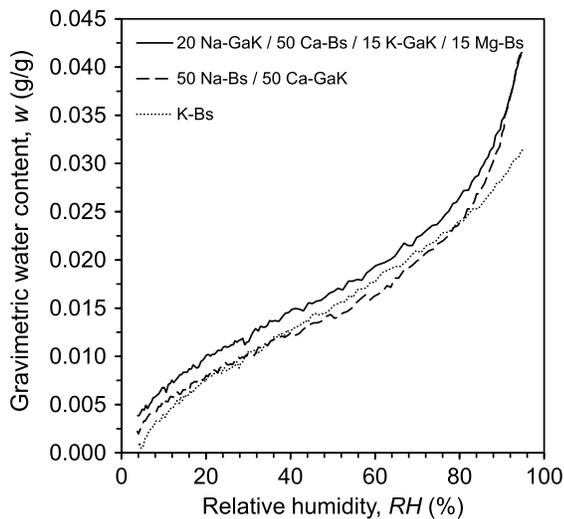


Fig. 5. Soil water desorption isotherms of three artificially mixed soil samples

whereas the w of the former soil sample is almost 1.3 times that of the latter sample. The reason is that soils with divalent cations adsorb more water as compared to soils with monovalent cations because the hydration enthalpies of Ca^{++} and Mg^{++} are much greater than those of Na^+ and K^+ .

To validate the proposed methodology for the quantification of ECs, the SWRC model in Eq. (7) is fitted to the measured soil water desorption isotherms in the range of $-370,000 \text{ kPa} < \psi < -320,000 \text{ kPa}$ using a least-squares regression to optimize the corresponding fitting parameters. The Solver add-in in Microsoft

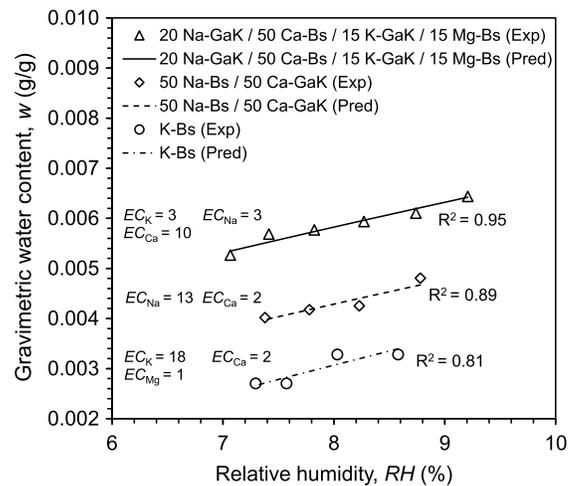


Fig. 6. EC_i values estimated by using SWRC for three artificially mixed soil samples

Excel is used to maximize an R^2 value for parameter optimization. The R^2 value is defined as

$$R^2 = 1 - \frac{\sum (w_i - w_i^m)^2}{\sum (\bar{w} - w_i)^2} \quad (8)$$

where w_i = measured gravimetric water content at increment i ; w_i^m = modeled gravimetric water content obtained from Eq. (7) at increment i ; and \bar{w} = mean of the measured w_i values. The obtained fitting parameters EC_K , EC_{Na} , EC_{Mg} , and EC_{Ca} for all soils are

