SHORT COMMUNICATION

Predicting cation exchange capacity from hygroscopic moisture in agricultural soils of Western Europe

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Abstract

Soil cation exchange capacity (CEC) depends on the extent and negative charge density of surfaces of soil mineral and organic components. Soil water sorption also depends on the extent of such surfaces, giving thus way to significant relationships between CEC and hygroscopic moisture (HM) in many soils. In this work, we explored whether CEC could be accurately predicted from HM in agricultural soils of Mediterranean and humid temperate areas in Western Europe. For this purpose, we examined 243 soils across a wide variation range of their intrinsic properties. Soil CEC was determined using 1 M ammonium acetate at pH 7 and HM at an equilibrium air relative humidity (RH) of 43% (HM_{43}). Most of the variation of soil CEC was explained by HM_{43} through a linear function (CEC = 1.4 + 0.78HM_{43}; R^2 = 0.962; standard deviation = 2.30 cmol$_c$/kg). Coefficients of the regression equation were similar for subgroups of soils differing in moisture regime, clay mineralogy, carbonate content and organic carbon content. Therefore, soil hygroscopic moisture measurements at a fixed RH level provided a simple, robust, inexpensive method for predicting soil CEC.

Additional key words: soil organic carbon; relative humidity.

Abbreviations used: ACCE (active lime); CCE (calcium carbonate equivalent); CEC (cation exchange capacity); HM (hygroscopic moisture); HM_x (hygroscopic moisture in equilibrium with a relative humidity x); OC (organic carbon); RH (relative humidity).

Cation exchange capacity (CEC) is an important soil property because it influences the ability of soil to retain essential nutrients; also, it protects soil from acidification and groundwater from cation contamination. CEC results from the presence of a variety of negatively charged mineral and organic surfaces. Because water vapour adsorption is a measure of specific surface area in soils (Quirk, 1955; Newman, 1983), CEC and hygroscopic moisture (HM) are closely related in soil populations with similar types and proportions of negative surfaces involved in cation exchange processes. For instance, coefficients *a* and *b* in the regression equation CEC = *a* + *b*HM, where CEC is expressed in cmol$_c$/kg and HM in g water/kg soil, were found to be 2 cmol$_c$/kg and 0.544 cmol$_c$/g water, respectively, in smectitic soils, and 1 cmol$_c$/kg and 0.454 cmol$_c$/g water, respectively, in kaolinitic soils of New Zealand (Churchman & Burke, 1991).

The aim of this work was to explore whether CEC could be accurately predicted from HM in western European agricultural soils ranging widely in physical, chemical and mineralogical properties. For this purpose, we used a total of 243 soil samples from different agricultural areas of Western Europe. Most of the samples (204) were obtained from regions with a Mediterranean climate mainly in Portugal and Spain, and the others (39) from regions under a temperate humid climate in France, Germany, Great Britain, Italy and The Netherlands. The studied soils belonged to the Alfisol, Entisol, Inceptisol, Mollisol, Ultisol and Vertisol orders in Soil Taxonomy (Soil Survey Staff, 1999). No saline, sodic or gypsiferous soils, or soils with organic carbon (OC) contents higher than 35 g/kg were included. Soil samples were air-dried, grounded to < 2 mm and stored for several weeks to more than 30 years before analysis. Soils had a wide variation range in carbonate-

Table 1. Summary of the properties of the 243 soil samples used to construct the regression models

Property[1]	Minimum	Maximum	Mean	Standard deviation	Median
Carbonate-free clay (g/kg)	23	706	215	134	186
Organic carbon (g/kg)	1.4	34.0	10.1	4.9	9.4
CCE (g/kg)[2]	30	679	254	175	237
ACCE (g/kg)[2]	12	234	88	58	68
pH (water)	4.3	8.6	–	–	–
CEC (cmol$_c$/kg)	2	71	18.3	11.7	15
HM$_{43}$ (g/kg)	2.2	80.0	21.7	14.8	17.7
Fe$_d$ (g/kg)	0.6	35.8	11.0	7.0	10.7

[1] CCE, calcium carbonate equivalent; ACCE, active lime; CEC, cation exchange capacity; HM$_{43}$, hygroscopic moisture at 43% relative humidity; Fe$_d$, citrate/bicarbonate/dithionite-extractable Fe; [2] For carbonate-containing soils ($n = 77$).

free clay content, OC, calcium carbonate equivalent (CCE), active lime (ACCE), pH, cation exchange capacity (CEC) and Fe oxides content (Table 1).

Each soil sample was leached with 1 M ammonium acetate (pH 7), isopropanol and 1 M NaCl (pH 7). CEC was determined by distillation of NH_4^+ in the final leachate with a Hoskins apparatus. The value of HM at an equilibrium air relative humidity (RH) of 43% (HM$_{43}$) was adopted in this study because, in practice, a RH level of 43% can be readily reached in the atmosphere of a closed space (*e.g.*, a desiccator) in equilibrium with a saturated potassium carbonate solution at temperatures over a wide range —its temperature independence makes potassium carbonate superior to other salts— and corresponds to a coverage of about 1.7 layers of water (Churchman *et al.*, 1991).

