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Estimating cation exchange capacity and clay content from agricultural soil testing data

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Clay content and the ability to reversibly retain cations affect many essential chemical and physical properties of soil, such as pH buffering and carbon sequestration. Cation exchange capacity (CEC) and base saturation are also commonly used as criteria in soil classification. However, determination of CEC and particle-size distribution is laborious and not included in routine soil testing. In this study, pedotransfer functions including soil test cations (STCat; $Ca^{2+} + Mg^{2+} + K^*$), pH and soil organic carbon (SOC, %) as explanatory variables were developed for estimating CEC, titratable acidity (TA; H⁺ + Al³⁺) and clay content (clay, %). In addition, reference values for potential CEC and its components were determined for Finnish mineral and organic soils. The mean of potential CEC extracted by 1 M ammonium acetate at pH 7.0 ranged from 14 (range 6.4–25) in coarse soils to 33 (21–45) cmol(+) kg⁻¹ in heavy clay soils, and from 42 (24–82) in mull soils to 77 (25–138) cmol(+) kg⁻¹ in peat soils. The average CEC of clay and SOC were 27 and 160 cmol(+) kg⁻¹, respectively. Titratable acidity occupied 53% and around 40% of the CEC sites in organic and mineral soils. STCat, pH and SOC explained 96% of the variation in potential CEC. STCat and pH can be used in estimating the clay content especially for soils containing over 30% clay. In coarse textured soils, in contrast, SOC hampers the STCat based estimation of clay content.

Key words: exchangeable cations, boreal environment, organic carbon, pedotransfer function, titratable acidity

Introduction

Cation exchange capacity (CEC) is one of the basic properties commonly reported when characterizing soil in a scientific context. Reflecting the negative charges on soil particles, CEC indicates the ability of a soil to reversibly retain cations by electrostatic forces (e.g. Bache 1976, Ross and Ketterings 1995). This phenomenon is linked to soil nutrient stock and supply, mobility of elements and pH buffering, all of which are important factors in agricultural land use. However, the available methods of CEC analysis are too laborious for CEC determination to be included in routine soil testing protocols (Sumner and Miller 1996, Ciesielski et al. 1997).

Predicting the CEC value from more readily available soil data via pedotransfer functions is a credible alternative for direct laboratory measurement (McBratney et al. 2002). Permanent charge of layer silicates originating from isomorphous substitution within the mineral structure and variable pH-dependent charge generated by dissociation of hydroxyl and carboxyl groups are the main components contributing to CEC (Bache 1976). Consequently, clay and organic matter contents explain the majority of variability in the CEC values in many studies (e.g. Bell and van Keulen 1995, Parfitt et al. 1995, Krogh et al. 2000, Fooladmand 2008, Sulieman et al. 2018, Mishra et al. 2019). However, due to spatial variation in clay mineralogy and composition of organic matter, different pedotransfer functions are needed in different regions (Seybold et al. 2005).

Estimating potential CEC on the basis of soil test results obtained with the acid (pH 4.65) ammonium acetate solution, which is used in soil testing in Finland (Vuorinen and Mäkitie 1955), is not entirely straightforward. Exchangeable Ca, Mg, K and Na are extracted from soil roughly equally with the acid and neutral ammonium acetate of the same molarity (Niskanen and Jaakkola 1986), but the challenges are mostly related to the amount of the variable charge associated with soil organic and mineral matter (Curtin et al. 1996). Part of these sites are available for and occupied by exchangeable cations, but in acid soils many of the sites are blocked by non-dissociated protons. Those sites are not available for cation exchange at soil pH but become accessible at pH 7.0 or at whatever higher pH CEC is determined, and should thus be included in the value of potential CEC. Niskanen and Jaakkola (1986)

estimated effective CEC on the basis of the acid ammonium acetate soil test, and in their material of 430 soil samples (average pH 5.8), exchangeable acidity occupied only 6% of the effective CEC. Therefore, accurate estimates for the effective CEC were obtained. However, potential CEC is a more relevant characteristic, for example, in soil classification and in the determination of liming requirements. When attempting to estimate the potential CEC at pH 7.0, the component of non-dissociated variable charge sites, operationally determined as titratable acidity (TA; $H^+ + A^{3+}$), is much higher in acid soils, as compared to the exchangeable acidity.

Soil texture is rarely measured in routine soil analyses aimed to adjust fertilization. However, clay and fine-sized particle (FINES; $\emptyset < 0.02$ mm) content plays a significant role in soil fertility and in estimating soil carbon (C) sequestration potential (Hassink 1996, Wiesmeier et al. 2019). Further, recent studies have shown that soil clay to C ratio plays a key role in determining soil structural stability and yield potential (Soinne et al. 2016, Soinne et al. 2021). There is often a close correlation between CEC and clay, encouraging an attempt to predict the soil clay content on the basis of CEC or its components. A low-cost estimate of clay content based on agricultural soil test data would enable more accurate determination of liming requirement, better targeting of soil improvement measures based on soil clay/C ratio and better estimation of soil C sequestration potential.

In this study, a data set of CEC values, measured at pH 7.0 and representing various mineral and organic soils of Finland, was compiled by collecting previously published and unpublished results from soil surveys and field studies. Supplementary analyses of archived samples were carried out to fill major gaps in the existing material. The acquired data was used to 1) calculate reference values for the CEC and its components in different soil types, 2) develop pedotransfer functions for predicting the CEC and its components from soil organic C (SOC) and clay contents, pH, and Ca²⁺, Mg²⁺, and K⁺ extracted in standard agronomic soil testing, and 3) develop pedotransfer functions for soil clay and FINES content using the above-mentioned characteristics as explanatory variables. The results benefit full exploitation of the soil testing data and practical interpretation of the CEC values at farm level.

