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RELATIONSHIPS BETWEEN BUFFER ACIDITY AND EXCHANGEABLE
ACIDITY IN LIME TRIALS WITH ULTISOLS AND HISTOSOLS¹

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ABSTRACT

Lime requirements ordinarily are based on buffer methods but could be based on unbuffered salt-exchangeable acidity. The relationships between exchangeable acidity (EA) and buffer acidity (BA) were studied across a range of pH levels established through lime trials in four Ultisols and one Histisol in North Carolina Coastal Plain and Piedmont regions. Buffer acidity was proportionately higher than EA in all soils at any pH level. Linear regression slopes between either BA or EA and pH, within each soil, were not significantly different when the latter relationship included samples with pH less than or equal to 5.4. Variations in EA accounted for by BA ranged from 41 to 67% among the soils investigated. Buffer acidity alone accounted for 64% of the variation in EA for samples from all soils with pH less than or equal to 5.4. Including a squared BA term and either HM or CEC increased the R^2 to 0.79 and 0.86, respectively, but neither equation provided a completely suitable prediction of EA across all five soils investigated.

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INTRODUCTION

Most soil test labs determine lime requirement (LR) through the decline in pH which occurs after equilibrating soils with buffer solutions. Decreases in pH are calibrated against the lime required to raise the soil pH to a targeted value (1, 14, 17). Most buffer methods seek to obtain a soil pH of 6-7, the rationale being that this pH range is suitable for optimal plant growth in mineral soils (15). Ideal pH ranges, however, are known to vary with soil organic matter content.

Several investigators have obtained accurate estimates of LR based on unbuffered salt-exchangeable soil acidity (4, 5, 6, 7, 8). Most U.S. labs prefer the former approach because they wish to avoid the additional soil extraction.

Mehlich (10) developed a buffer method for estimating exchangeable acidity (EA) without the extraction and titration steps. This buffer consisted of a mixture of triethanoamine (TEA), acetic acid, NH_4Cl , BaCl_2 and sodium glycerophosphate. Comparisons of salt-exchangeable acidity with acidity measured by this buffer for a number of mineral soils provided good correlations and linear regression slopes near unity (10, 16). However, none of the reported investigations on this buffer indicated whether similar relationships between EA and buffer acidity (BA) could be obtained when pH is altered within a given soil. Using field liming trials, this study was undertaken with the objective of evaluating relationships between EA and BA at different pH levels in four Ultisols and a Histisol.

MATERIALS AND METHODS

Soil samples (0-15 cm) were collected in 1987 from lime experiments at five different sites in the North Carolina Coastal

Table 1. Class, sample size and range of selected characteristics for the soils used in the investigation.

Series	Class	Sample size	pH	Exchangeable acidity	Buffer acidity	CEC	Humic matter
					cmol _c L		g L
Belhaven	O	48 (42)	4.3-5.7(5.4)	0.2(0.4)-4.4	2.8(3.6)-7.4	6.8-15.7(11.7)	48-155
Cape Fear	M-0	93(55)	4.8-6.6(5.4)	0.1(0.2)-1.7	0.1(2.8)-4.7	8.0-18.2(12.6)	35(38)-57
Goldsboro	M	48(37)	4.4-6.0(5.4)	0.1(0.2)-1.3	0.8(1.1)-2.5	2.7-6.2(5.1)	6-14
Cecil	M	30(24)	4.4-6.1(5.4)	0.1(0.2)-0.8	0.8(1.5)-2.8	4.2-7.8(7.2)	4-8
Wagram	M	48(45)	4.5-5.8(5.3)	0.2(0.3)-0.9	1.2(1.4)-3.0	2.1-4.3(4.3)	2-4

The classification of the series according to Soil Taxonomy is:

Terric Medisaprist; loamy, mixed, dysic, thermic.
 Typic Umbraquilt; clayey, mixed, thermic.
 Aquic Paleudult; fine-loamy, siliceous, thermic.
 Typic Hapludult; clayey, kaolinitic, thermic.
 Arenic Kandudult; loamy, siliceous, thermic.

O=organic; M-C=mineral-organic; M=mineral.

Values in parentheses indicate changes in sizes and ranges of sample subsets used for regression analyses of EA vs. BA or pH.

