RESEARCH ARTICLE



Comparison of five methods to determine the cation exchange capacity of soil

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Abstract

Background: Cation exchange capacity (CEC) is a routinely measured soil fertility indicator. The standard NH_4OAc (pH 7) extraction procedure is time-consuming and overestimates actual CEC values of variable charge soils. Unbuffered extractants have been developed to measure the effective CEC (eCEC), but they differ in the type of index cation and extraction procedures.

Aim: This study was set up to systematically compare CEC values and exchangeable cation concentrations among different procedures and evaluate their practical aspects.

Methods: Five procedures were compared for (e)CEC, that is, silver thiourea (AgTU), cobalt(III) hexamine (Cohex), compulsive exchange (CE, i.e., $BaCl_2/MgSO_4$), $BaCl_2$ (sum of cations in single-extract), and NH_4OAc (pH 7). We applied these methods to a set of 25 samples of clay minerals, peat, or samples from soils with contrasting properties.

Results: The CEC values correlated well among methods ($R^2 = 0.92-0.98$). Median ratios of eCEC (AgTU as well as CE) to the corresponding eCEC (Cohex) value were 1.0, showing good agreement between eCEC methods, but NH₄OAc exceeded Cohex values (ratios up to 2.5 in acid soil). For BaCl₂-extracteable cations, the ratio ranged from low (<1.0) in acid soils (acid cations not measured) to high (>1.0) in high-pH soil (dissolution of carbonates). Multiple-extraction methods (CE and NH₄OAc) yielded more variation and increased labor.

Conclusions: The chemical properties of the sample cause method-specific interactions with chemical components of extractants. We found the Cohex method with ICP-MS detection to be the most efficient and cost-effective technique for determination of eCEC and exchangeable cations.

KEYWORDS base cations, chemical analysis, nutrient extraction, soil fertility

1 | INTRODUCTION

Cation exchange capacity (CEC) is an important index of soil nutrient availability. The cations dominating the soil exchange complex also influence soil structural stability and pH buffering capacity (Brady & Weil, 2017; Huang et al., 2012). Several chemical methods have been developed to measure soil CEC using extractants composed of simple salt solutions (Karam, 1993). The first method uses a cation with high selectivity to bind on the exchange complex; the complex is saturated with that cation, and the CEC is determined by calculating the loss of that cation from solution. That cation with high selectivity is further termed the index cation. The second method is based on displacing the

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes. © 2023 The Authors. *Journal of Plant Nutrition and Soil Science* published by Wiley-VCH GmbH. exchanger cations with a second exchanger and measuring the quantity of desorbed cations. Ammonium acetate (NH₄OAc) buffered to pH 7 is a standard soil CEC measurement method (Schollenberger & Simon, 1945), which is also used for taxonomic classification of soils (Sumner & Miller, 1996). In this procedure, NH_4^+ ions displace cations from the soil exchange complex and are desorbed by a second exchange with K^+ ions. The resulting concentration of NH_4^+ in the leachate is then measured by colorimetry or digestion (Pleysier & Cremers, 1975; Sumner & Miller, 1996). However, this method may overestimate the CEC of variable charge soils, due to pH dependency of the exchange sites and higher ionic strength of the extractant relative to field conditions (Ciesielski & Sterckeman, 1997; Gillman et al., 1983; Jaremko & Kalembasa, 2014). Extraction with buffered NH₄AOc may also underestimate the CEC of tropical peats (Reeza et al., 2021) or overestimate the CEC of calcareous soils (Ketterings et al., 2014). However, Dohrmann (2006a) reported underestimated CEC values due to competition of Ca²⁺ cations, liberated by calcite dissolution during extensive washing, with NH₄⁺ for exchange sites. Several methods have been developed to determine the effective CEC (eCEC), which is measured at soil pH and ionic strengths more closely representing in situ conditions (Pleysier & Juo, 1980). These extractants require an index cation with high selectivity over soil exchangeable cations to effectively displace them from the soil exchange complex, even at lower ionic strength of the index cation.