Material and methods

Study area

In Finland, agricultural land (2.3 million ha) constitutes about 7.5% of the total land area. Medium- and coarsetextured mineral soils and clay soils make up about 22%, 36% and 28% of the agricultural area of Finland, respectively. Organic soils account for about 13% of the arable area (Lemola et al. 2018, Luke 2020). Typically, the fine clay fraction (<0.0002 mm) mostly consists of illite, chlorite, vermiculite and amorphous material, whereas coarse clay (0.0002–0.002 mm) and coarser fractions are increasingly composed of feldspars and quartz (Sippola 1974). The formation of geologically young Finnish soils has been influenced by the Weichselian glaciation, which ended about 11 500 years ago, and consequently, the soils of Finland are rather young and mostly relatively weakly developed. These soils are inherently acidic (Reuter et al. 2008) and rich in organic C at the European scale (Aksoy et al. 2016). Cryic temperature regime of Soil Taxonomy prevails in Finland (Yli-Halla and Mokma 1998), and commonly the clayey soils have an aquic moisture regime (Yli-Halla and Mokma 2001). According to the World Reference Base for Soil Resources (IUSS Working Group WRB 2015), clay soils of Finland are typically classified as Vertic Endogleyic Luvic Stagnosols or Luvic Gleysols, and fine silt soils as Stagnic Regosols. Coarse silt and fine sand soils with deeper layers rich in clay are commonly classified as Endogleyic Luvic Planosols, whereas Endogleyic Cambisols are common in deeper medium-textured soils and (Gleyic) Podzols in coarse-textured soils (Yli-Halla and Nyborg 2013). Cultivated organic soils are usually classified as Umbric or Histic Gleysols or Sapric Histosols (Yli-Halla and Peltovuori 2009).

Soil samples and analysis

This study was based on Finnish soil samples collected from the plough layer of cultivated soils, and a few virgin soils. Owing to the deficient description of land uses in the original paper of Marttila (1965), the distribution of the samples into cultivated and virgin soils is slightly unclear. This group of 45 samples consists of 31–33 cultivated and 14–12 virgin soils. Values of potential CEC determined at pH 7.0 were collected, together with other relevant data, from all published sources known and available for participating researchers and personal archives containing unpublished data from previous and ongoing projects of the participating researchers (Table 1). The retrieved data set was complemented with the determination of CEC in a few additional soils to overcome methodological incompatibilities and increase the number of organic soil samples. The CEC analysis was carried out by using neutral ammonium acetate (1 M CH_3COONH_4 , pH 7.0) extraction in soil/solution ratio of 1:5 (w/v). The sample

suspensions were agitated for 1 h and then allowed to stand overnight, after which the agitation was continued for 10 min. Thereafter, the suspensions were centrifuged, and the supernatants filtered. The extraction was repeated in 15 min length for 3 times combining all the supernatants. From the final solution, concentrations of Ca, Mg, K and Na were analyzed by ICP-OES. The TA was determined by back-titration to pH 7.0. The CEC value was calculated as the sum of the extracted cations and TA in cmol(+) kg⁻¹.

Particle-size distribution was determined by a pipette method (Elonen 1971). In the older data sets (Marttila 1965, Mäkitie and Virri 1965, Sillanpää 1982), SOC was determined with the Walkley – Black method while in the other data sets, including the new measurements for this study, total C was determined using dry combustion (Dumas method). In the acid soils of Finland, this total C can be taken to represent SOC (Nelson and Sommers 1996). Soil pH was measured in a soil-water suspension (1:2.5 v/v). The same procedure for the determination of CEC was used in all datasets listed in Table 1, except in Marttila (1965), where the samples were leached with 1 M CH_2COONH_A , pH 7.0, in a percolation tube.

Data set	n	Remarks	Calibration/Validation
Sillanpää 1982	21	A set of archived samples from cultivated soils in Finland reanalyzed due to a different method originally used	Calibration
Yli-Halla et al. 2000	24	Plough layer samples of pedons collected for soil classification of cultivated soils in southern and central Finland	Calibration
Soinne et al. 2021	21	Cultivated mineral soils from southwestern and east- central Finland (Oranki project)	Calibration
Unpublished	22	Archived plough layer results from cultivated experimental soils and pedons collected for soil classification purposes from various parts of Finland	Calibration
Unpublished	14	Results of plough layer samples from central Finland used in compiling Finnish soil database	Calibration
Palojärvi et al. 2002	10	Plough layer samples from conventionally and organically cultivated fields in southern Finland (MABIN project)	Calibration
Mäkitie and Virri 1965	10	Clayey plough layer samples from mid-Uusimaa, southern Finland	Calibration
Hyväluoma et al. 2020	2	Plough layer samples of organic soils from Ostrobothnia, western Finland	Calibration
Peltovuori et al. 2002	3	Plough layer samples of clayey and coarse textured soils from southern and western Finland	Calibration
Paasonen-Kivekäs and Yli-Halla 2005	2	Plough layer samples of fine sand soils from Ostrobothnia, western Finland	Calibration
Keskinen et al. 2016	41	Monitoring of cultivated soils covering the agricultural area in Finland; new analyses of archived samples of organic soils from the 2018 sampling campaign	Calibration: 33 soils Validation: 8 randomly selected organic soils
Marttila 1965	45	Cultivated and virgin soils from various parts of Finland	Validation
Mattila and Rajala 2020	16	Cultivated soils from Finland sampled in 2019 representing productive (K) and unproductive (0) fields	Validation. Not included in descriptive statistics (exchangeable cations and texture not reported)

Table 1. Data sets with number of soil samples (n) used in this study for the modelling (calibration/validation) of cation exchange capacity (CEC) and titratable acidity (TA)

The final data comprising 215 soil samples (data set of Mattila and Rajala [2020] not included) was classified in soil types according to the Finnish system (Aaltonen et al. 1949) where soils are grouped into mineral and organic soils on the basis of the soil organic matter (SOM) content (Table 2). SOC content was converted to SOM content using the van Bemmelen factor of 1.724, which is found to be appropriate for Finnish cultivated mineral soils (Heikkinen et al. 2021). For descriptive statistics, the mineral soils were further classified to heavy clays, clays, medium-textured soils (mostly different loam soils) and coarse soils (mostly loamy sands) based on their clay (<0.002 mm) content only, because the complete particle-size distribution had not been presented for every dataset. Organic soils were further divided to mull soils and peat soils according to their SOM content (see Table 2). For 71 of the samples, information on Ca, Mg and K acquired by the soil testing procedure used in Finland (AAAc; a single acid ammonium acetate-extraction, 0.5 M $CH_3COONH_4 - 0.5 M CH_3COOH$, pH 4.65) in soil/solution ratio of 1:10 (v/v) and shaking time of 1 h, Vuorinen and Mäkitie 1955) was available.

