

RESEARCH NOTE



Base-neutralizing capacity of Finnish mineral soils

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Abstract. The base-neutralizing capacity, BNC_7 (OH^- as $meq\ kg^{-1}$ needed to raise soil pH to 7), was determined graphically from curves obtained in KOH titration (at a constant ionic strength of $I = 0.1$). In 84 soil samples, BNC_7 amounted to 0—316 $meq\ kg^{-1}$, being highest in the heavy clay soils and lowest in the non-clay soils. In different textural groups, BNC_7 seemed most markedly to be dependent on the initial soil pH, followed by organic C or oxalate soluble Al, in the coarser clays also on clay content. The results evidence that in determination of lime requirement, attention should be paid to the capacity of soil acidity. In routine soil testing, detailed lime recommendations for various soil types are needed.

Index words: base-neutralizing capacity, soil acidity, titration, pH-buffering, lime requirement, soil testing

Introduction

Since KAMPRATH (1970) proposed the exchangeable Al as a criterion for liming, various lime recommendations have been discussed widely. Some of them are based on the amount of base required to bring a soil to a given pH and others on that needed to inactivate toxic substances. In Finnish soils Al, not only as monomeric trivalent ion but probably to a much greater extent as polymeric hydroxy-Al, increases the amounts of lime needed to amend the acidity (KAILA 1971). However, in routine soil testing the liming recommendations are based on $pH_{(H_2O)}$ and NH_4 -acetate (pH 4.65) extractable Ca. MÄN-TYLAHTI and YLÄRANTA (1980) have found

this method rather unsatisfactory especially for mineral soils where it overestimates the requirement. They proposed a titrimetric method for a more precise determination. The purpose of the present study was to estimate the base-neutralizing capacity of Finnish mineral soils in various textural groups. The soil factors accounting for its variation were investigated statistically.

Material and methods

The material consisted of 15 heavy clay soils (60 % or more clay fraction $< 2\ \mu m$), 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 analytical methods and soil characteristics are reported in a previous paper (HARTIKAINEN 1985).

The method of batch base-titration and its precision are presented in detail elsewhere (HARTIKAINEN 1986). In brief, 5 g of soil was treated in duplicate with 50 ml of solutions containing 0, 0.3, 0.6, 0.9, 1.2, or 1.5 meq base (KOH) at an ionic strength of $I = 0.1$ (adjusted by KCl), equilibrated for 4 d (stirred once). Thereafter pH was measured with an analogous pH-meter, using a separate reference electrode. The base-neutralizing capacity (BNC) was determined graphically from the titration curves and expressed as a quantity of base (meq kg^{-1}) needed to elevate the soil pH to 7.

Results and discussion

In 84 samples BNC_7 ranged from 0 to 316 meq kg^{-1} , the average and median being 107 and 95 meq kg^{-1} , respectively. As expected, it tended to increase with decreasing soil pH, the correlation of $\log \text{BNC}_7$ vs. $\text{pH}_{\text{CaCl}_2}$ being $r = -0.84^{***}$ ($n = 0.83$). In the three textural classes BNC_7 was markedly higher in the heavy clay soils than in other soil groups. The mean values with 95 % confidence limits and ranges were as follows:

	BNC_7	range
Heavy clays ($n = 15$)	164.8 ± 44.8	68–316
Coarser clays ($n = 41$)	101.9 ± 16.2	16–232
Non-clay soils ($n = 28$)	82.2 ± 20.4	0–212

In all samples, BNC_7 correlated closely also with NH_4 -acetate and NH_4 -oxalate soluble Al ($r = 0.85^{***}$ and 0.77^{***} , respectively), followed by organic C ($r = 0.72^{***}$) and clay content ($r = 0.50^{***}$). When its dependence on soil characteristics was investigated by the regression analysis, the statistically significant variables were: organic C (C_{org} , %), oxalate soluble Al (Al_o , mmol kg^{-1}), soil $\text{pH}_{\text{CaCl}_2}$, and clay content (clay, %).