The NH₄OAc method requires different analytical methods and multiple extractions to determine NH₄⁺ and exchangeable cations. In contrast, a one-step extraction and one-step (simultaneous) detection of exchangeable cations and CEC may be achieved by coupling unbuffered, that is, eCEC methods to analytical instruments for multielemental analysis. The inductively coupled plasma (ICP) instruments offer such approaches, except that they cannot detect the protonrelated exchangeable acidity. The ICP coupled to mass spectrometry (ICP-MS) has higher accuracy and a greater range of detection limits compared with the optical emission spectroscopy (ICP-OES; Harris, 2010); however, matrix effects may be stronger on ICP-MS than on ICP-OES (Chen, 1995). The different CEC protocols differ in the type and concentration of the exchanging cation, the soil:solution ratio, single or multiple extractions, the contact time, phase separation, and analytical detection methods. A low soil:solution ratio may result in flocculation of the soil and lower quantities of cations extracted, while a large ratio dilutes the index cation solution, decreasing the effectivity of exchange and thus lowering the measured CEC (Ouhadi & Deiranlou, 2011). Measured CEC values may also be affected by soil mineralogy (Brady & Weil, 2017). For example, the exchange of cations slows down by a partial collapse of the interlayer space due to the fixation of monovalent index cations (e.g., present in ammoniumbased extractants) in hexagonal cavities of the silicate layer. This explains why smectites and vermiculites as well as micaceous minerals such as illite exchange cations less readily (Dohrmann, 2006b; McBride, 1994).

Various methods have been developed to measure eCEC. The compulsive exchange or $BaCl_2$, MgSO₄ procedure (Gillman, 1979) is based on the saturation of soil with Ba^{2+} , followed by exchange with Mg²⁺ using a MgSO₄ solution. This reaction is driven (i.e., compulsive) by the formation of BaSO₄ precipitate. Soil CEC may also be determined by summing cations displaced by a single extraction with BaCl₂ (Hendershot & Duquette, 1986). However, the dissolution of soluble salts such as gypsum, calcite, and dolomite by BaCl₂ solution may release excess Ca or Mg into the leachate (Dohrmann, 2006b), leading to inflated CEC values. Silver thiourea Ag[SC(NH₂)_n]⁺ (AgTU; Chhabra et al., 1975) and cobalt(III) hexamine [Co[NH₃]₆]³⁺ (Cohex; Ciesielski & Sterckeman, 1997; Ciesielski et al., 1997) are single-extraction eCEC determination methods based on the concept of measuring the loss of index cation in the extractant. The Cohex method is less sensitive to the effects of dissolution of carbonates compared to the compulsive exchange method (Jaremko & Kalembasa, 2014). It has been suggested that precipitation of BaCO3 during exchange with BaCl2 followed by dissolution of BaCO3 during exchange with MgCl2 solution affects CEC values (Dohrmann, 2006b). The AgTU has been implemented in the European risk assessment of toxic metals in soil (Smolders et al., 2009), but neither AgTU nor Cohex methods are widely used, although the latter is formally adopted as an ISO-certified reference method (International Organization for Standardization, 2018).

There are only few studies that systematically compared CEC determination methods across a range of soil and soil constituents. Most of these comparisons are limited to soils of limited geographic distribution. For example, three methods have been compared on 48 soil samples (Ciesielski & Sterckeman, 1997), but all samples originated from France; hence, no highly weathered soils were included. The implications of operational improvements using ICP-MS as opposed to ICP-OES should also be considered with greater attention to allow true comparisons of cost and efficiency. The aim of this study was to compare the accuracy and precision, practical efficiency, and costeffectivity of five CEC methods across soil samples and clay minerals. The five methods are Cohex, AgTU, compulsive exchange, BaCl₂ singleextract, and NH₄OAc batch methods. Results obtained by ICP-OES and ICP-MS techniques, as well as base saturation yielded by the different methods, were compared.

2 | MATERIALS AND METHODS

2.1 Sample collection and preparation

Soil samples, clay deposits, one reference clay mineral, and one peat sample (n = 25) were sourced from the soil collection of the Division of Soil and Water Management, Katholieke Universiteit Leuven. Two internal laboratory reference soils were included for quality control purposes. The sample selection strategy was designed to maximize variation of the soil physiochemical properties based on known soil characteristics. Particle size was determined using an LS 13 320 Laser Diffraction Particle Size Analyser by Beckman Coulter. The texture class of each sample was determined according to the United States Department of Agriculture (USDA) classification system (National Employee Development Staff Soil Conservation Service, 1987) based on proportions of sand (0.63–2 mm), silt (0.002–0.63 mm), and clay

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TABLE 1 (Effective) cation exchange capacity ((e)CEC) values obtained by various methods for a diverse set of samples (n = 25). Cohex, AgTU and BaCl₂ (ICP-MS), compulsive exchange (ICP-OES), and NH₄OAc (Continuous Flow Analyzer) are results shown. Standard deviation (n = 2) in brackets where applicable.

