RESEARCH NOTE

Acid-neutralizing capacity of Finnish mineral soils

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Abstract. The acid-neutralizing capacity (ANC) was determined graphically from curves obtained in HCl titration (at a constant ionic strength $I = 0.1$) and was expressed as a quantity of acid (meq kg^{-1}) needed to reduce the soil pH to 3.8. The relationship between $ANC_{3.8}$ and soil characteristics was studied statistically.

In 84 soil samples, $ANC_{3.8}$ ranged from 12 to 184 meq kg^{-1}. The average $ANC_{3.8}$ was highest in the heavy clay soils and lowest in the non-clay soils, but the differences between the various textural soil groups were not significant. In all soil groups the initial pH_{CaCl_2} was relatively the most important factor explaining the variation in $ANC_{3.8}$. Organic C was also a significant variable; this was considered to indicate the importance of cation exchange reactions of organic matter in acid-buffering. With the exception of heavy clay soils, oxalate-soluble Al significantly explained the variation in $ANC_{3.8}$, suggesting that dissolution of Al hydroxides acted as a sink for H^+ ions and contributed to the neutralizing capacity at the reference pH of 3.8.

Index words: acid-neutralizing capacity, soil acidity, titration, pH-buffering

Introduction

From the agricultural and ecological point of view soil pH is a very enlightening attribute of a soil. In addition to intensity of acidity it indicates the chemical and biological condition of a soil. Addition of H^+ ions to the edaphic system generally, but not always, decreases soil pH; any alterations depend on the buffering properties of the respective soil. Soil acidification is actually defined as a decrease in acid-neutralizing capacity rather than as a decrease in pH (VAN BREEMEN et al. 1983).

The intensity of buffering depends on the type of buffer system present, whereas the capacity is determined by its size. In a study of HARTIKAINEN (1985) on the intensity of acid- and base-buffering, the acid quantities needed to reduce soil pH by 0.5 units were the higher the lower the initial soil pH was. It was further observed that in soils of different initial pH levels the variation in buffer values was explained by different soil factors. In the present study on the acid-neutralizing capacity and related soil characteristics, attention was paid to the capacity of soils in various

textural classes to counterbalance the effect of acidifying factors.

Materials and methods

a) Soil samples

The experimental material, collected from southern and central Finland, consisted of 15 heavy clay soils (60 % or more clay fraction < 2 μm), 41 coarser clay soils (30—59 % clay), 20 silt soils (main fraction 2—20 μm) and 8 fine sand soils (main fraction 20—200 μm). The characteristics of the soils are presented in Table 1.

The air-dried 2-mm sieved samples were analysed for pH in a 1:2,5 0.01 M $CaCl_2$ suspension and for organic C by the wet combustion method (GRAHAM 1948). Exchangeable basic cations displaced with 1 M NH_4OAc (pH 7.0) were determined by AAS (Ca and Mg) or by flame photometry (K and Na). Al, Fe, and Mn extracted with 0.05 M NH_4-oxalate (pH 3.3) (1:20 $^w/_v$) and Al extracted with 1 M NH_4OAc (pH 4.8) (according to McLEAN 1965) were determined by AAS.

b) Determination of acid-neutralizing capacity

Analogously to aqueous systems, the acid-neutralizing capacity (ANC) of the soils can be determined by titration with a strong acid to a given reference pH. In the present study, a batch titration method was used: 5 g of soil was treated with 50-ml volumes of solutions containing 0, 0.3, 0.6, 0.9, 1.2 or 1.5 meq HCl

at an ionic strength of I = 0.1 (adjusted by KCl).

After a 4-day equilibration (stirred once), the pH of the suspensions was measured with an analogous pH-meter, using a separate reference electrode. The titration graphs were drawn by expressing the measured pH as a function of acid added. The ANC was determined graphically from the curve and expressed as a quantity of acid (meq kg^{-1}) needed to reduce the soil pH to 3.8. In other words, the ANC stands for H^+ consumption between the pH of zero point of titration (ZPT), i.e. pH in 0.1 M KCl, and pH_{KCl} 3.8. The subindex of ANC denotes the reference pH.

The titration was carried out in duplicate. The precision of the method is described in details elsewhere (HARTIKAINEN 1985).

