



ELSEVIER

Forest Ecology and Management 80 (1996) 47–56

Forest Ecology
and
Management

Factors influencing decline in soil pH in Hawaiian *Eucalyptus* and *Albizia* plantations

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Accepted 3 August 1995

Abstract

Soil pH declined from 5.9 to 5.0 in 8 years beneath plantations of *Eucalyptus saligna* (Sm.) in Hawaii. In stands of *Albizia falcataria*, (L.) Fosberg, the soil pH change was more dramatic, declining from 5.9 to 4.6. We measured several components of soil acidity beneath four mixtures of the two tree species to gain insight on the processes responsible for the decline in soil pH. These components were studied using an empirical method of comparing acid quantity, degree of neutralization (depletion of base cations), and acid strength. The decline in soil pH differed between species as a result of differences in the degree of neutralization of the soil exchange complex; the larger decrease in soil pH under *Albizia* was produced by greater acidification of the exchange complex. Empirical titration curves suggested that differences in acid strength moderated the divergence in soil pH beneath the species. Had the acids accumulating in the soil under *Albizia* been as strong as those in the *Eucalyptus* soil, the difference in soil pH would have been greater. Though the two species had contrasting effects on soil pH, the differences in degree of neutralization, responsible for the pH decline, were small compared with differences in the amount of cations stored in tree biomass. Continued supply of nutrient cations (from weathering or fertilization) will ultimately control both the extent of soil pH decline and the level of productivity sustained by the forest.

Keywords: Soil acidification; Plantation forestry; *Albizia falcataria*; *Eucalyptus saligna*

1. Introduction

Plantations of fast growing tree species are one of the most effective ways to meet demands for fuelwood, lumber, and biomass. In the tropics, these plantations often use fast-growing exotic species.

Eucalyptus is the most widely planted genus of trees in the world, with plantations covering more than 16 million ha in more than 100 countries outside its native range of Australia and Southeast Asia (Westoby, 1989; Evans, 1992).

Concerns about declines in soil fertility and long-term productivity of fast-growing plantations have promoted interest in using nitrogen-fixing trees in mixed species plantations. *Albizia* is a genus of tropical N₂-fixers commonly included in mixed species plantations and agroforestry combinations

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(MacDicken and Vergara, 1989). Compared with *Eucalyptus* monocultures, mixed stands of *Eucalyptus* and *Albizia* may produce more biomass, contain larger above-ground nutrient pools, and cycle more nutrients through litterfall (Binkley et al., 1992).

Soil acidity affects plantation performance by influencing the availability of essential soil nutrients and the solubility of potentially toxic elements (Russell, 1973; Brady, 1984). Growth of some tree species is limited within distinct soil pH ranges; for example, *Leucaena leucocephala* is unable to grow at soil pH levels below pH 4.5 (Evans, 1992). Pines generally grow well at soil pH levels ranging from 3.5 to 6.0 (Evans, 1992). The crucial nature of soil acidity in determining the success of plantation establishment was stressed by Zobel et al. (1987): "It is fair to state that the most common cause of failures in establishing exotics . . . results from planting a species, or provenance, on soils with an unsuitable pH."

The effect of forest plantations on soil acidification is important where a decline in soil pH could contribute to nutrient deficiency or toxic conditions. Studies of fast-growing tree plantations on very acidic soils highlight variability between species and soil type (Chijicke, 1980; Sanchez et al., 1985; Voss et al., 1988). The long-term potential of multiple rotations of forest plantations depends on successfully matching the tree species to site soil conditions, and application of necessary management activities to sustain soil productivity.

We examined soil acidification associated with 8-year-old monocultures and mixed plantations of *Eucalyptus saligna* (Sm.) and nitrogen-fixing *Albizia falcataria* (L.) Fosberg (= *Paraserianthes falcataria* (L.) Nielsen). Our objectives were: (1) to characterize the change in soil pH during the first 8 years of plantation development, (2) to compare the effect of two fast-growing tree species on soil pH, and (3) to evaluate the equilibrium factors that account for species effects on soil pH.

2. Methods

The study was conducted in forest plantations growing on abandoned sugar cane land, near Hakalau

on the northeast coast of the island of Hawaii (19°30' N, 155°15' W). Annual rainfall averages 4600 mm with no distinct dry period (DeBell et al., 1989). The stands are situated on thixotropic isomesic Typic Hydudand soils of the Akaka series. A series of experimental plots with seven mixtures of *Eucalyptus* and *Albizia* were installed in 1982 in a randomized complete design in 4 blocks. Prior to the last sugar cane crop, 4 years prior to plantation establishment, 2000 kg ha⁻¹ of CaCO₃ was plowed into the soil. Fertilizer was applied during the first 3 years of plantation development (see Binkley et al., 1992).