						cmol _c kg ⁻¹				
Sample No.	pН	Organic carbon (%)	Clay (%)	Sample type ^a	Texture	Cohex	AgTU	CE	BaCl ₂	NH ₄ OAc (pH 7.0)
1	2.9	<0.1	73	Clay deposit	Clay	71 (7.1)	30 (0.2)	b	49 (2.1)	b
2	3.1	3.7	3.0	Topsoil	Loam	4.6 (0.4)	3.4 (0.2)	4.9 (0.4)	0.3 (0.1)	b
3	3.1	3.3	3.0	Topsoil	Sand	b	2.9 (0.1)	5.2 (0.1)	0.3 (0.1)	12 (0.7)
4	3.4	0.3	9.0	Subsoil	Loam	5.4 (0.2)	5.7 (0.1)	b	1.0 (0.1)	14 (0.1)
5	3.7	2.1	2.0	Topsoil	Sand	2.4	2.0 (0.1)	2.1 (0.3)	0.3 (0.1)	5.8 (0.5)
6	3.8	33	34	Topsoil	Loam	68 (0.9)	52	b	79 (6.6)	b
7	4.6	<0.1	30	Clay deposit	Clay	4.4 (0.3)	5.0 (0.1)	b	5.2 (0.1)	9.7
8	4.7	0.6	26	Topsoil	Loam	6.0 (0.3)	6.0 (0.1)	b	3.7 (0.1)	b
9	5.4	3.5	57	Topsoil	Clay	36 (2.3)	37 (0.2)	34 (0.6)	36 (0.9)	31
10	5.6	1.0	14	Topsoil	Loam	8.1 (0.3)	8.6 (0.1)	8.2 (0.3)	9.1 (0.1)	11 (0.6)
11	5.8	0.9	32	Topsoil	Loam	25 (2.0)	23 (0.4)	23 (0.3)	24 (1.5)	23 (1.0)
12	6.1	36	<0.1	Cocopeat	NA	58 (0.6)	56 (0.8)	b	110 (11)	65 (0.8)
13	6.2	1.0	10	Topsoil	Loam	6.9 (0.5)	7.1 (0.2)	7.2 (0.1)	8.5 (0.3)	9.6
14	6.2	6.7	4.0	Topsoil	Loam	11 (0.8)	8.8 (0.3)	11 (0.1)	12 (0.7)	11
15	6.3	15	44	Topsoil	Clay	80 (0.1)	80 (0.2)	89 (1.6)	98 (3.1)	68 (3.9)
16	6.3	0.9	10	Topsoil	Loam	7.8 (0.9)	8.5 (0.1)	8.7 (0.3)	9.3	11 (0.8)
17	6.6	1.5	2.0	Topsoil	Sand	8.1 (1.1)	6.2 (0.1)	7.1 (0.4)	9.8 (0.2)	7.9
18	6.9	0.4	12	Subsoil	Loam	8.1 (0.1)	11 (0.1)	8.7 (0.1)	12 (0.3)	b
19	6.9	3.6	4.0	Topsoil	Sand	13 (0.6)	8.0	11 (0.1)	17 (0.1)	b
20	7.2	3.1	14	Topsoil	Loam	14 (0.2)	13 (0.4)	14 (0.1)	18 (0.4)	11 (0.8)
21	7.2	1.4	49	Topsoil	Clay	19 (0.5)	20 (0.4)	23 (0.8)	25 (0.5)	39 (3.8)
22	7.3	2.9	39	Clay deposit	Clay	33	37 (0.5)	45 (1.2)	43 (0.9)	35
23	7.3	1.8	32	Topsoil	Loam	30 (1.2)	25 (0.1)	29	33 (1.6)	35 (0.6)
24	7.5	<0.1	100	Vermiculite	Clay	130 (2.7)	74 (4.2)	110 (1.4)	150 (0.8)	b
25	7.5	0.6	4.5	Topsoil	Sand	5.0 (0.1)	5.1 (0.1)	5.3 (0.1)	8.6 (0.1)	3.9 (0.5)

Abbreviation: CE, compulsive exchange.

^aTopsoils <20 cm depth; subsoils >20 cm depth.

^bCV >15%; result deemed unreliable.

(<0.002 mm). Carbon (C) and nitrogen (N) contents were determined by oxidative digestion followed by carbon dioxide (CO₂) and nitrogen (N₂) analysis by gas chromatography. Soil pH was measured using a 1:5 soil:solution ratio in a 0.01 M CaCl₂ solution matrix (10 mL). The samples were prepared for CEC analysis according to the following standard protocol. Soils and clays were sieved using 2 mm and 1 mm diameter sieve, respectively, crushed with mortar and pestle, and dried at 105°C. Heating may cause a partially reversible collapse of the interlayer of minerals such as smectites and a consequent decrease in the CEC (Kaufhold & Dohrmann, 2010; Phillips et al., 1986). However, this effect is minimal for soils dried at temperatures below 200°C (Ouhadi et al., 2010). Soil properties of individual samples and (e)CEC values obtained by different methods are shown in Table 1.