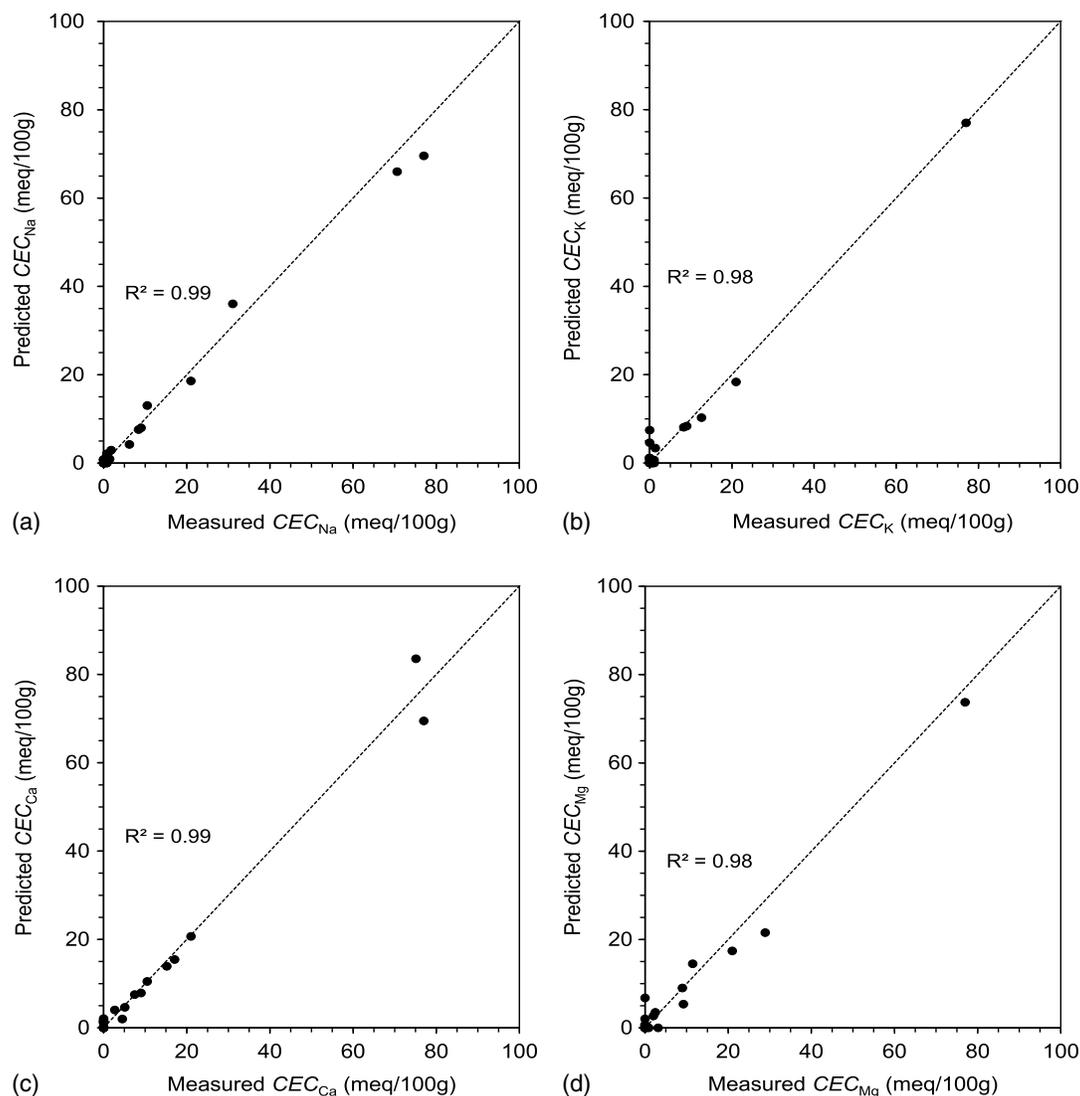


Fig. 7. Comparison between EC values of: (a) Na^+ ; (b) K^+ ; (c) Ca^{++} ; (d) Mg^{++} in all tested soils obtained by an independent experimental method and by using SWRC

listed in Table 3 as the predicted values. The measured exchangeable cation values using the AAS method for natural soils and the predetermined exchangeable cation values for cation-exchanged and artificially mixed soils are listed in Table 3 as the experimental values.

The performance of Eq. (7) in predicting the exchangeable cation values in a soil is assessed in Fig. 6. A comparison between the measured soil water sorption isotherms and the theoretical modeled water sorption isotherms of the soils used in Fig. 5 are represented in this figure. The compatibility between these measured and modeled isotherms results in close matches between the estimated exchangeable cation values and the experimental exchangeable cation values, as indicated in Table 3.

Comparing the experimental and predicted exchangeable cation values for each soil in Table 3 reveals that there is good agreement between these two sets of data for all soils; a difference of less than 15% of the soil's CEC. More specifically, Fig. 7 is plotted to illustrate the comparison between the experimental and predicted exchangeable cation values for each individual exchangeable cation in all tested soils. Good correlations with $R^2 \geq 0.98$ are found between the experimental and predicted exchangeable cation values for the four base cations.

Further Assessments

In general, the experimental and predicted exchangeable cation values in Fig. 7 are close to each other; the difference between predicted and experimental values is generally less than 12% of the soil's CEC. However, the difference between the predicted and experimental exchangeable cation values for a few soil samples (e.g., Mg^{++} -Bs) is higher. One of the sources of errors in the SWRC methodology is the limited number of measured soil water sorption points (4–6 points) in the range of $-370,000 \text{ kPa} < \psi < -320,000 \text{ kPa}$ to be fitted by the theoretical SWRC model. With the advancement of technology in relative humidity measurement in smaller ranges, the more the measured soil water sorption points in the range of $-370,000 \text{ kPa} < \psi < -320,000 \text{ kPa}$, the greater the accuracy of the methodology. Even with the current limitations, this methodology accurately estimates the dominant exchangeable cation that has the greatest effect on the soil's physical properties among all different types of exchangeable cations in the soil.