Soil was sampled from the 0–0.15 m depth, transported in coolers and analyzed fresh. The pH of fresh soil was measured in the following suspensions: 1:1 and 10:1 mixtures of fresh soil weight to volume of deionized water; 1:1 0.01 M CaCl₂. All pH readings were taken using a glass electrode after shaking soils for 30 min.

Exchangeable cations were extracted with 1 M NH₄NO₃ and analyzed with a Jarrell Ash Model 975 ICP (Thermo Jarrell Ash Corp., Waltham, MA). Values were corrected for moisture content and reported on an oven dry basis. Effective (unbuffered) cation exchange capacity (CEC_e) was calculated by the sum of exchangeable cations. Base saturation was calculated as the sum of Ca²⁺, Mg²⁺, K⁺, and Na⁺ divided by CEC_e. Water soluble anions were extracted in a 10:1 solution of deionized water to fresh soil and analyzed with a DIONEX anion chromatograph (DIONEX Corp., Sunnyvale, CA). Alkalinity of the water extracts was determined by titration to a pH 4.5 endpoint with 0.01 M HCl while the extracts were constantly stirred. Ionic strength was calculated as the sum of water soluble anions and alkalinity. Exchangeable-titratable acidity, consisting of various forms of Al, was determined in 1 M KCl extracts titrated to a 8.2 endpoint with 0.01 M NaOH. Bulk density values were used to convert the exchangeable cation concentrations to an area basis.

Oven dried plant samples were ground and sieved prior to digestion by the semi-micro Kjeldahl procedure (modified from Nelson and Sommers, 1980). Analysis of total N and P was performed with a Latchet spectrophotometer (Latchet Instruments, Mequon, WI). Tissue cation concentrations were assessed by ICP and atomic absorption spectrophotometry.

Cation stocks in tree biomass were calculated from estimates of above-ground biomass measured at year 8 (Binkley et al., 1992). Leaf biomass was assumed to equal 1 year of litterfall (Dunkin, 1989). This assumption is reasonable given the rapid growth of the stands and the rate at which lower leaves are shaded and abscised. Forest floor biomass was measured in one 0.1 m² quadrat per plot.

We developed titration curves to estimate the acid and base neutralizing capacities of soil beneath the different plantation mixtures (Fig. 1). The change in pH was plotted on titration curves after adding 0.01 or 0.005 M of HCL (or NaOH) to two 2:1 subsamples in 1 M NH₄Cl (for acid additions) or 1 M KCL (for base additions). Soils equilibrated for 24 h after each addition of acid or base. Soil pH was read after stirring the soil mixtures. Daily pH readings and acid or base additions continued until the pH fell below 4.0, or rose above 6.0. The amount of acid required to reach pH 4 was defined as acid neutralizing capacity (ANC), and base neutralization capacity (BNC) as the quantity of base required to reach pH 6.0 (BNC_{6.0}). BNC_{6.0} was used in comparisons as it represents the upper pH level for the natural soil system.

An empirical method was used to compare equilibrium soil factors responsible for differences in

acidity under the influence of the tree species (Binkley et al., 1989; Binkley and Valentine, 1991). The soil is equated to a weak acid solution system influenced by (1) acid quantity, (2) degree of neutralization, and (3) acid strength. The approach offers an alternative to the Henderson–Hasselbalch equation, which calculates the pH of weak acid solutions given acid strength and the concentrations of dissociated and undissociated acids. Henderson–Hasselbalch was derived for solutions containing only one source of H⁺ (monoprotic acid systems); because of the multiple buffering systems found in soils, it is not directly capable of calculating soil pH. Empirically derived titration curves allow stepwise adjustments of acid quantity, degree of neutralization, and acid strength of one soil to the levels found in another soil. The deviation between the three adjusted pH values from the original pH provides insights on the importance of each factor in controlling soil pH.