Plain and Piedmont regions. Each experiment contained an unlimed treatment and two to four lime rates, applied more than 18 months before sampling. These lime treatments were reflected by the range of pH, EA, BA and cation exchange capacity (CEC) values within samples from each experiment (Table 1). According to North Carolina soil test guidelines, three soils were classed as mineral ($<35 \text{ g L}^{-1}$ humic matter, HM), one as mineral-organic ($35\text{-}52 \text{ g L}^{-1}$ HM) and one as organic ($>52 \text{ g L}^{-1}$ HM).

Soil samples were air-dried, crushed and passed through a 2 mm sieve. Soil pH, HM, BA and Mehlich 3 extractable (11) Ca, Mg, K and Na were analyzed by the NCDA Agronomic Division Soil Testing Laboratory. Soil pH was determined in a 1:1 soil:water suspension followed by buffer pH (BpH) determination in a 1:1:1 soil:water:buffer suspension. Buffer acidity was calculated by the formula $BA = (6.6 - \text{BpH})/0.25$ (10). Cation exchange capacity was calculated by the summation of Ca, Mg, K, Na and BA. Humic matter was determined by photometry (12). Exchangeable acidity was extracted from the soil after 5 minutes contact with 1 M KCl at a 1:10 soil-solution ratio and determined by titrating to the phenolphthalein end point with 0.01 M NaOH.

Relationships between EA and BA, EA and pH, and BA and pH within each soil were established with regression procedures in the Statistical Analysis System (13). The maximum R^2 improvement option of the stepwise regression analyses procedure was used to select variables for multiple regression prediction of EA across all soils. Variables included were BA, HM, CEC, their squared terms and their interaction terms. A minimum of 2% improvement in the R^2 was required to maintain a variable in the equation. Individual observations were used to generate all regression equations.

RESULTS AND DISCUSSION

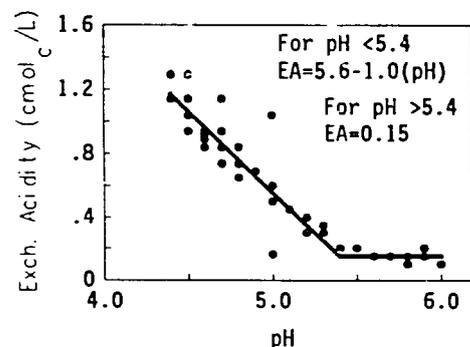
Subdividing Soil Samples for Regression Analyses

A preliminary screening of relationships between EA and either BA or pH within each soil revealed that trends were curvilinear when observations from all lime treatments were included. Below a pH of 5.5 the relationships were linear. Above this pH, EA levels were low and regression slopes approached zero. These trends were consistent with previous observations that soils have little exchangeable Al above pH 5.5 (15). Linear components of EA vs. pH relationships for each soil were defined by linear-plateau techniques (2). Intercepts for the two lines occurred at pH 5.4 in all soils, as shown for the Goldsboro soil in Figure 1. Coefficients of determination (r^2 values) among soils for this regression model ranged from 0.87 in the Goldsboro soil to 0.90 in Wagram soil. Subsequent evaluations of relations between EA and either pH or BA were, therefore, performed with samples of pH less than or equal to 5.4. Sample size and range in chemical properties for the subsamples in each soil are indicated in Table 1.

Buffer and Exchangeable Acidity Relationships with pH

Linear regression equations relating BA and EA to pH are shown in Table 2 for each soil. Except for the Cape Fear soil, EA provided a higher correlation with pH than BA. Regression slopes relating EA or BA to pH within each soil were not significantly different (5% probability level).

Results showed that BA was proportionately higher than EA for any given pH up to 5.4. At higher pH levels EA values were low and constant. Mehlich (10) compared BA with neutral 0.6 M BaCl_2 exchangeable acidity and BaCl_2 -TEA extractable acidity in several



1. Exchangeable acidity as a function of pH in the Goldsboro soil.

Table 2. Linear regression equations between BA or EA as a function of pH in the soils studied.

Dependent variable	Soil	Equation	r
BA	Belhaven	$y = 17.89 - 2.59x$	0.84
	Cape Fear	$y = 13.53 - 1.94x$	0.95
	Goldsboro	$y = 5.59 - 0.78x$	0.85
	Cecil	$y = 6.42 - 0.88x$	0.88
	Wagram	$y = 7.03 - 1.02x$	0.81
EA	Belhaven	$y = 16.92 - 3.07x$	0.92
	Cape Fear	$y = 10.35 - 1.88x$	0.89
	Goldsboro	$y = 5.44 - 0.97x$	0.88
	Cecil	$y = 3.32 - 0.58x$	0.92
	Wagram	$y = 3.77 - 0.65x$	0.94

All regression slopes were significant at the 5% probability level.