Soil type		SOM (%)	Clay (%)	n
Organic soils	Peat	≥ 40		37
	Mull	20-39.9		30
Mineral soils	Heavy clay		>60	22
	Clay	-20	30-59.9	48
	Medium	<20	12-29.9	41
	Coarse		<12	37

Table 2. Soil classification used in the study based on the soil organic matter (SOM) and clay (<0.002 mm) contents

For the soil test analysis in Finland, an equal volume of soils is taken for the analysis, whereas the CEC measurement is done on soil mass basis. For the regression models, STCat results (mg l^{-1}) were transformed to cmol l^{-1} taking into account the charge of each cation (i.e. STCat cmol(+) l^{-1} = STCa cmol $l^{-1} \times 2$ + STMg cmol $l^{-1} \times 2$ + STK cmol l^{-1}). In predicting the CEC, the sum of cation charges was used whereas in predicting the clay content, each cation was included separately (i.e. STCa cmol l^{-1} , STMg cmol l^{-1} and STK cmol l^{-1} , charges not taken into account) in the regression model.

An additional data set consisting of 571 soil samples mainly from the national soil monitoring of Finland (Keskinen et al. 2016) and Oranki-project (Soinne et al. 2021) was compiled for predicting the soil clay content and the fine particles content (FINES; \emptyset < 0.02 mm) on the basis of pH, C and STCat. The validation data used for clay and FINES content models was collected from on-going projects and included 31 samples from different fields in southern Finland.

Data analysis

Pedotransfer functions were constructed using linear regression analysis for the calibration data to estimate CEC, TA, Clay% and FINES% from various soil properties (pH, STCat, SOC and Clay). Regression models were fitted separately for all soils, mineral soils and organic soils in modelling of CEC and TA, and separately for all soils, clay soils (clay% > 30) and coarse soils (clay% < 30) in modelling of Clay% and FINES%. The square root transformation was applied for TA and STMg to meet model assumptions (normally distributed errors with constant variance). In some models, 1–2 observations were excluded as outliers based on their studentized residual values (> 3 or < -3). In all models, only predictors significant at the 0.05 level were included. Different models for the same predicted variable were compared by two statistics based on the model specific data: coefficient of determination (R²) was used to assess the model explanatory power and root mean square error (RMSE) to assess the model explanatory error. In addition to their performance (R² and RMSE), reported models were selected considering the availability of predictive variables for the potential users of these equations (e.g., SOC is not commonly analyzed in agronomic soil testing in Finland). All models were created using the SAS Enterprise Guide 7.1 (SAS Institute Inc., Cary, NC, USA).

Models with R² above 0.7 were tested with validation data and the performance of the models was evaluated using the statistics R² (prediction power), RMSE (error variation) and ME (mean error = bias). RMSE was calculated from the average square difference between the predicted value (y_{pred}) and the observed value y_{obs} (eq. a) and ME as the mean difference between y_{ored} and y_{obs} (eq. b):

a)

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (y_{pred} - y_{obs})^2}$$
 $ME = \frac{1}{N} \sum_{i=1}^{N} (y_{pred} - y_{obs})$

Results

Characteristics of the studied soils

According to descriptive statistics shown in Table 3, the $pH(H_2O)$ of the study soils ranged within four pH units from very acidic to neutral pH values. Almost all soils were acidic, and the median values of the different soil groups ranged between 5.1 and 5.9. The pH values within the individual soil types overlapped but, in general, organic soils tended to be more acidic than the mineral soils. The pH in most soils was thus much lower than the pH 7.0 at which the potential CEC is usually measured, suggesting an abundance of TA. Because the main grouping of soils was based on SOM content, the mean SOC content in peat soils (36%, range 23–53%) was over twofold compared

to mull soils (16%, range 12–23%) (Table 3). Within mineral soils, the SOC content ranged between 0.7% and 11%, and there was strong overlapping between the different textural groups. However, the mean SOC was higher for clay soils (4.3–4.6%) than for medium-textured or coarse soils (2.6–3.5%).

Collations		Mean ± SD	N.dia			Percenti	les		Max
Soil type	n	Weall ± 3D	Min	5 th	25 th	50 th	75 th	90 th	— Max
					pH (F	1 ₂ 0)			
Organic soils									
Peat	37	5.0 ± 0.8	3.5	3.9	4.3	5.1	5.6	5.9	6.5
Mull	30	5.4 ± 0.6	3.9	4.4	5.0	5.5	5.9	6.2	6.8
Mineral soils									
Heavy Clay	22	5.9 ± 0.5	5.1	5.1	5.5	5.9	6.2	6.3	6.8
Clay	48	5.7 ± 0.6	4.0	4.9	5.2	5.6	6.0	6.6	7.0
Medium	41	5.8 ± 0.5	4.7	5.1	5.6	5.9	6.1	6.5	7.0
Coarse	37	5.9 ± 0.6	4.0	5.0	5.6	5.9	6.4	6.6	7.2
					SOC	(%)			
Organic soils									
Peat	37	36 ± 9.1	23	24	27	35	44	47	53
Mull	30	16 ± 3.4	12	12	13	15	19	21	23
Mineral soils									
Heavy Clay	22	4.6 ± 2.0	2.0	2.3	3.4	4.1	4.8	8.1	8.7
Clay	48	4.3 ± 2.0	1.0	2.1	2.9	3.7	5.4	6.7	11
Medium	41	2.6 ± 1.3	0.7	0.9	1.6	2.5	3.3	4.7	6.3
Coarse	37	3.5 ± 1.9	1.0	1.5	2.0	3.0	4.7	6.3	7.9

Table 3. General statistics for soil organic carbon (SOC) and pH measured in water in different soil types

Potential CEC varied largely among soil types (4.7–138 cmol(+) kg⁻¹) (Table 4). Comparison of the CEC values revealed that the CEC values in organic soils partly overlapped with those of clay soils, and the CEC values in clay soils partly with other mineral soils. However, the mean CEC values systematically increased with soil types as follows: coarse (14 cmol(+) kg⁻¹) < medium-textured (16 cmol(+) kg⁻¹) < clay (25 cmol(+) kg⁻¹) < heavy clay (33 cmol(+) kg⁻¹) < mull (42 cmol(+) kg⁻¹) < peat (77 cmol(+) kg⁻¹) soils. Despite a large variation in TA (0–122 cmol(+) kg⁻¹), the mean values followed the same ascending order as for the CEC in terms of the soil types (Table 5). Mean TA values in mull and peat soils (20–49 cmol(+) kg⁻¹) were 1.8–4.3 times higher than in clay soils (11–12 cmol(+) kg⁻¹), and 3.5–8.3 times higher than in medium-textured or coarse soils (5.4–6.3 cmol(+) kg⁻¹).