2.2 | (e)CEC methods

All chemicals were of reagent grade and purchased from AppliChem $(Co[NH_3]_6Cl_3)$, VWR $(AgNO_3)$, ChemLab $(MgSO_4, KCl, ethanol)$, Sigma-Aldrich $(CS[NH_2]_2)$, and Janssen $(BaCl_2 \text{ and } NH_4OAc)$. Soil CEC measurements were performed in duplicate according to reference methods with operational details listed in Table 2. Sample masses were selected based on the estimated CEC, such that the expected loss in concentration of the index cation fell within an appropriate range (15%-50%) to optimize measurement accuracy while maintaining the displacing power of the index cation (Chhabra et al., 1975; Ouhadi & Deiranlou, 2011). For all methods, the sample was agitated for 2 h with the extractant in a 30 mL plastic centrifuge tube on an end-overend shaker. The compulsive exchange procedure was an exception,

TABLE 2 Standard methods of (effective) cation exchange capacity ((e)CEC) measurement performed in this study.

(e)CEC method	1			Solid-liquid				
Full name	Abbreviation	Result	Extracting solution	ratio min-max (g: mL)	Extraction time (min)	Phase separation	Quantitative analysis	Reference
Ammonium acetate (batch)	NH ₄ OAc	CEC	NH ₄ OAc (1 M, pH 7)/KCl (1 M)	0.02–0.4	120	Centrifugation for 15 min at 1377 RCF	Colorimetry (Continuous Flow Analyzer)	Sumner and Miller (1996)
Compulsive exchange	CE	eCEC	BaCl ₂ (0.1 M)/MgSO ₄ (0.02 M)	0.02-0.17	196		ICP-MS/ICP- OES	Houba et al. (1989)
BaCl ₂ (single extraction)	BaCl ₂		BaCl ₂ (0.1 M)	0.03-0.25	120			Hendershot and Duquette (1986)
Silver thiourea	AgTU		Ag (0.01 M)/ TU (0.1 M)	<0.01-0.17				Chhabra et al. (1975).
Cobalt(III) hexamine	Cohex		Co[NH ₃] ₆]Cl ₃ (0.0166 M)	0.02-0.20				Ciesielski and Sterckeman (1997)

consisting of three 1-h shaking events, as well as shaking overnight. Phase separation of soil extracts was achieved by centrifugation at 1377 relative centrifugal field (RCF) for 15 min for all extraction methods. All leachates were analyzed using both ICP-OES (Thermo Scientific iCAP 7400 Duo) and ICP-MS (Agilent 7700x). For CEC determination with the NH₄OAc method, NH₄-N was measured with a 5100 SANplus Segmented Flow Analyzer (Skalar). For methods involving multiple extractions, the extract volumes used for calculating dilution factors were corrected for the volume of entrained solution on a massbasis, by recording tube weights before addition of the final extractant dose.

2.2.1 | Method 1: NH₄OAc at pH 7, batch method

The NH₄OAc procedure was performed by saturating soil samples (0.5–10 g) with 25 mL NH₄OAc (1 M, pH 7) solution, prepared as described by Sumner and Miller (1996). After shaking and subsequent centrifugation, the supernatant was collected for analysis of exchangeable cations. The residues were then washed with 30 mL ethanol (97%) and centrifuged, and the supernatant was discarded. This was repeated to total three washes. After discarding the last ethanol, the tubes with soil were weighed to calculate entrained ethanol mass in the soil, and samples were saturated with 30 mL KCl (1 M). The samples were shaken and subsequently centrifuged as previously described. The supernatant was analyzed for NH₄-N. The CEC values were calculated from the measured molar concentration of NH₄-N in the supernatant after correction for the volume of entrained ethanol.

2.2.2 | Method 2: Compulsive exchange (MgSO₄/BaCl₂) at soil pH

The compulsive exchange procedure was performed by saturating samples (0.5–5 g) with 30 mL BaCl₂ (0.1 M) solution, described by Houba et al. (1989). After shaking and subsequent centrifugation, the

supernatant was discarded. This was repeated for a total of three extractions. The samples were then saturated with 30 mL $BaCl_2$ (0.0025 M) and subsequently agitated overnight on an end-over-end shaker. After discarding the supernatant and recording gross tube masses, the samples were saturated with 30 mL $MgSO_4$ (0.02 M) solution. After shaking and subsequent centrifugation, the extracts were collected for analysis of Mg. The eCEC values were calculated from the loss of Mg in solution after correction for the volume of entrained solution.