Results and discussion

The magnitude of ANC depends on the reference pH chosen. According to VAN BREEMEN et al. (1983), a pH of 5 might be appropriate for agricultural soils and that of 3 more reasonable for forest soils. The reference pH of 3.8 used in the present study is intermediate, but from an ecological point of view it may be universal for soils of undefined utilization.

The $ANC_{3.8}$ ranged from 12 to 184 meq kg^{-1}, the average and median being 68.8 and 58.0 meq kg^{-1}, respectively. It decreased with increasing initial soil acidity; the correlation of $ANC_{3.8}$ vs. soil pH_{CaCl_2} was r = 0.77*** (n = 84). The correlation between log

Table 1. Characteristics of soil samples. Means with confidence limits at 95 per cent, w = range.

	pH ($CaCl_2$)	Org. C % of D.M.	Oxal. extr. Al	Fe mmol kg^{-1}	Acet. extr. Al mmol kg^{-1}	Basic cations meq kg^{-1}
Heavy	5.1±0.3	5.0±1.3	97±28	91±15	10.5±5.8	229±68
clays w	4.2—6.0	1.0—9.0	45—255	30—149	2.2—39.4	103—613
Coarser	5.2±0.2	4.2±0.6	62±6	72±9	6.4±1.4	128±13
clays w	4.3—6.5	0.5—11.9	28—111	31—171	1.3—18.9	61—219
Non-clay	5.2±0.3	3.5±0.7	60±12	62±6	7.1±2.3	98±17
soils w	3.8—6.4	0.7—7.7	17—141	33—112	1.4—21.2	24—206

Table 2. $ANC_{3.8}$ (meq kg^{-1}) of soils in different textural groups. Means with confidence limits at 95 per cent level.

	$ANC_{3.8}$	Range
Heavy clays	76.1 ± 17.9	22—134
Coarser clays	69.3 ± 9.4	40—158
Non-clay soils	64.1 ± 12.7	12—184

$ANC_{3.8}$ and pH was not significantly closer (r = 0.78***). Furthermore, the neutralizing capacity tended to increase with the increase in exchangeable basic cations, the correlation coefficient being r = 0.46***. It should be pointed out that when a heavy clay sample exceptionally rich in NH_4OAc soluble cations was excluded, the value of r rose to 0.64***.

On the other hand, $ANC_{3.8}$ did not correlate with the clay content of soils (r = 0.12). In fact, there were great variations in the neutralizing capacity within the textural groups, but the differences between the various soil classes were not noticeable (Table 2). Certainly, the average $ANC_{3.8}$ was highest in the heavy clay soils and lowest in the non-clay soils.

When the dependence of $ANC_{3.8}$ (y) on the soil characteristics was studied by the regression analysis, only soil pH_{CaCl_2}, the content of organic C (%) and oxalate-extractable Al (mmol kg^{-1}) were statistically significant variables (P = 0.05). In various textural soil groups the relationship conformed to the following equations:

Heavy clay soils:
y = 65.68 pH + 10.29 org. C — 307.59
R^2 = 0.82***
Standard error of estimate S = 14.66
Coarser clay soils:
y = 55.91 pH + 2.12 org. C + 0.45 oxal. Al — 257.81
R^2 = 0.88***
S = 10.61
Non-clay soils:
y = 51.91 pH + 7.95 org. C + 0.26 oxal. Al — 246.97
R^2 = 0.81***
S = 14.94

On the basis of β-coefficients the initial soil pH was the most decisive factor in all soil groups. In the non-clay soils the relative importance of organic C content was greater than that of oxalate soluble Al, whereas a reverse rank was found in the coarser clay soils.

More detailed studies are needed to clarify the causes for different buffer capacities of different soils and the mechanisms responsible for buffer action, but some interpretations can be discussed. Generally, in all textural groups the same factors explained the variation in the acid-neutralizing capacity. However, in the heavy clay soils, where the organic C and oxalate-soluble Al were highly correlated (r = 0.77***), the oxalate-soluble Al was excluded from the equation. Although it explained 17 % of the variation it was insignificant owing to the small number of samples.

