

An empirical analysis of the factors contributing to 20-year decrease in soil pH in an old-field plantation of loblolly pine

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Abstract. The pH of weak-acid solutions is controlled by acid concentration ($\text{HA} + \text{A}^-$), the degree of acid dissociation (A^-/HA), and the strength of the acids present (pK_a). We developed an empirical approach that allows the relative importance of each of these factors to be estimated for soils. This empirical model was applied to soils collected from an old-field plantation of loblolly pine (*Pinus taeda* L.) at 5 and 25 years of age. During this period, soil pH dropped by 0.3 to 0.8 units, and extractable calcium, magnesium and potassium declined by 20 to 80%. The empirical model indicates that the decline in pH resulted largely from the reduction in base saturation of the exchange complex. However, the average acid strength of the exchange complex decreased during the 20 years, preventing a greater decline of perhaps 0.1 to 0.2 units in the observed pH. The rate of decrease in the acid neutralizing capacity to pH 3.5 was about 1.3 kmol_c/ha annually, while the increase in base neutralizing capacity was about 2.7 and 1.6 kmol_c/ha annually to pH 5.5 and 8.2, respectively. Extractable alkali and alkaline earth cations declined by about 2.2 kmol_c/ha annually, matched by the rate of increase in aluminium. These changes demonstrated the dynamic nature of poorly buffered soils, and indicated that changes in soil acidity may be expected over a period of decades (especially following changes in land-use).

Concern over possible effects of acid deposition on soils has stimulated research in the processes and rates of soil acidification (see Van Breeman et al. 1983; Ulrich & Pankrath 1983; Reuss & Johnson 1986). Tabatabai (1985) concluded that, "it is clear that since forest soils are usually acidic in reaction, measurable effects are not possible in such soils." However, the few studies that have been able to examine changes in soil pH over periods of one to several decades (Brand et al. 1986; Tamm & Hallbacken 1986; Nilsson 1986; Falkengren-Grerup 1987; Anderson 1987) have concluded that soil pH may change by 0.5 to 1.0 units in 20 to 50 years. Recent work by Binkley and others (1988) indicated that substantial changes in soil solution chemistry can occur in forest soils typical of the Southeastern U.S. when pH changes

are as small as 0.3 units. The possible causes of changes in soil pH can be listed (Binkley & Richter 1987) and modelled (Schnoor 1984; Reuss et al. 1986; Reuss & Johnson 1986), but the relative importances of potential factors have not been quantified for any situation where soil acidification has occurred. Although soil analysis methods have been developed for describing a variety of the components of soil acidity (see Hesse 1971; Thomas 1982; McLean 1982; Thomas & Hargrove 1984), these methods do not allow for a clear analysis of the relative importances of factors that might account for differences in pH between soils.

In this paper, we develop an empirical approach that provides a first approximation of the relative importances of factors responsible for acidification of the soil in a loblolly pine (*Pinus taeda* L.) plantation from age 5 to 25 years. We first illustrate this empirical approach with simple solutions of weak organic acids, and then illustrate how this approach can be used to explain the observed change in soil pH.

The empirical approach

The pH of a weak-acid solution tends to be low when the total concentration of acid is high ($HA + A^-$ is high), when the acid is largely undissociated (A^-/HA is low), and when the affinity of the acid anion (A^-) for H^+ is low (the pK_a is low) (see Stumm & Morgan 1981). Simple acid/base equations can be used to calculate changes in the pH of weak-acid solutions. Soils behave as weak acids due to sorption processes on mineral and organic colloids. Soil pH tends to be low when the total negative charge on colloids is large, when the proportion of the colloid charge balanced by H^+ (or Al^{3+}) is high, and when the affinity of the colloid surfaces for H^+ (or Al^{3+}) is low (= low pK). Because soils are mixtures of diverse colloids, simple acid/base equations cannot adequately represent the acid/base behavior of soils (see Bloom & Grigal 1985; Perdue 1986). However, the fundamental aspects of acid/base chemistry can be applied to soils through the use of empirically derived titration curves.