2.2.3 | Method 3: BaCl₂ single-extract at soil pH

The BaCl₂ single-extract method was performed by saturating soil samples (0.5-5 g) with 20 mL of BaCl₂ (0.1 M), prepared as described by Hendershot and Duquette (1986). After shaking and subsequent centrifugation, the extracts were collected for analysis of exchangeable cations. The eCEC values were approximated as the sum of cations in the sample extracts as follows:

CEC (cmol_c kg⁻¹) =
$$\sum$$
 [Ca], [Mg], [K](cmol_c kg⁻¹). (1)

2.2.4 | Method 4: Silver thiourea (AgTU) at soil pH

The AgTU procedure was performed by saturating the soil samples (0.1-5 g) with 30 mL Ag (0.01 M)/TU (0.1 M) solution. The AgTU solution was prepared as described by Chhabra et al. (1975) with a modified order of chemical addition to prevent flocculation of the solution as follows. An aliquot of MQ water (500 mL) was added to 1 L thiourea (0.2 M) and homogenized, followed by slow addition of 500 mL AgNO₃ (0.04 M) under strong stirring. The soil suspensions were shaken end-over-end for 2 h and centrifuged. The extracts were then collected for analysis of exchangeable cations and also Ag. The eCEC values were calculated from the loss of Ag in solution.

2.2.5 | Method 5: Cobalt(III) hexamine chloride method at soil pH (Cohex)

The Cohex extraction method was performed by saturating samples (0.5-5 g) with 25 mL Co[NH₃]₆]Cl₃ (0.0166 M), prepared as described by Ciesielski et al. (1997). After shaking and subsequent centrifugation, the extracts were collected for analysis of exchangeable cations and also Co. The eCEC values were calculated from the loss of Co in the solution.

3 | RESULTS

3.1 Soil and clay properties

Soil samples were collected worldwide, representing young to highly weathered soils, classified between Cambisols and Ferralsols (Table S1). The soil properties hence ranged widely (Table 1). The pH (0.01 M CaCl₂) of the soil samples ranged 2.9–7.5, with a median value of 6.2. The organic carbon percentage ranged from 0.3 to 33, with a median value of 1.6. The clay content varied from 2.0 to 57, with a median value of 11. The Boom formation clay sample (Sample 1) consisted primarily of smectite (33%), quartz (32%), randomly interstratified smectite-illite (17%) and smaller proportions of kaolinite, K-feldspar and plagiosclase. The Westerwald formation clay sample (Sample 7) consisted primarily of quartz (69%), kaolinite (17%), and smaller quantities of illite, smectite, and K-feldspar. Sample 24 was reference vermiculite clay.

3.2 Operational details in (e)CEC measurements

Possible operational details underlying differences in CEC measurements were assessed by performing preliminary experiments, presented in the Supporting Information (Tables S5-S7 in "Method variation experiments"). With the Cohex method, it was found that shaking time (0.5-16 h) does not have a significant effect on CEC measured. The soil:solution ratio $(0.05-0.1 \text{ g mL}^{-1})$ did not significantly affect ICP-OES measurements; however, changing soil:solution ratios caused slight measurement discrepancies with ICP-MS. This may be due to the sensitivity of the ICP-MS instrument to carry-over effects of extracts (Al-Hakkani, 2019). With the NH₄OAc method, it was found that increasing the number of extractions with the saturating cation as well as the number of extractions with the second exchanger cation increased the CEC measured in one reference soil; however, the effect was not clear for the other soil. The contrasting results may be due to loss of soil during the ethanol washing procedure. Stock solutions of different concentrations that were diluted to the same theoretical final cation concentration yielded similar measured cation concentrations. The measured concentrations differed less than 10% from the theoretical stock solution concentrations. These results were true for both ICP-OES and ICP-MS measurements. Thus, spectroscopic measurements of exchangeable cation concentration in 10 x diluted BaCl₂ (0.1 M) soil extracts were not influenced by matrix effects.

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3.3 (e)CEC values and precision of methods

The median coefficient of variation (CV%) among analytical replicates for (e)CEC measurements determined by ICP-MS was lower than that determined by ICP-OES for most extraction methods, as shown in Table S2. This indicates that ICP-MS is a more accurate method of analysis for CEC determination, as agreed in analytical chemistry literature (Wilschefski & Baxter, 2019). The compulsive exchange method was the only exception. The CV% decreased with increasing CEC (Figure S1). This shows that lower CEC-values were less accurately determined, compared to higher CEC-values, due to the difficulty of detecting smaller changes in concentration of the index cation in the leachate.

The compulsive exchange and NH₄OAc methods presented practical difficulties, such as loss of soil colloids while decanting supernatant, or insufficient mixing of heavily textured (clay) samples resulting in lower soil-solution contact during the final exchange. The flocculation of soil samples by ethanol using the NH₄OAc method prevented loss of soil during decantation more effectively, compared to multiple BaCl₂ exchanges with the compulsive exchange method. It is recommended that clays should be mixed with the extractant using a vortex instrument or end-over-end shaker to ensure sufficient soil-solution contact with the compulsive exchange method. Samples which did not produce reliable results (CV% > 15%) were eliminated. The number of samples eliminated from the different methods was 1 (Cohex, highly dispersive sand), 8 (CE, dispersive loams and cocopeat, and clay samples), and 7 (NH₄OAc, dispersive loams and clay samples).