In the heavy clays the relationship between BNC_7 (y) and soil characteristics conformed to the equation:

$$y = 10.70 C_{\text{org.}} + 0.50 \text{Al}_o - 90.34 \text{pH} + 519.27$$

The coefficient of multiple determination R^2 was 0.93^{***} and the standard error of estimate S was 23.77.

In the coarser clays, also the clay content was included in the equation:

$$y = 6.31 C_{\text{org.}} + 0.74 \text{Al}_o + 0.90 \text{clay} - 54.56 \text{pH} + 276.56$$

$$R^2 = 0.91^{***}, S = 16.44$$

In the non-clay soils the equation was:

$$y = 9.21 C_{\text{org.}} + 0.31 \text{Al}_o - 54.43 \text{pH} + 311.74$$

$$R^2 = 0.91^{***}, S = 16.87$$

The relative importance of various variables affecting the BNC_7 values may be compared on the basis of the β -coefficients:

	pH	$C_{\text{org.}}$	Al_o	clay
Heavy clays	-0.52	0.31	0.31	—
Coarser clays	-0.61	0.23	0.29	0.15
Non-clay soils	-0.68	0.30	0.19	—

BNC_7 seems to depend most markedly on soil $\text{pH}_{\text{CaCl}_2}$, followed by organic C in the non-clay soils and by oxalate soluble Al in the coarser clay soils. In the heavy clay soils these variables appear to be equally important. The results show a similar trend as reported in an earlier study of KAILA (1971) where the relative importance of oxalate soluble Al explaining the variation in titratable non-exchangeable acidity was in the clay soils greater than that of organic C, but in the other mineral soils it was less important. The soils being classified according to their clay content reduced the range and, thus, the importance of clay in various groups.

The differential base-buffer values (OH^- as meq kg^{-1} needed to raise soil pH sequentially by 0.5 units) and their dependence on soil properties have been studied earlier (HARTIKAINEN 1986). In soils of various pH ranges the soil characteristics explaining the variation in base-buffer values varied markedly: oxalate soluble Fe, various fractions of Al (exchangeable, non-exchangeable acidic

and oxalate soluble Al), clay content and organic C. The clay content was of significance only in the strongly acid soils ($\text{pH}_{\text{ZPT}} \leq 4.8$) where its role in base-buffering in the beginning of titration was concluded to be due to H^+ ions on the permanent charges of minerals. As the exchange of H^+ ions from permanent charges is stated to constitute only a relatively small amount of exchangeable acidity (VEITH 1977), at least in the later phase of the titration the role of clay was assumed to be attributable to other buffering mechanisms, e.g. by release of Al from the inter-lattice space of Al-chlorites.

In principle, the BNC value stands for a cumulative effect of factors responsible for buffer action during a stepwise titration. Thus, the components that contribute to BNC depend on the reference pH chosen. Oxalate soluble Fe excluded, all factors earlier found by HARTIKAINEN (1986) to affect the buffer values in various pH categories were in effect included in the variables explaining the variation in BNC_7 in the present study.

In all textural soil groups pH, i.e. intensity of acidity, was a decisive variable. However, several forms of acidity account for the total acidity of a given soil. Numerous compounds contain undissociated H^+ , and a stepwise dissociation of H^+ occurs with increasing pH. Thus, the other variables involved, even though related to the capacity of acidity, are indirectly connected also with the nature of acidity. There is a close relationship between pH and various fractions of Al (e.g. MARION et al. 1976). Yet, soil pH is a poor measure

of Al concentration of soil solution, because organic matter controls the relationship between pH and Al^{3+} activity in acid soils (HOYT 1977, BLOOM et al. 1979, JAMES and RIHA 1984).

The results evidence that if the titration method cannot be adopted in routine soil testing, it is necessary to frame individual lime recommendations for various textural soil types. In the determination of lime requirements, attention should be paid to soil factors related to the capacity of soil acidity.