The relationship between ANC and pH is consequential, because a higher activity of H^+ ions (lower pH) can be considered a result of a reduced inactivation ability of soil. The other factors explaining the variation in ANC depend on the reference pH chosen. Virtually, the reference pH determines which buffer systems are involved. ULRICH (1981) has demonstrated the characteristic chemical soil state for various buffer ranges and calculated the pH of 3.8 (in equilibrium soil solution) to represent the upper limit of the iron buffer range. In the present study, the oxalate-soluble Fe was insignificant in explaining the variation in $ANC_{3.8}$, which suggests that the iron buffer range was not reached. The oxalate-soluble Al, on the contrary, was a significant variable, infering that the dissolution of Al hydroxides might act as a sink for H^+ ions. The buffering by this mechanism can be expected to be ample but ecologically harmful.

The contribution of organic C may be attributable to the significance of organic matter as cation exchanger and indicate the role of exchange reactions in acid-buffering. The H^+ ions exchange cations directly only on slightly acid (variable) charge sites (VEITH and SCHWERTMANN 1972) the main source of

which in Finnish soils is generally organic matter. Thus, an influx of H^+ to soil implies a reduction in effective cation exchange capacity even though not necessarily in pH. However, especially at higher reference pHs, the organic C may be a poor measure of the buffering capacity due to organic matter. The pK_a values of organic constituents range from 3.8 to 6.2 (Martin and Reeve 1958, Hargrove and Thomas 1982), wherefore also the efficiency of organic matter as proton acceptor can be concluded to vary.

Further studies on the ANC values at various reference pHs are needed to give estimates on the susceptibility of our soils to various acidifying factors. On the other hand, also studies on the type and kinetics of proton consuming reactions are necessary in order to infer the ecological consequences of acid-buffering reactions.

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SELOSTUS

Suomalaisten kivennäismaiden haponneutralointikapasiteetti

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Laboratoriokoe tehtiin Etelä- ja Keski-Suomesta kerätyillä 84 maanäytteellä, joista 15 luokiteltiin aitosaveksi, 41 hiesu- tai hietasaveksi, 20 hiesuksi ja 8 hiedaksi. Ilmakuivista maista otettiin 5 g:n eriä, joihin lisättiin 50 ml titrausliuosta, jossa oli 0, 0.3, 0.6, 0.9, 1.2 tai 1.5 mekv HCl:ää. Jokaisen titrausliuoksen ionivahvuus (I) oli säädetty KCl:llä 0.1:ksi. Neljän päivän reaktioajan jälkeen suspensioiden pH mitattiin ja mittaustuloksista piirrettiin käyrä, jossa pH esitettiin happolisäyksen (mekv kg⁻¹ maata) funktiona. Haponneutralointikapasiteetti (ANC) ratkaistiin graafisesti ja ilmoitettiin happomääränä (mekv kg⁻¹), joka tarvittiin laskemaan maan pH 3.8:aan.

Tutkituissa näytteissä $ANC_{3.8}$ vaihteli 12—184 mekv kg⁻¹. Keskimääräinen neutralointikapasiteetti oli suurin (76 mekv kg⁻¹) aitosavissa, seuraavaksi suurin (69 mekv kg⁻¹) hiesu- ja hietasavissa ja pienin (64 mekv kg⁻¹) hiesu- ja hietamaiden muodostamassa ryhmässä. Maalajiryhmien väliset erot eivät kuitenkaan olleet tilastollisesti merkitseviä. Koko aineistossa neutralointikapasiteetti ei korreloinut saveksen pitoisuuden kanssa. Saves-% ei myöskään ollut tilastollisesti merkittävä selittäjä regressioyhtälöissä, joilla pyrittiin kuvaamaan $ANC_{3.8}$:n ja maan ominaisuuksien välistä suhdetta. Voimakkaimmin $ANC_{3.8}$ riippui maan alkuperäisestä pH:sta. Orgaanisen

hiilen pitoisuus oli merkittävä selittäjä kaikissa maalaji-ryhmissä, minkä katsottiin olevan osoitus orgaanisen aineksen kationinvaihtoreaktioiden merkityksestä hapon puskuroinnissa. Aitosavien ryhmää lukuunottamatta oksalaattiuuttoinen Al oli kolmas merkitsevästi $ANC_{3.8}$:n vaihtelua selittävä tekijä. Tämä viittaa siihen, että Al-hydroksidien liukenemiseen perustuva puskurointimekanismi alkaa tuntuvasti vaikuttaa neutralointikapasiteetin arvoon, kun referenssi-pH:ksi on valittu 3.8.