The CEC values in Table 1 are given as means of duplicate analysis, and all values with CV > 15% are not reported. The values refer to ICP-MS detected ones except for the CE method. The mean of eCEC and CEC among all methods could be given as a crude index of the CEC of the soils, and this ranged from 2.5 to 120 cmol_c kg⁻¹, mean 26 cmol_c kg⁻¹. This average (e)CEC of the samples generally increased with increasing clay content (Pearson correlation coefficient r = 0.71), increasing pH (r = 0.19), and increasing organic carbon percentage (r = 0.50), corroborating common knowledge.

3.4 (e)CEC values obtained by different methods

The CEC values of the five methods were correlated to each other in all pairwise combinations; the coefficients of determination were always greater than 0.90 (Table S3). The slopes for conversions of eCEC between the compulsive exchange and Cohex methods did not differ significantly from 1.0. The slopes for conversions between AgTU or Cohex and NH₄OAc methods also did not differ significantly from 1.0. Soil samples with high clay content tended to show greater discrepancies between CE (eCEC) and Cohex (eCEC) values (Table 1). The ratio of the (e)CEC to the corresponding eCEC (Cohex) value was calculated and reported in Table 3. The ratios for AgTU and CE were closer to 1.0 than those of NH₄OAc and BaCl₂, which ranged up to a value of 2.5. Plots of (e)CEC values of various methods versus the eCEC (Cohex) are

TABLE 3Ratio of (effective) cation exchange capacity ((e)CEC)values determined by AgTU, BaCl2 (ICP-MS), compulsive exchange(ICP-OES), and NH4OAc (Continuous Flow Analyzer) methods versusthe Cohex method (ICP-MS).

	AgTU	CE	BaCl ₂	NH₄OAc
(e)CEC/eCEC Cohex minimum-maximum;	0.4–1.4 1.0	0.9–1.4 1.0	0.1–1.8 1.2	0.8–2.5 1.1
median				

Abbreviation: eCEC, effective cation exchange capacity.

shown in Figure 1. The buffered CEC method (NH₄OAc) yielded larger values than the Cohex (eCEC) methods for soils with lower pH as well as the cocopeat sample.

The ratios of (e)CEC measured by different methods relative to eCEC (Cohex) were plotted against sample pH in Figure 2 to identify factors explaining differences among methods. The ratio of eCEC (compulsive exchange) and eCEC (AgTU) to eCEC (Cohex) remains relatively

constant across the pH range, whereas clear trends are found for other methods. The ratio of CEC (NH₄OAc) to eCEC (Cohex) decreases with increasing sample pH (r = -0.71; Figure 2).

The ratio of eCEC (BaCl₂) to eCEC (Cohex) increases with increasing sample pH (r = 0.76), and this trend is slightly more prominent when excluding clays and cocopeat (r = 0.85; Figure 2). Lower eCEC (BaCl₂)/eCEC (Cohex) ratios were obtained for low-pH soils, and the reverse case was observed for high-pH soils. The eCEC (AgTU) relative to eCEC (Cohex) ratio slightly decreases with increasing eCEC (Figure 1).

3.5 | Base saturation values obtained by different methods

The percentage base saturation (%BS, i.e., sum of equivalent charges of Ca, Mg, Na, and K relative to the CEC) of individual soil samples according to different extraction methods is shown in Table 4. The median



FIGURE 1 Cation exchange capacity (CEC) (A: NH_4OAc , n = 19), effective CEC (eCEC) (B: AgTU, n = 24), eCEC (C: $BaCl_2$, n = 24), and eCEC (D: compulsive exchange, n = 19) versus eCEC (Cohex). Solid reference line (y = x), simple linear equation with intercept = 0, and associated correlation coefficient (R^2) values are shown. pH (0.01 M CaCl₂) ranges of individual samples are indicated by different symbols.



FIGURE 2 Ratio of cation exchange capacity (CEC) (A: NH₄OAc, n = 19), effective CEC (eCEC) (B: AgTU, n = 24), eCEC (C: BaCl₂, n = 24), and eCEC (D: compulsive exchange, n = 19) relative to eCEC (Cohex) versus sample pH (0.01 M CaCl₂). Pearson coefficient indicating correlation between ratio value (Y) and pH (X) shown for all samples (r) as well as soils only (r_{soils}). Solid reference line (y = 1) is shown. Texture class of individual samples is indicated by different symbols, where "clay" refers to texture class of topsoils, as opposed to reference clays ("pure clay") or clay deposits (cf. Table 1).