Several problems can be addressed as challenges in the application of chemical methods for the quantification of ECs. In soils with calcite and soluble salts, not all exchange sites will be occupied by the saturating cation when using ammonium acetate

(e.g., Sumner and Miller 1996). Furthermore, cations such as NH_4^+ and K^+ can be trapped in soil interlayers and may not be readily available for cation exchange during the saturation processes. This fixation of ions in some clay minerals (e.g., vermiculites and smectite) can occur, resulting in the underestimation of the exchangeable cation value (e.g., Bower 1950; Sumner and Miller 1996). The hydrolysis of water molecules that occurs during the process of rinsing soil with deionized water and the dissolution of soluble minerals and soluble salts in the soils containing them are other problems related to the usage of chemical methods for the determination of ECs (e.g., Sumner and Miller 1996; Laird and Fleming 2008). Most of the challenges do not exist when the SWRC-based methodology is used.

The close match between the experimental and predicted exchangeable cation values illustrates that the usage of SWRC at extremely low matric potential is a promising methodology for the quantification of ECs. With the aid of current technology utilizing the automated VSA, this new methodology is simple, quick (it lasts for less than a couple of hours), requires less sample handling, and does not result in the typical errors in the current instrumental methods due to chemical, ionization, matrix, emission, and spectral interferences. Therefore, the SWRC-based methodology can be actively used in the characterization of soils for geotechnical or soil science applications.

Discussion

One of the characteristic features of SWRC is hysteresis that exhibits for all water regimes (hydration, adsorbed, and capillary). The reason for hysteresis can be attributed to the change in rigidity of the water adsorption on the exchangeable ions between the platelets (Keren and Shainberg 1975), change in clay morphology undergoing different hydraulic paths (Woodruff and Revil 2011), and the dissimilar contribution of the forces between exchangeable cations and their surrounding interlayers during adsorption and desorption paths (Lu and Khorshidi 2015). It is suggested to use the drying path in inferring the exchangeable cation and surface properties of soils (e.g., Quirk 1955; Likos and Lu 2006; Lu and Khorshidi 2015). Thus, the measured desorption curves were used to quantify the exchangeable cations in soils.

At lower water contents, the water phase can exist as hydration and film water in micro, macro, and nano pores. Following the wetting path on an oven-dried sample, the hydration regime precedes the adsorbed film regime (Lu and Khorshidi 2015). Khorshidi and Lu (2016a) quantitatively showed that cation hydration occurs before surface hydration. The lowest matric potential for the initiation of the formation of the monolayer surface water can be as low as $-280,000$ kPa (Khorshidi and Lu 2016b). This value is still higher than the range of the matric potential values that is considered for the proposed method for the quantification of exchangeable cations ($-370,000$ kPa $< \psi < -320,000$ kPa). Therefore, water in soil is entirely bonded to the exchangeable cations in all pores, and no other forms of water coexist with this form of water. This water is indeed in equilibrium with the corresponding (global) matric potential in the entire sample because the sample is allowed to reach the global equilibrium while measuring the water sorption isotherms.

Despite the aforementioned advantages of the SWRC-based methodology over current techniques in quantification of exchangeable cations in soils, there are still some drawbacks that might restrict the application of this method. The proposed method is applicable only for soils with pH values greater than 6. Moreover, if the soil fabric is highly sensitive to drying or wetting and there are

dissoluble minerals, cations, and chemical compounds in the soil fabric, not only current techniques but also the suggested method can face certain difficulties for quantifying the exchangeable cations.

Twenty-three soil samples including nine different soils ranging from expansive to nonexpansive were used to validate the proposed methodology. Although this number of soil samples should be enough to draw conclusions, the application of this SWRC-based methodology for quantification of exchangeable cations of any other types of soils can be further investigated. Indeed, the application of the proposed methodology for all soils with any pH values can be studied if the accuracy of the water sorption measurement by VSA increases by the technological advancements.

Summary and Conclusions

Several methodologies have been proposed for the determination of soil properties [e.g., cation exchange capacity, specific surface area, and the expansibility coefficient] using the soil water retention curve at high suctions. Following the SWRC approach, a new methodology for the quantification of base exchangeable cations in soils with a pH > 6 is presented.

The new methodology is based on a theoretical relationship between the matric potential and cation hydration developed for homoionic soils. Using a thermodynamic equilibrium, this relationship is extended to capture the soil water retention in soils with multiple cation species. The new SWRC model at extremely high suctions illustrates the relationship between the matric potential and the amount and type of individual exchangeable cations in soil. Given the CEC of the soil, the exchangeable cation values for four base cations of a soil can be determined as fitting parameters by fitting the SWRC model to the measured soil water sorption isotherm.

A suite of artificially mixed homoionic soils and natural bulk soils are used for the validation of the methodology. The SWRC-based exchangeable cation values for these soils are comparable to the measured or predetermined exchangeable cation values. The main advantage of this new SWRC-based method, as compared to other existing methods, is its simplicity, which leads to fewer errors during the process of conducting the experiments. This method eliminates the common errors that usually occur during the extraction process and the analysis of exchangeable cations concentrations using different techniques with chemical, ionization, matrix, emission, and spectral interferences.

The new methodology provides a practical method for the use of SWRC in the fields of geotechnology, geoenvironmental, and soil science for the quantification of ECs in soils.

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