Soils contain combinations of acids of varying strengths resulting from different types of organic matter and clay minerals that constitute the exchange complex. With this approach, acid quantity (ANC_{4.0} + BNC_{6.0}) is determined by the size of the exchange complex (Fig. 1). Degree of neutralization (ANC/(ANC + BNC)) is the portion of the exchange complex occupied by base cations (dissociated acid por-

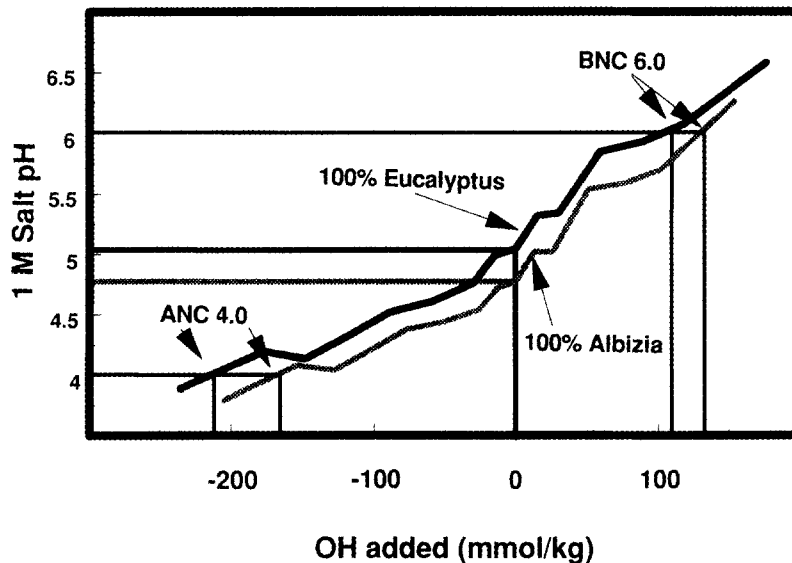


Fig. 1. Titration curves for pure *Eucalyptus* and *Albizia* plots. Negative OH⁻ values indicate acid additions.

Table 1
Components of soil acidity

Percent <i>Eucalyptus</i>	Soil pH in		Exchangeable	
	Water	CaCl ₂	Acidity (mmol _c kg ⁻¹)	BNC ₆ (mmol _c kg ⁻¹)
100	4.95 a (0.07)	4.54 a (0.07)	1.47 a (0.49)	101.5 a (16)
75	4.85 ab (0.02)	4.37 b (0.04)	2.43 ab (0.67)	116.4 ab (10)
25	4.77 ab (0.12)	4.39 ab (0.08)	2.73 ab (1.3)	118.8 ab (3)
0	4.62 b (0.12)	4.27 b (0.04)	4.68 b (0.86)	129.7 b (10)

Values are mean and standard deviation ($n = 3/\text{treatment}$). Within a column, different letters indicate that means differ at $P \leq 0.05$ between treatments.

tion), relative to sites retaining the acid cations H^+ and Al^{3+} (undissociated portion). Acid strength regards the affinity of the exchange sites for H^+ . Strong acids (low pK_a) dissociate more readily at equilibrium and maintain the soil solution at a lower pH than weak acids. Acid strength defines the shape of the titration curve. The effect of acid strength on pH variation between two soils is determined as the residual difference in pH after the curve of one soil has been adjusted for the acid quantity and degree of neutralization of the other.

Statistical comparisons of treatment and block effects were based on analysis of variance (ANOVA; Steel and Torrie, 1980). Multiple comparison of means were made using Tukey's honestly significant difference (HSD) method, setting the confidence level at 0.05. Linear regression analysis was employed to compare the strength of the relationships between pH

and either base saturation or degree of acid neutralization. Statistical analysis was executed with Statistical Package for Social Sciences (SPSS/PC + V2.0) software (SPSS Inc., 1988).

3. Results

During the first 2 years growth, soil pH in water dropped from 5.9 to 5.4 under the pure *Eucalyptus* and to 5.2 under the pure *Albizia* stands (DeBell et al., 1989). By year 8, pH declined by 0.9 units (to 5.0) under the *Eucalyptus* plots and by 1.3 units (to 4.6) under the *Albizia* plots (Table 1).

At age 8, soil pH in water and 0.01 M CaCl₂ differed significantly in the surface 0–15 cm depth between pure *Eucalyptus* and pure *Albizia* plots

Table 2
Exchange and dissociation properties

Percent <i>Eucalyptus</i>	Base saturation ^a (%)	Acid neutralization ^b (%)	Acid quantity (mmol _c kg ⁻¹)	Sum of cations (mmol _c kg ⁻¹)
100	46.45 a (8.9)	67.88 a (2.9)	314.92 a (21.0)	24.55 a (3.3)
75	44.58 a (3.0)	61.04 ab (2.2)	298.73 a (12.1)	21.88 a (2.2)
25	43.85 a (7.0)	60.41 ab (3.6)	301.69 a (29.1)	22.35 a (4.9)
0	35.67 a (5.8)	56.28 b (2.5)	297.93 a (35.9)	27.99 a (3.8)

^a Percent base saturation.