Factor 1: acid quantity (Q)

The pH of a pure solution of an acid can be calculated from the simple equilibrium equation:

$$K_{eq} = \frac{(H^+)(A^-)}{(HA)} \quad (1)$$

where K_{eq} is the thermodynamic equilibrium constant for the acid, (H^+) is the activity of free H^+ , (A^-) is the activity of the acid anion, and (HA) is the activity of the undissociated acid. In soils, (A^-) would represent the colloidal surfaces with adsorbed alkali + alkaline-earth cations (termed “base cations” by soil scientists), and (HA) would represent adsorbed H^+ and Al^{3+} . In pure solutions, if any one of the three activities is known, the others can be calculated. Consider two solutions of acetic acid (CH_3COOH , $K_{eq} = 1.76 \times 10^{-5}$), one with 1 mmol of acetic acid per liter, and the other with 2 mmol/L. Since (H^+) and (A^-) must be equal, and (HA) must equal the 1 mmol/L minus the dissociated ions, the (H^+) of the weaker solution (assuming for simplicity that activity equals concentration) would be:

$$1.76 \times 10^{-5} = \frac{(H^+)^2}{(0.001) - (H^+)} \quad (2)$$

Solving with the quadratic formula gives a (H^+) of 1.24×10^{-4} and a pH of 3.91. The same calculation for the more-concentrated solution gives a pH of 3.75.

The pH of solutions may also differ if they have the same quantity of dissociated acid (A^-) , but different quantities of undissociated acid (HA) . Equation 1 can be rearranged such that:

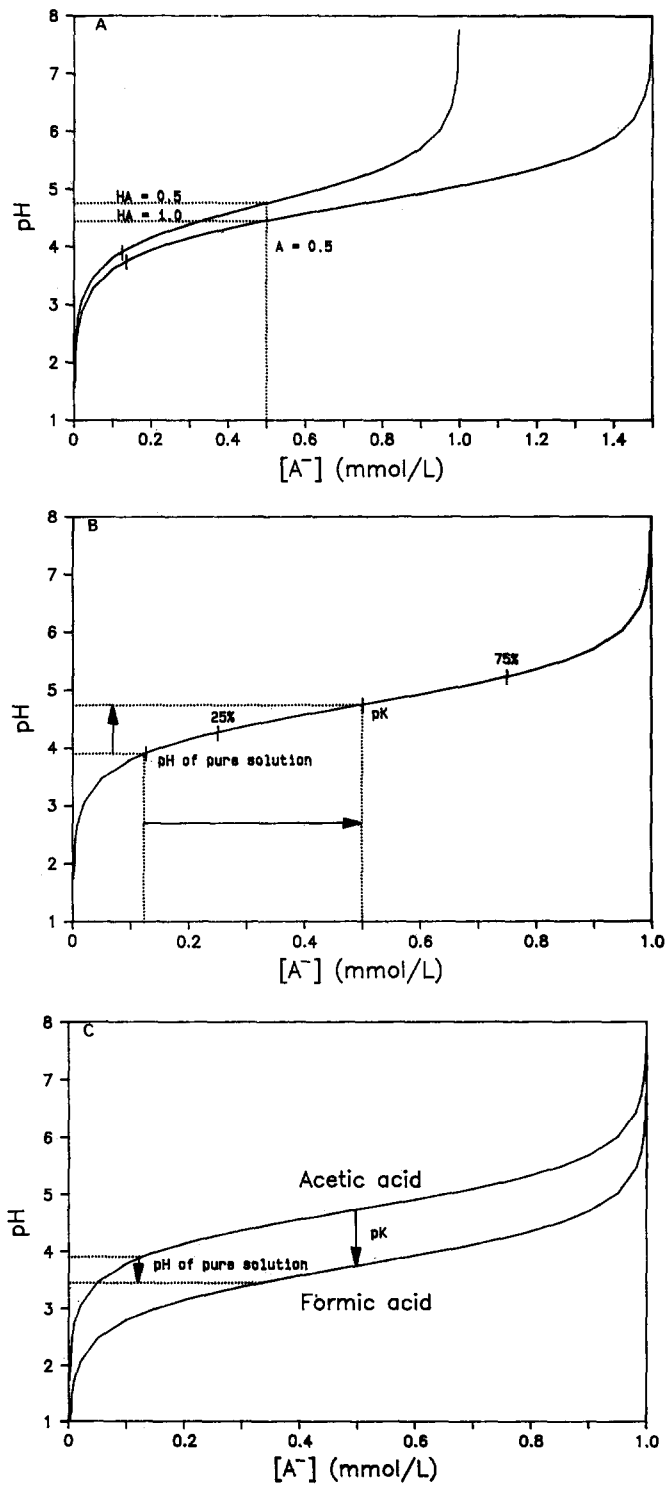
$$(H^+) = \frac{K_{eq} \times (HA)}{(A^-)} \quad (3)$$

Taking the logarithm of each side, and changing the signs, gives:

$$pH = pK - \log \frac{(HA)}{(A^-)} = pK + \log \frac{(A^-)}{(HA)} \quad (4)$$

Equation 4 (the Henderson-Hasselbalch equation) can be used to calculate the change in pH that results from increasing (HA) while (A^-) is held constant.