Table 4. General statistics for potential cation exchange capacity (CEC, $cmol(+) kg^{-1}$) in different soil types (see number of soil samples (n) in Table 2 and 3).

Soil type		Min		Max				
Son type	Mean ± SD	IVIIII	5 th	25 th	50 th	75 th	90 th	Max
			C	EC (cmol(+	·) kg ⁻¹)			
Organic soils								
Peat	77 ± 28	25	47	55	68	104	119	138
Mull	42 ± 13	24	25	33	39	46	60	82
Mineral soils								
Heavy Clay	33 ± 6.4	21	23	29	33	39	40	45
Clay	25 ± 5.6	13	17	21	24	27	31	44
Medium	16 ± 4.6	4.7	10	12	15	18	22	27
Coarse	14 ± 4.3	6.4	8.0	11	13	17	20	25

The descriptive statistics are presented for the contents of exchangeable Ca^{2+} , Mg^{2+} , K^+ and Na^+ in Table 5. As for the mean contents of exchangeable Ca^{2+} , medium-textured and coarse soils had the lowest values (7.2–7.7 cmol(+) kg⁻¹) and organic soils the highest values (17–22 cmol(+) kg⁻¹). The lowest mean contents of exchangeable Mg^{2+} , on average of 1.2 cmol(+) kg⁻¹, were found in medium-textured and coarse soils and the highest (6.1 cmol(+) kg⁻¹) in heavy clay and peat soils.

Soil type	Mean ± SD	Min	Percentiles					— Max	
Son type	Mean ± 50	IVIIII	5 th	25 th	50 th	75 th	90 th	IVIAX	
				TA (cmol(+	+) kg ⁻¹)				
Organic soils									
Peat	49 ± 35	4.3	12	23	32	76	102	122	
Mull	20 ± 12	0.6	4.4	13	20	25	30	59	
Mineral soils									
Heavy Clay	12 ± 6.7	2.2	4.9	8.1	9.4	15	22	29	
Clay	11 ± 6.1	1.1	2.3	6.2	9.1	15	18	27	
Medium	6.3 ± 2.8	0.6	2.5	4.7	5.9	7.5	9.3	15	
Coarse	5.4 ± 3.5	0.0	1.3	3.2	4.7	6.0	9.7	18	
				Ca ²⁺ (cmol(+) kg ⁻¹)				
Organic soils									
Peat	22 ± 12	4.4	5.9	13	19	30	37	53	
Mull	17 ± 9.9	0.6	3.8	11	15	20	33	39	
Mineral soils									
Heavy Clay	14 ± 4.3	5.3	7.9	12	14	17	20	22	
Clay	10 ± 4.7	2.4	5.0	7.2	10	13	15	30	
Medium	7.7 ± 3.9	1.5	1.8	5.0	7.3	8.5	14	17	
Coarse	7.2 ± 4.4	0.8	1.2	4.4	6.1	8.6	5.0	19	
				Mg ²⁺ (cmol	(+) kg ⁻¹)				
Organic soils									
Peat	6.1 ± 4.5	0.5	0.8	2.7	4.9	8.7	13	17	
Mull	4.1 ± 2.6	0.5	0.7	2.3	3.9	6.0	6.8	11	
Mineral soils		0.0	017	2.0	0.0	010	0.0		
Heavy Clay	6.1 ± 2.3	2.2	3.2	4.3	5.9	7.7	8.9	11	
Clay	2.8 ± 1.5	0.7	1.0	1.8	2.3	3.5	4.5	7.8	
Medium	1.4 ± 0.7	0.4	0.5	0.8	1.3	1.9	2.1	3.8	
Coarse	0.9 ± 0.6	0.2	0.2	0.5	0.8	1.2	1.6	2.9	
course	0.5 2 0.0	0.2		K ⁺ (cmol(+		1.2	1.0	2.5	
Organic soils					/ 6 /				
Peat	0.48 ± 0.55	0.10	0.13	0.21	0.31	0.38	1.17	2.37	
Mull	0.48 ± 0.33 0.32 ± 0.17	0.10	0.13	0.21	0.28	0.38	0.57	0.82	
Mineral soils	0.02 ± 0.17	5.11	0.12	0.21	0.20	0.00	0.07	0.02	
Heavy Clay	0.77 ± 0.27	0.30	0.31	0.56	0.79	0.94	1.04	1.41	
Clay	0.63 ± 0.30	0.20	0.28	0.40	0.53	0.80	1.04	1.38	
Medium	0.31 ± 0.17	0.20	0.12	0.20	0.25	0.36	0.56	0.84	
Coarse	0.31 ± 0.17 0.32 ± 0.19	0.09	0.12	0.17	0.30	0.45	0.56	0.83	
coarse	0.52 ± 0.15	0.05	0.10	Na ⁺ (cmol(·		0.45	0.50	0.05	
Organic soils					ן מיי ו				
Peat	0.20 ± 0.14	0.05	0.07	0.11	0.17	0.24	0.42	0.59	
Mull	0.20 ± 0.14 0.14 ± 0.14	0.03	0.07	0.07	0.11	0.24	0.42	0.70	
Mineral soils	0.14 ± 0.14	0.05	0.05	0.07	0.11	0.14	0.21	0.70	
Heavy Clay	0.16 ± 0.07	0.06	0.10	0.12	0.16	0.19	0.20	0.40	
Clay	0.18 ± 0.07 0.13 ± 0.12	0.00	0.10	0.12	0.10	0.19	0.20	0.40	
Medium	0.13 ± 0.12 0.14 ± 0.27	0.00	0.03	0.10	0.10	0.14	0.21	1.80	
Coarse	0.14 ± 0.27 0.09 ± 0.07	0.00	0.00	0.08	0.10	0.12	0.17	0.36	