North Carolina mineral and organic soils. He observed that BA measured comparable sources of acidity to exchangeable acidity when the proportion between the latter form and BaCl_2 -TEA acidity was low. Marked reductions in BaCl_2 -TEA acidity were not observed until pH was raised to levels where most of the exchangeable acidity was neutralized.

Relationships Between EA and BA

Linear regression equations and correlation coefficients between EA and BA are shown in Table 3 for each soil. Variations in EA accounted for by BA ranged from 41% in the Goldsboro soil to 67% in the Cape Fear soil. These results contrasted with the high correlation (0.97) Mehlich (10) obtained between 0.6 N BaCl_2 exchangeable acidity and BA for 91 mineral soils from North Carolina, Southeastern United States and the Colombian Amazon. Regression slope values for the three mineral soils and one organic soil in the present study also were considerably lower than the respective values of 0.96 and 1.6 reported for similar soil classes in the previous study.

Benavides (3) also obtained a high correlation (0.96) between EA and BA on 68 mineral soils from the Colombian Amazon. He found the slope for the regression equation to be 1.4. Tran and van Lierop (16) obtained a linear relationship between EA and BA for 37 coarse-textured soils with EA and pH ranges of 0.3 to 5.4 $\text{cmol}_c \text{ kg}^{-1}$ and 3.8 to 5.2, respectively. However, the precision of this relationship ($r = 0.77$) was similar to the ones reported in the present study.

Discrepancies between our results and those reported by Mehlich (10) and Benavides (3) may be related to differences in the composition of the soil samples included in each investigation.

Table 3. Linear regressions equations and correlation coefficients between EA and BA for the soils at pH<5.4.

Soil	Equation	r
Belhaven	EA = - 1.90 + 0.74(BA)	0.75
Cape Fear	EA = - 1.83 + 0.71(BA)	0.82
Goldsboro	EA = - 0.30 + 0.58(BA)	0.64
Cecil	EA = - 0.53 + 0.47(BA)	0.78
Wagram	EA = - 0.10 + 0.34(BA)	0.66

All regression slopes were significant 5% at the probability level.

Variations in BA and EA in the previous studies resulted from the large number of sites sampled in different geographic regions. In the present investigation, variations in acidity parameters were related to both site differences and lime treatments within each site. Nevertheless, our findings would suggest that EA at variable pH levels within a given soil cannot be predicted by a linear relationship developed across a broad range of soils.

Multiple Regression Equations

Linear regression slopes between EA and BA among the five soils (Table 3) were noted to increase with levels of HM and CEC (Table 1). Since both of these soil parameters have been shown to influence LR interpretations with other buffer methods (9), it is also possible that the low correlation between EA and BA within soils could be improved by accounting for the variations in HM and CEC among the samples. These soil properties were therefore evaluated individually in regression equations relating EA and BA across all soils in the study.

For equations with HM the variables considered were BA, HM, their squared terms and the interaction among the linear terms. Buffer acidity alone accounted for 64% of the variability in EA across all soil samples. The inclusion of BA² as the second term increased the R² to 0.76. Humic matter was the third and final variable included and the R² was increased to 0.79. The final regression equation was:

$$EA = 0.7808 - 0.3181(BA) + 0.1267(BA)^2 - 0.0094(HM) \quad [1]$$

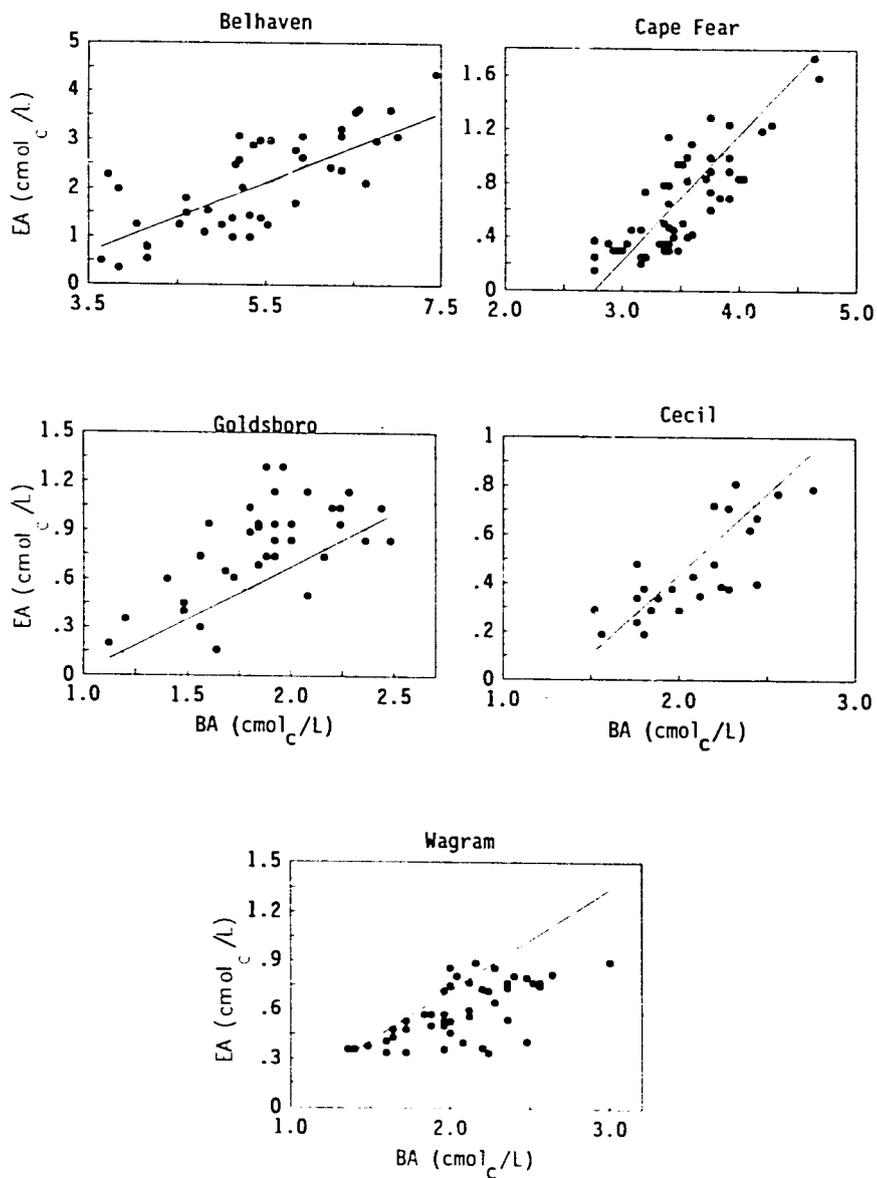
Regression coefficients for all variables retained in the final equation were significant (P = 0.05).

Variables considered in the equation with CEC were BA, CEC, their squared terms and the interaction among the linear terms. When CEC was added to the equation after BA, the proportion of variability in EA accounted for increased from 64 to 86%. The third and final variable included in the equation was CEC² which increased the R² to 0.88. The final equation was:

$$EA = - 0.6408 + 0.6565(BA) + 0.0632(CEC) - 0.0161(CEC)^2 \quad [2]$$

Once the squared CEC term was added to the equation the regression coefficient for CEC was not significant. Nevertheless, it was maintained in the equation because of its contribution to the R².

Measured EA and EA predicted by equations [1] and [2] are compared in Figure 2 as a function of measured BA in each of the five soils. Lines for predicted EA were obtained through linear regressions of EA, calculated by each equation, for the levels of BA and HM or CEC in samples for each soil. Both equations provided a good fit to the observed data in the Belhaven soil which contained the highest levels of BA, EA, CEC and HM. In the Cape Fear and Cecil soils the equation with CEC provided a closer fit to the observed



2. Measured (symbols) and predicted (lines) EA as a function of BA for each soil. Dashed and solid lines denote linear regressions of EA estimated by equations [1] and [2], respectively.

trends between EA and BA than the equation containing HM. However, the latter equation provided a better fit to the observed data in the Wagram soil. Neither equation provided a reasonable fit to the observed data in the Goldsboro soil which had the poorest correlation between observed EA and BA (Table 3).

Although estimates of EA from measured BA were improved by consideration of either CEC or HM, both of which are routinely measured in soil tests, neither variable provided a good estimate across all soils investigated. Further investigations with a greater number of soils varying in HM and CEC are needed to validate, refine and/or improve these relationships. Application of this concept has the potential for improving the LR determination and resultant lime recommendation. Since soil acidity derived from organic matter is also expressed by CEC, the latter variable may be more useful in relating EA and BA.

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