%BS values of the Cohex and ${\rm BaCI}_2$ methods were greater than 100%, while that of the AgTU method was smaller.

accounted for in the cost analysis of Table S4. Single-extraction methods were less time-consuming to perform than multiple-extraction methods, as shown by the procedural durations.

3.6 Cost analysis and efficiency

Both CEC and individual cation concentrations could be measured in single batches with ICP-MS. However, two sets of samples with different dilution factors were required for ICP-OES measurements, as lower dilution factors were necessary for analyses of cations compared to those for optimal detection of trace elements (Ba, Co, and Ag index cations). Duplicate dilutions required for ICP-OES measurements were

4 | DISCUSSION

4.1 | (e)CEC values obtained by different methods

Strong correlations among extraction methods (Table S3) support findings of other studies (Bascomb, 1964; Chhabra et al., 1975; van der Ent et al., 2019; Madeira et al., 2003; Purnamasari et al., 2021;



TABLE 4 Percentage base saturation (%BS) obtained by AgTU, BaCl₂ (ICP-MS), NH₄OAc (Continuous Flow Analyzer), and Cohex (ICP-MS) methods for a diverse set of soils (clay and cocopeat samples excluded); n = 24. Standard deviation (n = 2) of sum of cations in brackets where applicable.

Sample No.	pН	Cohex	AgTU	BaCl ₂ ^a	NH ₄ OAc
2	3.1	5.0 (0.1)	11 (0.1)	5.6 (0.1)	b
3	3.1	b	14 (0.1)	5.4 (0.1)	1.1 (0.1)
4	3.4	13 (0.1)	10 (0.1)	b	5.6 (0.1)
5	3.7	12	12 (0.1)	16 (0.1)	4.1 (0.1)
6	3.8	130 (2.5)	130 (7.3)	b	b
7	4.6	140 (0.3)	100 (0.1)	b	55 (1.4)
8	4.7	71 (0.1)	49 (0.1)	b	b
9	5.4	96 (1.2)	75 (0.5)	110 (0.9)	99 (4.2)
10	5.6	110 (0.5)	78 (0.1)	110 (0.1)	76 (0.1)
11	5.8	95 (0.4)	77 (0.4)	110 (1.5)	99 (0.3)
12	6.1	160 (1.7)	160 (1.4)	b	190 (9.4)
13	6.2	120 (0.6)	85 (0.1)	120 (0.3)	68 (1.4)
14	6.2	110 (0.2)	100 (0.1)	120 (0.7)	71 (5.0)
15	6.3	100 (4.0)	78 (1.3)	110 (3.1)	110 (2.2)
16	6.3	120 (0.7)	79 (0.1)	110	81 (0.1)
17	6.6	100 (0.4)	110 (0.2)	140 (0.2)	89 (3.4)
18	6.9	200 (0.1)	98 (0.1)	140 (0.3)	b
19	6.9	130 (0.1)	130	160 (0.1)	b
20	7.2	130 (0.7)	100 (0.1)	130 (0.4)	270 (0.3)
21	7.2	120 (1.3)	85 (0.1)	110 (0.5)	120 (1.0)
23	7.3	110 (0.8)	93 (0.5)	110 (1.6)	180 (1.7)
25	7.5	190 (0.1)	130 (0.1)	160 (0.1)	340 (0.1)
Minimum- maximum; median	3.1–7.5; 6.2	5.0–210; 120	10–160; 90	4.5–150; 110	1.1–340 100

^a%BS calculated as [100% \times sum of cations (BaCl₂ single-extract)/eCEC (Ba/Mg)].

^bCV >15%; result deemed unreliable.

Zgorelec et al., 2019). A nearly one-to-one relationship between CE (eCEC) and Cohex (eCEC) values agrees with the works of Ciesielski and Sterckeman (1997) and Jaremko and Kalembasa (2014). Large differences between eCEC (CE) and eCEC (Cohex) for heavily textured samples is likely a result of lack of soil-solution contact with the MgSO₄ solution. The median ratios of eCEC to corresponding Cohex (eCEC) values for AgTU (1.0) and CE (1.0) show good agreement among the three eCEC methods (Table 3). However, NH₄OAc exceeded the Cohex values (median ratio 1.1, up to 2.5 in acid soil), and that ratio ranged unacceptably wide (ratio 0.1-1.8) for the BaCl₂-extracteable cations.

The larger CEC (NH₄OAc) values of acidic soils and high-organic matter cocopeat compared to Cohex (eCEC) values (Figure 1) show that buffering by the NH₄OAc extract (pH 7) clearly raises the CEC of soils with pH-dependent sorption sites. This has been shown before in

comparisons between CEC (NH₄OAc) and either AgTU (Gillman et al., 1983) or BaCl₂ (Horn et al., 1982; Madeira et al., 2003; Mustapha et al., 2020; Purnamasari et al., 2021; Zgorelec et al., 2019). The negative correlation between the ratio of CEC (NH₄OAc) to eCEC (Cohex) and sample pH (Figure 2) confirms the effect of pH in samples with variable charge exchange sites.