Table 5. General statistics for contents (cmol(+) kg⁻¹) of titratable acidity (TA; $H^+ + AI^{3+}$) and exchangeable calcium (Ca²⁺), magnesium (Mg²⁺), potassium (K⁺) and sodium (Na⁺) in different soil types (see number of soil samples (n) in Table 2 and 3)

The mean contents of exchangeable K⁺ approached an average of 0.70 cmol(+) kg⁻¹ in clay soils, while it averaged 0.36 cmol(+) kg⁻¹ among other soil types. Most soil types had rather similar and very low mean contents of exchangeable Na⁺ (0.09–0.20 cmol(+) kg⁻¹). In terms of specific cation ratios, the average ratio of exchangeable Ca to Mg was 7.5 in coarse, 5.5 in medium-textured, 3.8 in clay and 2.3 in heavy clay soils, and 4.1 in mull and 3.5 in peat soils. The relative proportions of cations and TA varied less between the soil groups than did the absolute concentrations (Table 6). The average TA occupied more than half of potential CEC sites in organic soils, being more abundant than Ca²⁺, but it was not much lower in mineral soils, where it was around the same level as Ca²⁺. This outcome highlights the importance of TA as a major component of potential CEC in this soil material. The scarcity of K⁺ in organic soils was also striking.

Soil type	ТА	Ca ²⁺	Mg ²⁺	K+	Na⁺
			(%)		
Organic soils					
Peat	57 ± 25	32 ± 18	9.7 ± 7.8	0.8 ± 1.4	0.3 ± 0.4
Mull	49 ± 23	40 ± 18	10 ± 6.1	0.8 ± 0.4	0.4 ± 0.3
Mineral soils					
Heavy Clay	35 ± 16	43 ± 11	19 ± 6.7	2.4 ± 1.0	0.5 ± 0.2
Clay	42 ± 19	43 ± 17	11 ± 5.4	2.6 ± 1.2	0.5 ± 0.5
Medium	41 ± 16	47 ± 16	9.0 ± 4.5	2.0 ± 1.0	0.9 ± 1.8
Coarse	41 ± 22	49 ± 20	6.9 ± 4.2	2.4 ± 1.4	0.7 ± 0.8

Table 6. Percentages (mean \pm SD) of titratable acidity (TA; H⁺ + Al³⁺) and different cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) occupying the potential cation exchange capacity (CEC) sites in different soil types (see number of soil samples (n) in Table 2 and 3)

Linear regression models for estimating cation exchange capacity (CEC)

STCat (cmol(+) I⁻¹) extracted with acid ammonium acetate soil test solution and soil pH explained 83% of the variation in the CEC (eq. 1; Table 7). When the two major soil types (organic and mineral soils) were analyzed separately, pH and STCat explained 89% of the variation in CEC in mineral soils (eq. 3) and root mean square error (RMSE) decreased to 3.21, whereas in organic soils, RMSE was above 8 (eq. 8) (Table 7, Fig. 1). Validation of the models with independent dataset produced relatively good agreement with observed and predicted values for mineral and organic soils (R² = 0.69 and 0.83, respectively, Table 7). The functions, however, slightly underestimated CEC (ME < 0) in mineral soils (Table 7, Fig. 1).

Table 7. Pedotransfer functions for estimating potential cation exchange capacity (CEC, cmol(+) kg⁻¹) using sum of soil test cations (STCat cmol(+) l^{-1} = STCa cmol $l^{-1} \times 2$ + STMg cmol $l^{-1} \times 2$ + STK cmol l^{-1}), pH and soil organic carbon (SOC, %) as explanatory variables, and statistics of calibration data and validation data

CEC	_			Calibratio	on		Valio	dation	
Eq. No.	Predictors Regression equation		n	RMSE	R ²	n	RMSE	ME	R ²
	All soils								
1	STCat, pH	CEC = 145.68 + 1.91 × STCat - 24.36 × pH	63	7.71	0.83	24	8.88	-0.18	0.78
2	STCat, pH, SOC	CEC = 70.97 + 1.25 × STCat - 11.40 × pH + 0.71 × SOC	63	3.95	0.96	24	6.16	-0.10	0.85
	Mineral soils								
3	STCat, pH	CEC = 82.88 + 1.30 × STCat - 12.97 × pH	29	3.21	0.89	15	7.05	-0.30	0.69
4	STCat, pH, SOC	CEC = 50.83 + 1.17 × STCat - 8.38 × pH + 1.48 × SOC	29	2.26	0.95	15	6.72	-0.16	0.62
5	SOC	CEC = 11.23 + 2.41 × SOC	114	7.00	0.33				
6	Clay	CEC = 10.29 + 0.31 × Clay	114	4.37	0.74	34	6.26	-0.10	0.66
7	SOC, Clay	CEC = 4.89 + 1.67 × SOC + 0.27 × Clay	114	2.89	0.89	34	6.39	-0.14	0.82
	Organic Soils								
8	STCat, pH	CEC = 147.84 + 1.98 × STCat - 24.60 × pH	34	8.42	0.72	9	4.94	0.08	0.83
9	STCat, pH, SOC	CEC = 78.47 + 1.33 × STCat - 12.95 × pH + 0.69 × SOC	34	4.98	0.90	9	4.12	-0.02	0.86
10	SOC	CEC = 17.17 + 1.51 × SOC	46	16.56	0.54	20			
11	SOC, pH	CEC = 70.10 + 1.30 × SOC - 9.11 × pH	46	15.37	0.62	20			



Fig. 1. Predicted cation exchange capacity (CEC, cmol(+) kg⁻¹) modelled using soil test cations (STCat cmol(+) l⁻¹ = STCa cmol l⁻¹ × 2 + STMg cmol l⁻¹ × 2 + STK cmol l⁻¹) and pH as predictors for a) the whole data, b) for mineral soils and c) for organic soils plotted against observed CEC (cmol(+) kg⁻¹). Open circles represent the results of the calibration data and blue circles represent the validation data. Data point excluded from the regression analysis as an outlier is marked with red square.