In the present study an alternative procedure to determine HM was adopted: for each sample HM was determined at different RHs over the 30–50% RH range and then HM$_{43}$ was estimated from the fitted regression line. For the HM measurement at each RH, 4–6 g of soil placed in a weighing bottle were equilibrated with the air in a 200 dm^3 cupboard fitted with a small fan to reduce the time of equilibration to about 1 day. The RH in the cupboard was measured with a MicroLite Temperature/RH Data Logger (fourtec – Fourier Technologies, USA) and only when the RH for the 24 hours preceding weighing of the soil oscillated by less than 2% in absolute value the HM measurement was deemed to be acceptable. In passing, it should be mentioned that, in practice, HM$_{43}$ can also be estimated from the HM value at x RH by using the equation:

$$HM_{43} = HM_x \times [1 + (x - 43) \times 0.0117] \quad [1]$$

where HM$_{43}$ and HM$_x$ are the HM values at a relative humidity of 43% and x, respectively. This equation was

derived from the results for 49 soils studied elsewhere (Sánchez-Alcalá *et al.*, 2014) and is valid for the 30–50% RH range.

Figure 1 testifies to the strong correlation between CEC and HM$_{43}$ ($R^2 = 0.962$). The standard deviation was 2.30 cmol$_c$/kg (*i.e.*, 95% of all observations should fall within ± 4.6 cmol$_c$/kg from the regression line).

Table 2 shows the intercept and slope of the CEC–HM$_{43}$ regression lines corresponding to the four pairs of soil subgroups obtained by classifying the soils according to OC content (above or below 10 g/kg), CEC for the clay fraction (above or below 70 cmol$_c$/kg), presence of carbonate, and moisture regime (xeric or udic; Soil Survey Staff, 1999). Significantly ($p < 0.05$) different intercepts were found between calcareous and noncalcareous soils, and significantly ($p < 0.05$) different intercepts and slopes between soil groups differing in CEC for the clay fraction. Linear slopes
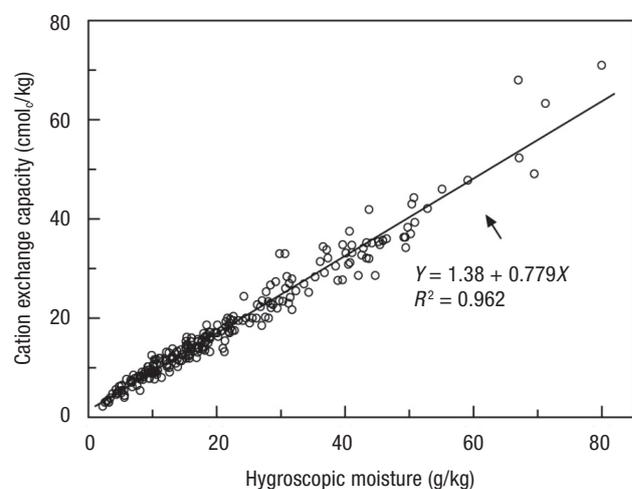
Figure 1. Cation exchange capacity as a function of hygroscopic moisture in equilibrium with a relative humidity of 43%.

Inside figure:
$$Y = 1.38 + 0.779X$$
$$R^2 = 0.962$$

Table 2. Intercept and slope of the regression equation of cation exchange capacity (CEC) against hygroscopic moisture at 43% RH

Soil group	Number of soils	Intercept[1] (cmol$_c$/kg)	Slope[1] (cmol$_c$/g water)
All soils	243	1.38	0.779
Soils with organic carbon > 10 g/kg	96	2.26	0.752
Soils with organic carbon ≤ 10 g/kg	147	0.95	0.792
Soils with CEC for clay > 70 cmol$_c$/kg	143	1.63a	0.781A
Soils with CEC for clay ≤ 70 cmol$_c$/kg	100	1.88b	0.722B
Calcareous soils	77	0.31a	0.795
Noncalcareous soils	166	1.41b	0.793
Soils with xeric moisture regime	203	1.31	0.780
Soils with udic moisture regime	40	2.29	0.744

[1] Different letters following the intercept or slope of the regression lines for each pair of soil subgroups indicate significant differences at the $p < 0.05$ level.

also differed significantly in soils with high CEC values (> 70 cmol$_c$/kg) in their clay fraction as compared to the other soils. This was likely due to the higher smectite contents in soils with high CEC values. Unlike them, soils from temperate areas have illite as their most common silicate clay, which has lower surface charge density and presence of internal surfaces accessible to hydrated cations. The two slopes, however, differed by less than 8% in all instances.

Finally, as expected from the high CEC of the organic soil components, the explained variance in soil CEC increases significantly ($p < 0.05$) (although slightly), if OC is introduced as a new variable in the equation:

$$CEC = 0.48 + 0.778HM_{43} + 0.09OC \qquad [2]$$

with $R^2 = 0.963$ and a standard deviation of 2.26 cmol$_c$/kg.

In summary, the regression equation of Figure 1 affords the simple, robust, inexpensive prediction of soil CEC even if precise information about the soil components influencing CEC is lacking. This performs better than the modest predictive ability of other variables, even when used in combination in a multiple regression model (see, for example, Manrique *et al.*, 1991).

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