The effect of sample pH on the ratio of BaCl₂ to Cohex eCEC values (Figure 2) may be explained by cations other than exchangeable Ca, Mg, Na, and Ca in BaCl₂ extract. The summing of exchangeable cations does not include exchangeable acidity (Al³⁺ and H⁺), although these ions contribute to the eCEC of low-pH soils (Hendershot & Duquette, 1986). Zgorelec et al. (2019) also found that Al, H, Mn, and Fe contributed to CEC of acid soils. High-pH soils, on the other hand, may contain carbonates which become soluble in Ba solutions (Dohrmann, 2006b; Horn et al., 1982; Jaremko & Kalembasa, 2014; Mustapha et al., 2020; Zgorelec et al., 2019). The higher sum of cations (BaCl₂) compared to eCEC (Cohex) of the cocopeat sample (see Table 1) is explained by the large quantity of soluble Na salts (i.e., not present on the exchange complex) in this material.

The ratio of AgTU versus Cohex (eCEC) values decreases with increasing eCEC as shown in Figure 1. This may be due to the lower concentration of Ag versus Co index cation at lower soil:solution ratio (Ouhadi & Deiranlou, 2011), and precipitation of Ag_2S at pH > 8 (Chhabra et al., 1975) may have precluded reliable eCEC measurements in several alkaline soils. However, a lack of clear trends does not allow full support of these hypotheses.

4.2 | The CEC values of clay minerals and clay deposits

The mean (e)CEC of the Boom Clay and Westerwald formation was 50 and 6.1 cmol_c kg⁻¹, respectively, reflecting their contrasting mineralogical compositions. The CEC of Boom formation clay is strongly correlated to its bulk-smectite and illite content, with average CEC contributions of smectite and illite components estimated to be 80 and 30 cmol_c kg⁻¹, respectively (Frederickx et al., 2018). The CEC of kaolinite clays, dominating Westerwald formation clay, range from 3 to 10 cmol_c kg⁻¹ (Brady & Weil, 2017). The mean (e)CEC value of pure vermiculite clay is 116 cmol_c kg⁻¹, falling within the expected range (Brady & Weil, 2017).

4.3 | Base saturation values obtained by different methods

The tendency of high-pH samples to exhibit %BS > 100% across methods (Table 4) may be a result of cation summation dependence on Ca concentration, which is usually the largest proportional contributor to the soil exchange complex (Brady & Weil, 2017; Zgorelec et al., 2019). The dissolution of gypsum and calcium carbonate from high-pH soils during extraction may have released excess Ca (Dohrmann, 2006b). Lower %BS of low-pH soils is logically related to exchangeable acidity.

4.4 | Cost analysis and efficiency

The higher cost of ICP-MS was compensated for by cost of duplicate ICP-OES measurements (Table S4). Thus, ICP-MS is a more efficient analysis technique compared to ICP-OES. The disadvantage of eCEC methods is that they required an a priori estimate of the eCEC for setting the optimal soil weight for the analysis, thereby increasing labor time if eCEC is completely unknown. The Cohex method was found to be the most convenient method for routine eCEC measurements, as it may be performed in a single extraction and needs no preparation of the index cation reagent, as is the case for the AgTU for which storage and Ag reduction issues occur Ciesielski & Sterckeman (1997). Zachara et al. (2002) also recommended the Cohex method for practical reasons.

5 CONCLUSION

Evaluation of soil fertility requires a contextual interpretation of soil CEC test results. This is the first report of a comparison of CEC values obtained by the buffered CEC (NH_4OAC), $BaCl_2$ (single extraction), compulsive exchange, AgTU, and Cohex methods for a single soil sample set. We found that AgTU, compulsive exchange, and Cohex methods yielded similar eCEC values. Buffered CEC (NH₄OAc) and sum of cations (BaCl₂ single-extract) differed from eCEC (Cohex) values for soils with variable charge properties and soluble salt content. Multipleextraction posed practical difficulties for determination of (e)CEC of highly dispersive or heavily textured soils. Our study confirmed the contribution of acidic cations to (e)CEC by the observation of lower %BS with low-pH soils for all extraction methods. Inflated Ca concentration predictions due to calcium carbonate dissolution in high-pH soils may have caused overestimation of %BS values. We found Cohex extraction coupled to ICP-MS analysis to be the most efficient and cost-effective method of simultaneous soil CEC and exchangeable base cation content measurement.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

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