Including SOC in the model increased the explanation power of the regression model such that the STCat, pH and SOC explain 96% of the variation in the CEC in all soil types (eq. 2; Table 7, Fig. 2). The validation data showed good agreement between the observed and predicted values ($R^2 = 0.85$, Table 7), and further, the absolute value of the ME of the validation data was lower, though still below 0.

In mineral soils, SOC solely explained 33% of the variation (eq. 5) and pH was not a statistically significant predictor when included in the model with SOC. In contrast for the organic soils, including pH in the model with SOC resulted in both variables to be statistically significant and increased the explanatory power from 54% (eq. 10) to 62% (eq. 11).



Fig. 2. Predicted cation exchange capacity (CEC, cmol(+) kg⁻¹) modelled using soil test cations (STCat cmol(+) $l^{-1} =$ STCa cmol $l^{-1} \times 2 +$ STMg cmol $l^{-1} \times 2 +$ STK cmol l^{-1}), pH and soil organic carbon (SOC, %) as predictors for a) the whole data, b) for mineral soils and c) for organic soils plotted against observed CEC (cmol(+) kg⁻¹). Open circles represent the results of the calibration data and blue circles represent the validation data. Data point excluded from the regression analysis as an outlier is marked with red square.

In mineral soils, 74% of the variation in CEC was explained by clay content (eq. 6) and together with SOC, clay explained 89% of the variation in CEC (eq. 7) (Table 7, Fig. 3). Soil pH showed not to be a statistically significant predictor when included in the model. The regression coefficients indicated CECs of 27 cmol(+) kg⁻¹ for clay and 167 cmol(+) kg⁻¹ for SOC. For the validation dataset, the strength of the linear relationship (R²) between observed values and values predicted using eq. 7 (Table 7) was 0.82, and ME indicated potential underestimation of the CEC (Table 7, Fig. 3).



Fig. 3. Predicted cation exchange capacity (CEC, cmol(+) kg⁻¹) in mineral soils modelled using a) clay (%) and b) clay and soil organic carbon (SOC, %) as predictors plotted against observed CEC (cmol(+) kg⁻¹). Open circles represent the results of the calibration data and blue circles represent the validation data.

Linear regression models for estimating titratable acidity (TA)

Soil pH and SOC explained the majority of the TA (eq. 12–16, Table 8, Fig. 4 and 5). In minerals soils, including the clay content in the explanatory variables (eq. 15) increased R^2 and reduced the RMSE (Table 8, Fig. 5). Validation of the developed TA models with independent dataset indicated that eq. 13 for all soils and eq. 15 for mineral soils produced best agreement with observed and predicted values estimated based on MRSE and R^2 (Table 8, Fig. 4 and 5). The validation data indicated risk for equations 12 and 14–16 to underestimate the TA (Table 8).

TA						on		Vali	dation	
Eq. No.	Predictors	Regression equation	on	n	RMSE	R ²	n	RMSE	ME	R ²
	All soils									
12	SOC, pH	SQRT(TA) = 10.97 -	SQRT(TA) = 10.97 + 0.067 × SOC - 1.45 × pH			0.84	53	0.86	-0.003	0.93
		TA = (10.97 + 0.06	7 × SOC - 1.45 × pH)²		6.76					
13	SOC, pH, SOC×pH	SQRT(TA) = 9.19 + 0	0.20 × SOC - 1.13 × pH - 0.02 × pH × SOC	159	0.65	0.86	53	0.64	0.004	0.93
		TA = (9.19 + 0.20 ×	SOC - $1.13 \times pH - 0.02 \times pH \times SOC)^2$		5.87					
	Mineral soils									
14	SOC, pH	SQRT(TA) = 7.523 -	+ 0.200 × SOC - 0.946 × pH	112	0.50	0.72	34	0.45	-0.002	0.71
		TA = (7.523 + 0.200	0 × SOC - 0.946 × pH)²		2.97					
15	SOC, Clay, pH	SQRT(TA) = 7.282 +	0.162 × SOC + 0.012 × Clay - 0.952 × pH	112	0.41	0.81	34	0.43	-0.005	0.77
		TA = (7.28 + 0.16 ×	SOC + 0.01 × Clay - 0.95 × pH) ²		2.23					
	Organic soils									
16	SOC, pH	SQRT(TA) = 15.030	+ 0.051 × SOC - 2.138 × pH	46	0.78	0.87	19	1.04	-0.041	0.95
		TA = (15.030 + 0.05	51 × SOC - 2.138 × pH) ²		11.6					
140	a)	50) b)	140	c)					
120				120						
100		40		100						
		• 30)							
TA predicted 0 8	•	• •	0	80	<u> </u>	0	° 。	••	0	
	~~ ~~	• 20		60	0	0	•	•		
40	2 0 ⁰ 0			40	0	00				

Table 8. Pedotransfer functions for estimating titratable acidity (TA, cmol(+) kg⁻¹) using soil organic carbon (SOC, %), pH and clay content (%, for mineral soils) as explanatory variables, and statistics of calibration data and validation data

Fig. 4. Predicted titratable acidity (TA, cmol(+) kg⁻¹) modelled using pH and soil organic carbon (SOC, %) as predictors for a) whole data, b) for mineral soils and c) for organic soils plotted against observed TA (cmol(+) kg⁻¹). Open circles represent the results of the calibration data and blue circles represent the validation data. Data points excluded from the regression analysis as outliers are marked with red squares.

TA observed

30

40

20

20

0

20 40 60 80

TA observed

100 120 140

50

10

C

0

10

100 120 140

TA observed

20

20 40 60 80



Fig. 5. Predicted titratable acidity (TA, cmol(+) kg⁻¹) modelled using a) pH, soil organic carbon (SOC, %) and pH x SOC as predictors for whole data and b) pH, clay and SOC for mineral soils plotted against observed TA (cmol(+) kg⁻¹). Open circles represent the results of the calibration data and blue circles represent the validation data. Data points excluded from the regression analysis as outliers are marked with red squares.