The same result can be obtained through manipulation of titration curves. Consider a 1 mmol/L solution of acetic acid. At pH 4.75, both (A^-) and $(HA) = 0.5$ mmol/L. If (A^-) were held constant, and (HA) were doubled to 1 mmol/L, $(A^-) + (HA)$ would go from 1 mmol/L to 1.5 mmol/L, a 50% increase. The lower curve in Fig. 1a is derived from the first curve by proportionally increasing (by 50%) the change in (A^-) (which would equal the OH^- added in a titration) required to change pH at all points along the



curve. The new pH for $(A^-) = 0.5 \text{ mmol/L}$ and $(HA) = 1 \text{ mmol/L}$ can be read from the graph by moving vertically to $(A^-) = 0.5 \text{ mmol/L}$ to the lower curve. The equation for adjusting the curve for changes in $(HA + A^-)$ is:

$$(A^-)_j = (A^-)_i \times \frac{[(A^-) + (HA)]_j}{[(A^-) + (HA)]_i} \quad (5)$$

where $(A^-)_j$ is the position on the X-axis for the new curve, $(A^-)_i$ is from the original curve, and $[(A^-) + (HA)]_j$ and $[(A^-) + (HA)]_i$ are the total quantities of acid present in the new solution and in the original solution.

The curve-adjusting routine in Equation 5 is more cumbersome than simple calculations with the Henderson-Hasselbalch equation, but it provides the same answers. The advantage of the curve-adjusting routine is that it can be used with empirically determined curves that do not fit simple equations.

Factor 2: acid dissociation (D)

If a solution of acetic acid were titrated with a strong base, the pH would reflect the degree of dissociation of the acid caused by this titration. In this case, the total quantity of acid remains constant $[(A^-) + (HA)]$, but (A^-) increases and (HA) decreases. In soils, this would represent changes in alkali + alkaline-earth saturation, without changing the total exchange capacity. The change in pH due to the increase of (A^-) can again be calculated from the Henderson-Hasselbalch equation, or read from the curves as the change on the Y-axis associated with the amount of change on the X-axis. For example, if a solution of 1 mmol/L acetic acid is titrated such that (A^-) increased from 0.12 mmol/L in the pure solution to 0.5 mmol/L , the pH would have increased from 3.9 to 4.75 (Fig. 1b).

Factor 3: acid strength (S)

The pH of solutions may also differ if the acid concentrations and degree of dissociation were the same, but the strength of the acids differed. In soils,

Fig. 1. (A) Increasing the undissociated acid concentration (HA) from 0.5 mmol/L to 1.0 mmol/L with the dissociated concentration constant $[(A^-) = 0.5 \text{ mmol/L}]$ lowers the solution pH from 4.75 to 4.45. (B) Titration of a pure solution of 1.0 mmol/L of acetic to the point where half of the acid is dissociated requires 0.38 mmol/L of OH^- , and raises the pH from 3.91 to 4.75. (C) Formic acid is stronger than acetic acid, and will have a lower pH at any given level of dissociation.

this would represent a change in the affinity of the colloids for H^+ , as might occur with a change in the chemical composition of soil organic matter. For example, formic acid ($HCOOH$, $K_{eq} = 1.77 \times 10^{-4}$) is stronger than acetic acid. A 1 mmol/L solution of acetic acid has a pH of 3.91, and the pH of a 1 mmol/L solution of formic acid would be 3.46 (Fig. 1c). The degree of dissociation of the acetic acid $[(A^-)/\{(A^-) + (HA)\}]$ would be 0.12, compared with 0.34 for the formic acid. In order for the acetic acid to be 0.34 dissociated, the pH would have to be 4.46. If both acids were 34% dissociated, the pH of the formic acid solution would be 1 unit lower than that of the acetic acid solution. This can be determined graphically by comparing the difference in pH from two curves at equal (A^-) and (HA) (Fig. 1c).

Application of the empirical model to soils

The total charge of colloids represents the total acidity and alkalinity of soils. At any given pH, a portion of the charge on colloidal surfaces will be protonated or have exchangeable $Al^{3+} [= (HA)]$, and rest of the charge $[= (A^-)]$ will be balanced by alkali + alkaline-earth cations. Aluminum is grouped with H^+ because of its protolytic reactions (cf. Bohn et al. 1985). The protonated portion $[(HA)]$ at any given pH represents the titratable acidity, also called the base neutralizing capacity (BNC) (Van Breemen et al. 1983). The dissociated portion $[(A^-)]$ accepts H^+ , and is the titratable alkalinity or acid neutralizing capacity (ANC). The dissociated portion of the colloidal surfaces can be measured as the exchangeable alkali + alkaline-earth cations. A single equilibrium constant cannot represent the acid/base chemistry of complex mixtures of colloids, but empirical titration curves capture the spectrum of acid dissociation tendencies ($= dpH/dOH^-$) across a range of pH.