For agricultural purposes, a reference pH lower than 7 is, of course, more appropriate and more realistic. It should be taken into account that the beneficial effects of a higher pH on microbial activity and availability of plant nutrients are, at least to some extent, masked by current fertilization practice. If all essential elements are provided in adequate quantities, lime amounts only sufficient to eliminate toxic elements (e.g. exchangeable or soluble Al) or to reduce their concentrations to a low level are needed to obtain maximal yields (KAMPRATH 1970, SCHWERTMANN and ATTENBERGER 1979, WEBBER et al. 1982). Some viewpoints do, however, justify liming over this critical pH level. Important consequences of base treatment include an increase in the effective charge density, resulting in a reduction in leaching losses of essential basic cations, as well as an increase in the acid-neutralizing capacity of soils.

Acknowledgement. The author wishes to thank the Maj and Tor Nessling Foundation for the grant which made it possible to complete this study.

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Ms received April 15, 1986

SELOSTUS

Suomalaisten kivennäismaiden emäksen-neutralointikapasiteetti

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Laboratoriossa tehdyssä titrauskokeessa selvitettiin 84 maanäytteen (15 aitosavi-, 41 hiesusavi- tai hietasavi-, 20 hiesu- ja 8 hietanäytettä) kykyä neutraloida emästä. Ilmakuiviin 5 g:n maaeriin lisättiin 50 ml emäsluosta, jossa oli 0, 0.3, 0.6, 0.9, 1.2 tai 1.5 mekv KOH ja ionivahvuus säädetty 0.1:ksi KCl:llä. Suspensioiden annettiin reagoida 4 päivää, minkä jälkeen niiden pH mitattiin. Emäksenneutralointikapasiteetti ratkaistiin graafisesti käyrältä, jossa mitattu pH esitettiin emäslisäyksen (mekv kg^{-1} maata) funktiona. Se ilmoitettiin emäsmääränä (mekv kg^{-1}), joka tarvittiin nostamaan maan pH 7:ään.

Emäksenneutralointikapasiteetti (BNC_7) vaihteli 0—316 mekv kg^{-1} . Keskimääräinen BNC_7 näytti olevan aitosavissa selvästi suurempi (165 mekv kg^{-1}) kuin hiesuja hietasavissa (102 mekv kg^{-1}) tai hiesujen ja hietojen muodostamassa maalajiryhmässä (82 mekv kg^{-1}). Koko aineistossa saveksen pitoisuus korreloi kuitenkin suhteellisen löyhästi BNC_7 :n kanssa ja selitti vain 25 % sen

vaihtelusta. Maa-aineksen ominaisuuksien ja BNC_7 :n välistä suhdetta kuvaavissa regressioyhtälöissä savespitoisuus oli merkitsevä selittäjä vain hiesu- ja hietasavista muodostetussa maalajiryhmässä. β -kertoimien perusteella BNC_7 riippui kaikissa maalajiryhmissä voimakkaimmin maan alkuperäisestä pH:sta l. happamuuden intensiteetistä. Myös orgaaninen hiili ja oksalaattiuuttainen Al olivat merkitseviä selittäjiä. Näiden happamuuden luonnetta ja kapasiteettia kuvaavien tekijöiden merkitys eri maalajiryhmissä näytti kuitenkin jonkin verran vaihtelevan: Al oli suhteellisesti tärkeämpi hiesu- ja hietasavissa, orgaanisen hiilen pitoisuus hiesu- ja hietamaissa, mutta aitosavissa kumpikin tekijä oli yhtä tärkeä. Koska kalkitustarpeen arvioinnin tulisi perustua maan lähtö-pH:n lisäksi myös happamuuden kapasiteettitekijöihin, tulos viittaa siihen, että kivennäismaille annettavia kalkitusuusi-tuksia laadittaessa on syytä kiinnittää huomiota eri maalajien välisiin eroihin.