Linear regression models for estimating clay content with soil test cations and pH

Together with pH, STCa, STMg and STK explained 76% of the variation in clay% in mineral soils (eq. 17) (Table 9, Fig. 6) and including SOC in explanatory variables further improved the explanatory power of the model (eq. 18) (Table 9, Fig. 7). Regression models fitted separately for clay soils and coarse mineral soils revealed that clay% estimation for coarse soils was uncertain. Including SOC in the model improved the model for coarse soils but still only 46% of the variation was explained (eq. 22 and 23). For the clay soils, STCat and soil pH explained 78% of the variation and SOC was not statistically significant as an explanatory variable (eq. 21). Soil test cations were included separately as the share of Mg increased with increasing clay content, whereas the share of Ca decreased (Fig. 7). Explaining FINES content with soil test variables turned out to be uncertain and only 50 or 53 % of the variation in FINES content could be explained with STCat and pH or STCat, pH and SOC, respectively (eq. 19 and 20) (Table 8). Validation of the equations 17, 18 and 21 with independent dataset produced larger RMSE's and in addition, the validation data pointed towards a risk for underestimating the clay content (Table 8).

Clay/Fines	Clay/Fines				on	Validation				
Eq. no.	Predictors	Regression equation	n	RMSE	R ²	n	RMSE	ME	R ²	
	All soils									
17	Mg, Ca, K, pH	Clay = 72.62 + 24.23 × sqrt(Mg) + 4.32 × Ca + 17.15 × K - 16.13 × pH	571	9.38	0.76	31	10.72	-0.23	0.79	
18	Mg, Ca, K, pH, SOC	Clay = 116.54 + 24.17 × sqrt(Mg) + 5.82 × Ca + 13.29 × K - 22.80 × pH - 2.37 × SOC	571	8.54	0.80	31	10.61	-0.16	0.74	
19	Мg, Са, К, рН	Fines = 105.77 + 34.35 × sqrt(Mg) + 5.16 × Ca + 10.34 × K - 19.35 × pH	571	19.98	0.50					
20	Mg, Ca, pH, SOC	Fines = 168.07 + 35.37 × sqrt(Mg) + 7.41 × Ca - 28.85 × pH - 3.28 × SOC	571	19.31	0.53					
	Clay soils									
21	Mg, Ca, K, pH	Clay = 82.08 + 21.52 × sqrt(Mg) + 2.76 × Ca + 10.30 × K - 13.83 × pH	146	6.52	0.78	28	9.03	-0.13	0.73	
	Coarse soils									
22	Mg, Ca, K, pH	Clay = 33.53 + 6.08 × Mg + 2.39 × Ca + 8.70 × K - 6.32 × pH	425	6.55	0.34					
23	Mg, Ca, K, pH, SOC	Clay = 71.52 + 8.28 × Mg + 3.78 × Ca + 6.81 × K - 12.54 × pH - 1.75 × SOC	425	5.94	0.46					

Table 9. Pedotransfer functions for estimating mineral soil clay content (%) and FINES content (%, fine-sized particles; \emptyset < 0.02 mm) using soil test cations (STCa, cmol l⁻¹; STMg, cmol l⁻¹; STK, cmol l⁻¹) pH and soil organic carbon (SOC, %) as explanatory variables, and statistics of calibration data and validation data



Fig. 6. Predicted clay content (%) in a) all soils, b) coarse-textured and c) clay soils having soil test cations (STCa, cmol l^{-1} ; STMg, cmol l^{-1} ; STK, cmol l^{-1}) and pH as explanatory variables plotted against observed clay content. Open circles represent the results of the calibration data and blue circles represent the validation data.



Fig. 7. The share of Ca and Mg of the total soil test cations (STCa, cmol I⁻¹; STMg, cmol I⁻¹; STK, cmol I⁻¹) plotted against clay content in coarse- and medium-textured soils and clay soils.

Discussion

The basic soil test data available on farms at field level, i.e. plant available cations (STCat) and pH were found to explain 83% of the variation in CEC. This was anticipated, as the soil test procedure (AAAc, pH 4.65) extracts around 80% of the total exchangeable cations (Vuorinen and Mäkitie 1955) and pH links to exchangeable acidity as described below. Previously, Niskanen and Jaakkola (1986) congruently reported STCat and pH to explain over 80% of the variation in effective CEC in soils from Helsinki, Finland. Including information on SOC in the current model increased the explanatory power up to 96%. Organic matter is known to exhibit a major contribution to CEC, and organic compounds may even reduce the relative contribution of the clay fraction by blocking of the negative charges (e.g. Syers et al. 1970, Parfitt et al. 1995, Seybold et al. 2005). However, in the mineral soils of the current study, clay alone explained 74% of the variation in CEC, and with SOC the explanatory power increased to 89%. Similarly, in Danish soils, 90% of the variability in CEC values could be modelled by clay and organic matter content (Krogh et al. 2000), whereas in Iran, the explanatory power of SOM, clay and sand on CEC was 97% (Fooladmand 2008). The average CEC attained for clay in the present study (27 cmol(+) kg⁻¹) is in the range typical of illite as the predominant mineral (e.g. Martel et al. 1978, Kahr and Madsen 1995, White 1997). For SOC, the corresponding value of 167 cmol(+) kg⁻¹ agrees with the value of 184 cmol(+) kg⁻¹ SOC reported for unfractionated soil materials by Thompson et al. (1989), but also considerably higher values have been reported, e.g. 284–291 cmol(+) kg⁻¹ organic matter found by Krogh et al. (2000) in Denmark.

The potential CEC extracted by neutral ammonium acetate (TA determined by back-titration to pH 7.0) varied considerably among the different soil types. In mineral soils (CEC 14–33 cmol(+) kg⁻¹), the means and trends in soil CEC appeared to be similar to previously reported values for topsoils and subsoils of cultivated and virgin mineral soils (Kaila 1971a, 1972, Sippola 1974, Martel et al. 1978, Niskanen and Jaakkola 1986, Manrique et al. 1991, Krogh et al. 2000). In terms of different soils grouped by their taxonomic order, Manrique et al. (1991) found the means of potential CEC to range between 8.9 cmol(+) kg⁻¹ for Oxisols (n = 299) and 38 cmol(+) kg⁻¹ for Vertisols (n = 1274). In the present study, the means of potential CEC also followed the typical increasing trend with an increase in clay content among soil types (Kaila 1972, Sippola 1974).