Site description and methods

Loblolly pine seedlings were planted at various densities in January and February of 1957 in a field at the Calhoun Experimental Forest (in Union County, South Carolina) that had been cropped with cotton in 1955. The spacings ranged from 1.8 by 1.8 m up to 3.6 by 3.6 m (Balmer et al. 1975), and each spacing was replicated in 0.24 ha plots once in each of 4 blocks. In this study, we used only the 1.8 by 1.8 m spacing plots. The soil is classified as a clayey, mixed, thermic Aquic Hapludult of the Helena series, characterized by an upper layer of loamy sand to sandy loam, underlain by compact, mottled yellow-and-red clay.

The first soil sampling occurred in the spring of 1962, 5 years after plantation establishment. Six soil cores (1.9 cm diameter) were composited from samples taken in a circle, 75 cm from each of 16 trees, and these samples were then composited to give one sample for each of the 4 plots. The depths were: 0–7.5 cm (Ap horizon), 7.5–15 cm (Ap horizon), 15 cm to the B horizon (the top of which ranged from 20 cm to 60 cm due to sheet erosion), and within the B horizon. The soils were resampled several times; in the 1982 sampling we report in this paper, 20 cores taken at random were composited into a single sample for each plot.

The soils were analyzed for chemical properties soon after collection, and then stored air-dried. In 1987, we analyzed the samples for pH, extractable cations, and titratable acidity and alkalinity. We modified methods to use as little soil as possible in our multiple analyses. Soil pH had been measured in a water-paste in 1962, so we remeasured pH in a water-paste in the 1962 samples to check for changes during storage. The upper three depths averaged about 0.2 units higher in 1987 than the measurements in 1962, but the B horizon was about 0.2 units lower in 1987.

For the present study, we measured the pH of the supernatant of a 5:1 mixture of 0.01 *M* BaCl₂ and soil (2 g). The mixture was stirred well and allowed to settle for 30 minutes before the pH was measured with a combination electrode in the supernatant. Twenty mL of 2 *M* NH₄Cl was added to give a concentration of 1 *M* NH₄Cl and a solution:soil ratio of 10:1. Acid neutralizing capacity (ANC, titratable alkalinity) was indexed by adding incremental amounts of 0.05 to 0.1 *M* HCl, and allowing 24–36 hour equilibration before pH measurement of the supernatant (after Binkley 1986). Base neutralizing capacity (BNC, titratable acidity) was measured in a similar series of 1 *M* KCl/soil suspensions with incremental additions of 0.05 to 0.1 *M* NaOH. The titrations were continued until an endpoint of 3.5 was reached for ANC, and 8.2 was reached for BNC. The BNC to pH 5.5 was interpolated from the titration curves. Extractable cations were measured by atomic absorption in the supernatant after centrifugation of the acidified NH₄Cl extracts. These acidified samples may overestimate the cations that would be extracted by a shorter, neutral extraction; however, the comparisons among sampling years should hold.

Means for the two dates were compared with simple t-tests.

Results

Almost all soil properties changed significantly over the 20 year period. Soil pH dropped by 0.3 to 0.8 units in all horizons (Table 1), ANC declined

Table 1. Soil acidity properties. Means of 4 samples per year and depth; standard deviations in (), p level of significance of changes in [].

Depth	Year	pH _{BaCl2}	pH _{KCl}	ANC _{pH3.5}	BNC _{pH5.5}	BNC _{pH8.2}
cm					mmol _c /kg	
0-7.5	1962	4.97 (0.06)	4.63 (0.28)	9.7 (0.6)	3.9 (0.7)	30.3 (4.1)
	1982	4.14 (0.03)	3.94 (0.04)	8.3 (0.8)	7.8 (1.0)	36.8 (3.7)
	Change	-0.83 [0.00]	-0.69 [0.01]	- 1.4 [0.03]	3.9 [0.00]	6.5 [0.06]
7.5-15	1962	5.00 (0.05)	4.69 (0.10)	9.6 (0.9)	2.9 (0.4)	25.9 (2.2)
	1982	4.40 (0.04)	4.26 (0.07)	9.7 (0.5)	6.2 (0.2)	29.1 (1.9)
	Change	-0.60 [0.00]	-0.43 [0.00]	0.1 [0.86]	3.3 [0.00]	3.2 [0.07]
15-B	1962	4.95 (0.18)	4.72 (0.15)	9.9 (0.7)	2.7 (0.3)	24.7 (1.3)
	1982	4.43 (0.05)	4.35 (0.06)	9.6 (0.05)	6.1 (0.5)	28.1 (2.7)
	Change	-0.47 [0.00]	-0.37 [0.00]	- 0.3 [0.84]	3.4 [0.00]	3.4 [0.07]
B	1962	4.70 (0.18)	4.50 (0.11)	22.2 (3.9)	6.8 (0.6)	56.4 (20.6)
	1982	4.27 (0.08)	4.18 (0.05)	17.2 (4.7)	14.2 (7.2)	54.2 (8.4)
	Change	-0.43 [0.00]	-0.32 [0.00]	- 5.0 [0.15]	7.4 [0.08]	2.2 [0.84]