In productive agricultural soils, the distribution of major cations is generally considered to be $Ca^{2+} > Mg^{2+} > K^+$ > Na⁺ (e.g. Graham 1959, Bohn et al. 2001). In terms of basic cations of the present study, the average degree of base saturation of potential CEC was higher in mineral (60%) than in organic (47%) soils, and the distribution of base cations and the Ca to Mg ratio followed the typical trends. In the plough layer of Finnish mineral soils, Kaila (1972) found exchangeable Ca²⁺ to be the dominant cation (mean 61–78%), being followed by Mg²⁺ (9–30%), K⁺ (3–5%) and Na⁺ (1–2%). In the same study, the mean ratio of Ca to Mg decreased from about 9 in sand soils to about 2 in heavy clay soils (Kaila 1972). Similarly, in our data, the Mg²⁺ appeared to occupy more CEC sites than Ca²⁺ with increasing clay content. Acid soils are also characterized by exchangeable aluminum (Al³⁺) and hydrogen (H⁺), although rarely being the predominant cations (Bohn et al. 2001). In the present study, however, the prominent or predominant part of potential CEC was occupied by the TA in mineral (mean 35–42%) and organic (mean 49–57%) soils.

For a farmer, an estimate of the TA component of the potential CEC may be of more use than the estimate of the potential CEC as a whole, since the acidity reveals the extent of binding sites that could be released for nutrient cations by neutralization with liming. The TA comprises exchangeable Al³⁺ and H⁺ often determined in unbuffered KCl extracts (Coscione et al. 1998, Dai and Richter 2000) and in addition, pH-dependent dissociation of H⁺ from the functional groups in organic matter and edges of clay minerals and release of adsorbed hydroxy-Al cations (Bache 1976). Besides the pH-dependent acidity, soil pH is related to the amount of exchangeable Al³⁺, which tends to decrease with increase in soil pH due to formation of Al oxides (Cabrera and Talibudeen 1977). Organic matter is known to complex Al and thus control its amounts and lability in soil (Cabrera and Talibudeen 1977, Wesselink et al. 1996). These relationships explain the observed contribution of SOC, pH and clay on the TA such that an increase in SOC or clay increases, and an increase in pH decreases the amount of TA. The mean contents of TA in the present study were comparable to those in Kaila (1971b), who reported the mean TA of about 9, 12 and 49 cmol(+) kg⁻¹ for Finnish coarse (n = 141), clay (n = 100) and organic (n = 57) soils, respectively. In the study of Kaila (1971b), the average titratable, nonexchangeable acidity extracted by KCl at pH 8.2 was about 8-12 times higher within the soil groups than the corresponding exchangeable acidity displaced by unbuffered KCI. Kaila (1972) and Niskanen and Jaakkola (1986) found that exchangeable acidity displaced by unbuffered KCl had a relatively minor importance in most soil groups (<10% of effective CEC).

On a weight basis, the highest CEC values are generally reported for the organic soils among the soil types due to the lower bulk densities. Previous studies have shown a markedly higher mean or median CEC as well as larger variation in CEC values in organic soils than those of mineral soils (e.g. Krogh et al. 2000). In the present study, the variation in potential CEC values $(24-138 \text{ cmol}(+) \text{ kg}^{-1})$ of organic soils was somewhat smaller when compared with the range of $22-257 \text{ cmol}(+) \text{ kg}^{-1}$ (median 61 cmol(+) kg⁻¹) obtained for Danish organic soils (SOM > 10%, n = 68) by Krogh et al. (2000).

Use of soil test data to unravel soil clay content

Methods used for analyzing clay content are known to be laborious and therefore costly and thus, not feasible in surveys where large numbers of samples are analyzed. In routine soil tests for farmers, soil texture is determined by sensory identification (finger assessment) and reported to the farmer on a nominal scale as a soil type included in the Finnish soil texture triangle (Halonen and Juusela 1957). Clay soils are classified as clays or heavy clays having clay content of 30–60% or above 60%, respectively. Our results showed that for clay soils, the clay content can be estimated relatively well with soil test data obtainable for most of the fields in Finland. However, for coarse textured soils, where SOM contributes significantly to cation exchange sites, the use of STCat in estimating clay content might result in a significant error.

Arthur et al. (2015) reported regression relationships for estimating clay content based on the link between hygroscopic water and clay content. Their models predicted clay contents well for most soils (RMSE varying between 3–6%), however, large SOC and prevalence of 1:1 clay minerals in soil increased the prediction error of the equations (Arthur et al. 2015). The high SOC content has a larger effect in medium- and coarse-textured soils where SOC significantly increases the specific surface area of the soil whereas in clay soils, the contribution of SOC to sorption sites becomes insignificant compared with that of clay as the clay content increases. The SOC content of mineral soils in our data set was relatively high, the mean being 2.6% and 3.5% also in medium- and coarsetextured soils, respectively. According to Arthur et al. (2015), in soils with SOC% higher than 2.4, there is a risk of a consistent increase in prediction error with increasing SOC contents especially in low clay soils. Predicting clay content based on Finnish soil test data resulted in larger RMSE than estimations based on the hygroscopic water reported by Arthur et al. (2015). However, for soils first classified as clays with finger assessment, the regression model based on ST data can be used to get more precise information on the clay content of the soil.

Conclusions

In the present study, pedotransfer functions were developed for predicting the soil clay content, potential CEC and TA. The estimation of potential CEC was based on 148 mineral and 67 organic soil samples collected from plough layers from various parts of Finland, which were further grouped into different soil types. In the studied soils, the means of potential CEC and TA increased from coarse-textured soils to heavy clay soils and mull soils to peat soils. The results highlighted the importance of TA as a prominent or predominant component of the potential CEC. The results of Finnish soil test (acid ammonium acetate-extraction, pH 4.65) can be used in estimating the potential CEC as STCat and pH explain 83% of the variation and together with SOC 96% of the variation. In estimating TA, knowledge of SOC is required and SOC and pH explained 86% of the variation. Soil test data can also be utilized in estimating the clay content especially for soils with clay content over 30%. However, SOC hampers STCat based estimations on clay content especially in coarse-textured soils.

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