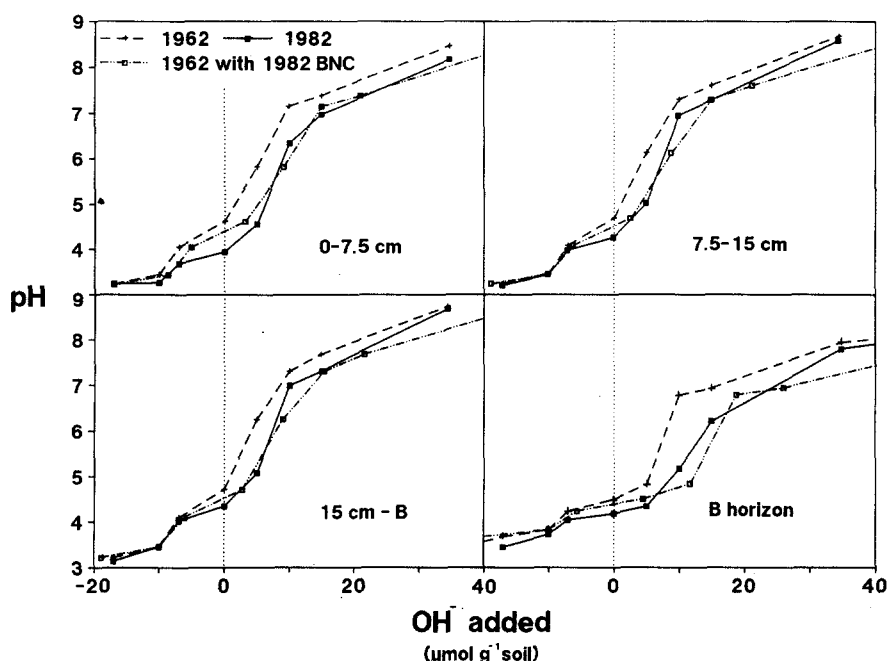


Fig. 2. Titration curves for 4 soil depths in 1962 (upper solid line) and 1982 (lower solid line), and the calculated curve for the 1962 soils if the total quantity of acid ($\text{BNC}_{8.2} + \text{ANC}_{3.5}$) equalled the 1982 soils.

marginally and BNC increased markedly. The content of exchangeable alkali + alkaline-earth cations dropped by 20 to 80% (Table 2), matched closely by increases in exchangeable aluminum.

We evaluated the importance of each of the three factors with a series of comparisons in which two factors for the 1962 soils were left unchanged, and the third factor was adjusted to the 1982 soils. The importance of the increase in acid quantity (Q , $\text{BNC}_{8.2} + \text{ANC}_{3.5}$) was assessed by adjusting the 1962 titration curves proportionately to the right to match the ($\text{BNC}_{8.2} + \text{ANC}_{3.5}$) in 1982 (Fig. 2), as illustrated for the simple acetic acid example in Fig. 1. For the 0–7.5 cm depth, this was an increase of 3.9 mmol_e/kg (Table 1). The expected pH in 1962 with the 1982 level of $\text{BNC}_{8.2} + \text{ANC}_{3.5}$ was then read by moving vertically (=holding (A^-) constant) from the actual 1962 line to the adjusted line. If the 0–75 cm depth soil in 1962 had the increased quantity of acids present in 1982, the pH_{KCl} would have been 4.55 rather than the observed 4.63 (Fig. 3).

In 1962, the 0–7.5 cm soil had 6.99 mmol_e/kg more alkali + alkaline-

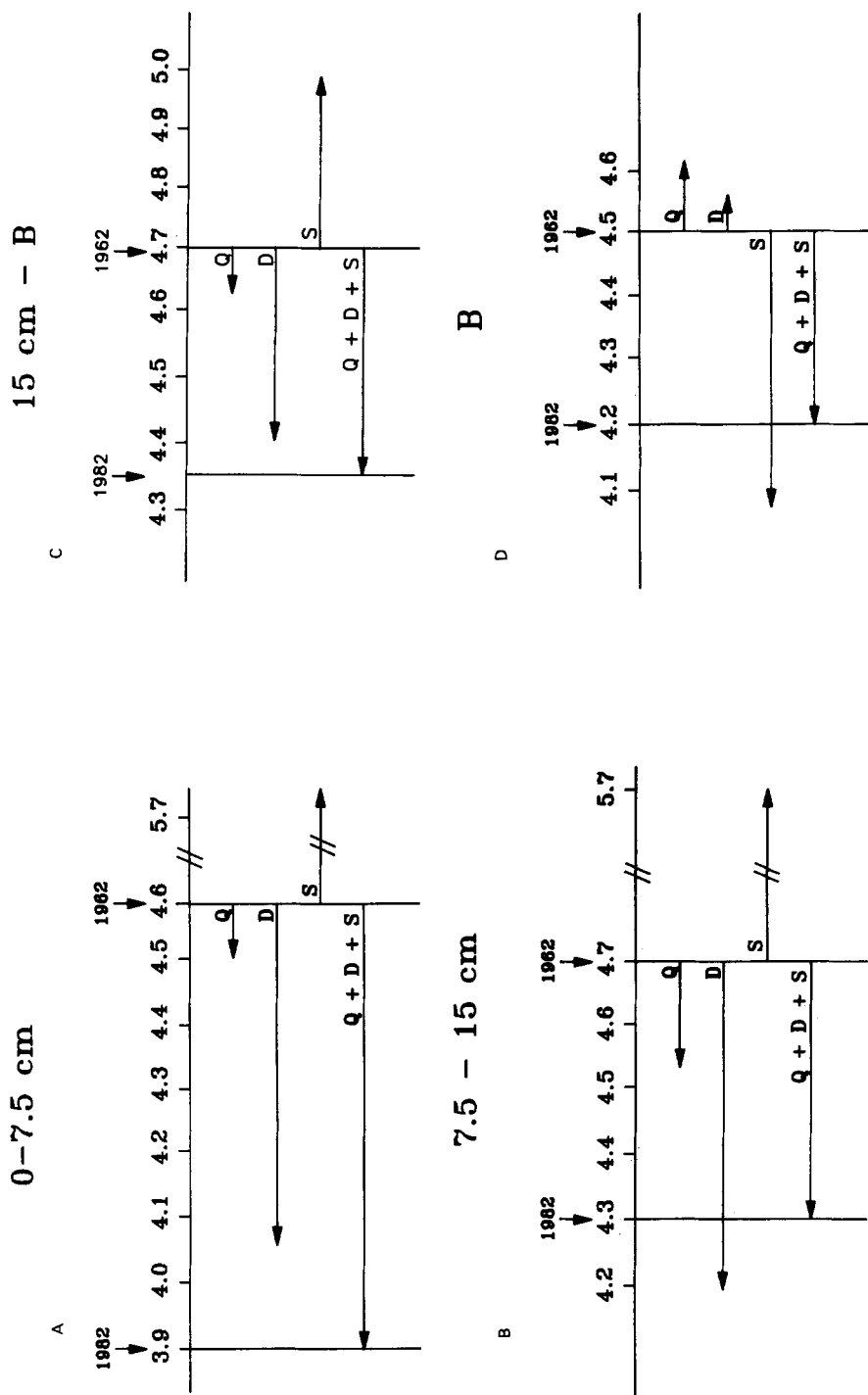


Fig. 3. Expected soil pH in 1982 if single factors ($Q = \text{BNC}_{e2} + \text{ANC}_{3,5}$; $D = \text{alkali} + \text{alkaline-earth cation content}$; $S = \text{acid strength}$) equalled the 1982 values.

Table 2. Exchangeable cations. Means of 4 samples per year and depth, standard deviation (), p level of significance of changes in [].

Depth	year	Calcium	Magnesium	Potassium	Sum of "bases"	Aluminum
cm		mmol _c /kg				
0-7.5	1962	5.94 (2.81)	1.16 (0.68)	1.23 (0.49)	8.33 (3.87)	11.79 (0.83)
	1982	0.65 (0.53)	0.47 (0.35)	0.22 (0.18)	1.34 (0.96)	18.84 (2.1)
	Change	- 5.29 [0.01]	- 0.69 [0.12]	- 1.01 [0.01]	- 6.99 [0.01]	7.05 [0.00]
7.5-15	1962	5.07 (2.71)	0.90 (0.65)	1.03 (0.44)	7.00 (3.65)	13.33 (0.01)
	1982	0.88 (0.36)	0.32 (0.18)	0.28 (0.33)	1.49 (0.76)	17.84 (1.84)
	Change	- 4.19 [0.02]	- 0.58 [0.14]	- 0.75 [0.04]	- 5.51 [0.03]	4.51 [0.00]
15-B	1962	3.82 (1.53)	1.18 (0.39)	1.43 (0.44)	6.42 (2.10)	13.34 (1.22)
	1982	1.83 (0.62)	0.83 (0.26)	0.32 (0.10)	2.97 (0.95)	17.75 (3.77)
	Change	- 1.99 [0.05]	- 0.35 [0.19]	- 1.11 [0.00]	- 3.45 [0.02]	4.41 [0.07]
B	1962	10.62 (1.17)	3.97 (2.37)	2.73 (0.82)	17.31 (4.16)	22.44 (5.48)
	1982	8.63 (1.00)	3.29 (1.12)	1.14 (0.69)	13.06 (2.64)	25.00 (3.00)
	Change	- 1.99 [0.04]	- 0.68 [0.62]	- 1.59 [0.03]	- 4.25 [0.13]	2.66 [0.44]

earth cations than in 1982. This represents $6.99 \text{ mmol}_c/\text{kg}$ increased protonation of the exchange complex in 1982. We evaluated the importance of the decrease in alkali + alkaline-earth cations (Factor #2, D) by estimating the 1962 pH_{KCl} if the alkali + alkaline-earth cations were reduced to the 1982 level [setting (A^-) for the 1962 curve equal to (A^-) for 1982]. For the 0–7.5 cm depth soil, this involved reading the pH from the 1962 titration curve at $6.99 \text{ mmol}_c/\text{kg}$ of OH^- added. The expected 1962 pH_{KCl} with the 1982 content of alkali + alkaline-earth cations would be 4.06 rather than the observed 4.63 (Fig. 3).

To assess the importance of the change in acid strength (S) of the exchange complex, we proportionately decreased the $(\text{BNC}_{8.2} + \text{ANC}_{3.5})$ of the titration curve for the 1982 0–7.5 cm soil to match the of the 1962 soil, and then moved along the curve $6.99 \text{ mmol}_c/\text{kg}$ to account for the greater in alkali + alkaline-earth cations in 1962 [set (A^-) equal to the 1962 value]. If the soil in 1962 had its original level of $\text{BNC}_{8.2} + \text{ANC}_{3.5}$ and alkali + alkaline-earth cations, but had the weaker acid strength of the 1982 soil, the pH_{KCl} in 1962 would have been about 5.77 rather than the observed 4.63 (Fig. 3). This difference in acid strength is illustrated in Fig. 4, where the

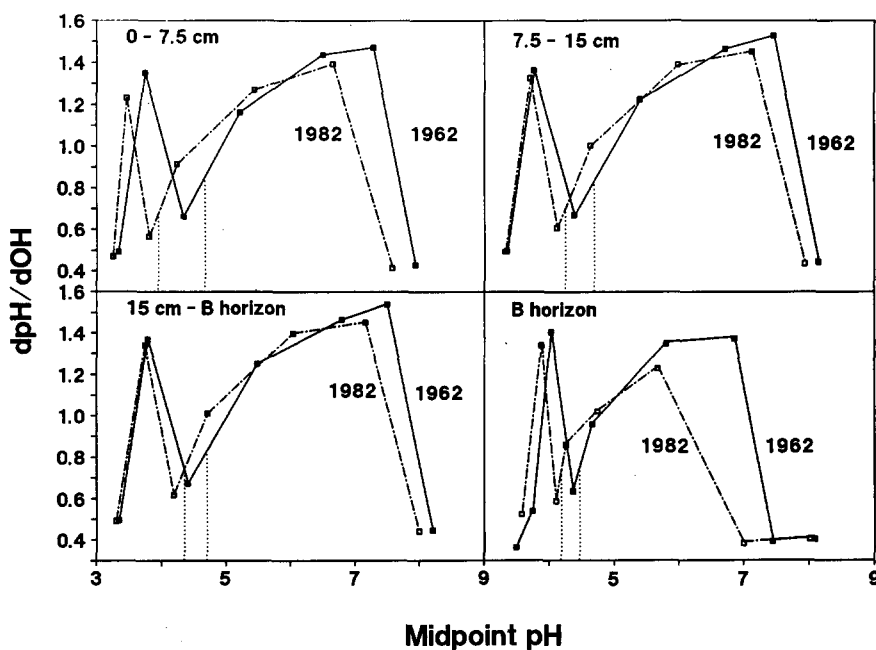


Fig. 4. Buffer capacity of 1962 and 1982 soils as a function of soil pH. High values indicate low buffer capacity. Vertical dotted lines indicate ambient pH.

buffering capacity (dpH/dOH^-) is plotted as a function of pH. If the acid strength and acid quantities were the same, the curves would be coincident. If only the acid quantities differed, the curves would have the same shape, but the curve for the more-poorly buffered soil would lie above that of the well-buffered soil. In this case, both the acid quantity and shapes of the curves differed, indicating a substantial change in the nature of the exchange complex.

The same calculations were performed for the other soil depths (Fig. 3). In general, the majority of the decrease in pH over 20 years was due to the reduction in alkali + alkaline-earth cations, which represents increased protonation of the soil acids and decreased base saturation of the soil. The increase in acid quantity played a smaller role. However, the decline in pH would perhaps have been about 0.1 to 0.2 units greater if the average acid strength of the exchange complex had not weakened.

These interpretations of the relative importances of factors that regulate soil pH are tentative, as they depend upon the extent to which our short-term titration curves in the laboratory characterize the real differences in the soils. Therefore, our interpretations are first approximations derived from the information available, rather than firm conclusions.

Discussion

The pH of this soil was very poorly buffered. The soil in 1962 had about $45 \text{ kmol}_c/\text{ha}$ of alkali + alkaline-earth cations (Table 3), and the average annual reduction in the alkali + alkaline-earth cations was $2.2 \text{ kmol}_c/\text{ha}$. The rate of accumulation of nutrient cations in biomass was not measured. However, the average rate for a 20-year-old loblolly pine stand in North Carolina was about $2.0 \text{ kmol}_c/\text{ha}$ annually (Binkley & Knoerr, unpublished data), so we expect most of the cation loss from the soil was due to

Table 3. Changes in soils pools (kmol_c/ha) from 1962 to 1982. Assumes bulk density = 1.35 for the upper 3 horizons, and 1.62 for the B horizon. The average thickness of the 15-B layer was calculated as 25 cm, and the thickness of the B horizon is 30 cm.

Horizon	Sum of "bases"	Aluminum	ANC _{pH3.5}	BNC _{pH5.5}	BNC _{pH8.2}
0-75.	- 7.1	7.1	- 2.0	3.9	6.6
7.5-15	- 5.5	4.5	0.1	3.3	3.2
15-B	- 11.7	15.3	- 1.0	11.5	11.5
B	- 20.6	12.6	- 24.3	35.9	10.8
Sum	- 44.9	39.5	- 27.4	54.6	32.1

accumulation in biomass, with probably about 10% being leached from the soil.

We would like to be able to separate the contributions of organic and aluminum compounds of varying pK_a 's to the change in acid strength, but we know of no direct method for such analysis. We did not measure soil organic matter in these samples, but earlier analyses (C. Wells, unpublished data) indicated that organic carbon increased by about 100 kg/ha annually between 1962 and 1982. The acidity of organic matter ranges between 1.5 to 3.0 mol_c/kg, or about 3.0 to 6.0 mol_c/kg of C (Bohn et al. 1985: 145). Therefore, the annual rate of increase of organic acidity was probably 0.3 to 0.6 kmol_c/ha during this period. The annual rate of accumulation of exchangeable aluminum was about 2.0 kmol_c/ha (Table 3), substantially larger than the rate of increase in organic acidity.

It is not possible to compose a complete H^+ budget for this stand, but the changes in soil pools provide estimates of H^+ fluxes unavailable in earlier H^+ budgets. The rates of change in the ANC and BNC of the soil were on the order of 1.3 to 2.7 kmol_c/ha annually; these rates are large relative to more-easily measured fluxes commonly included in H^+ budgets (see Binkley & Richter 1987). To our knowledge, the change in apparent strength of the exchange (acid) complex has not been included in other evaluations of changes in soil acidity. This change in apparent acid strength was less important than the reduction in alkali + alkaline-earth cations, but did moderate the decrease in pH by 0.1 to 0.2 units. The changes in soil pools and acid strength in this soil were larger than we had expected; long-term data of this sort for other soils are needed to evaluate the general importance of changes in acid quantity and strength.

Despite the relatively rapid acidification of this soil, we do not expect the changes in soil acidity to directly affect site productivity. The pH of the soil is well within the range commonly found for loblolly pine stands. However, the decline in extractable nutrient cations may indicate reduced nutrient supplies, and deficiencies of nutrient cations (especially K^+ , see Turvey & Allen 1987) may have developed.

How representative is this site of other forest soils in the Southeastern U.S.? Turner et al. (1986) estimated that 250 000 ha of Aeric Hapludults in the region may be sensitive to acidic deposition. Our results demonstrate that substantial changes in soil chemistry should be expected to occur on a time scale of a few decades, especially when agricultural fields are converted to forests. The need for more information on a variety of sites is clear. Identification of the relative contributions of atmospheric deposition and within-ecosystem processes will require monitoring major H^+ fluxes and the components of change in soil pools at a network of sites over a period of decades.

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