^b Percent acid neutralization = $ANC/(ANC + BNC_6)$.

Values are mean and standard deviation ($n = 3/\text{treatment}$). Within a column, different letters indicate that means differ at $P \leq 0.05$ between treatments.

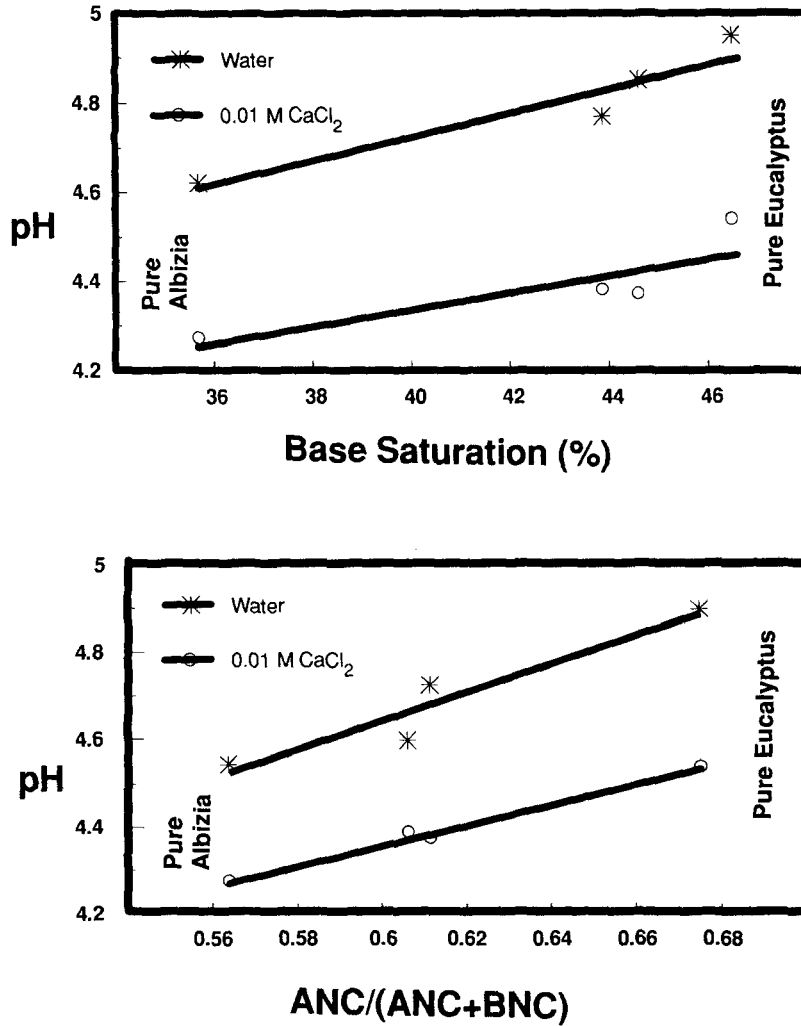


Fig. 2. Soil pH versus percent base saturation ($n = 3$) and acid neutralization ($n = 3$).

Table 3

Water soluble anions, H concentration, and 10:1 water pH^a

Percent <i>Eucalyptus</i>	F (mmol _c kg ⁻¹)	Cl (mmol _c kg ⁻¹)	SO ₄ -S (mmol _c kg ⁻¹)	NO ₃ -N (mmol _c kg ⁻¹)	Alkalinity (mmol _c kg ⁻¹)	Sum of anions (mmol _c kg ⁻¹)	H (mmol _c kg ⁻¹)	pH
100	4.60 (1.9)	72.18 (13)	263.1 (106)	56.0 (43)	5.18 (2.2)	401.1 (158)	0.095	5.18
75	5.16 (6.8)	44.16 (33)	145.0 (52)	13.8 (50)	4.42 (3.9)	212.6 (45)	0.096	5.17
25	6.02 (4.1)	49.03 (36)	98.6 (81)	262.6 (62)	0	416.3 (160)	0.125	5.06
0	2.60 (1.3)	53.71 (42)	118.5 (89)	391.9 (49)	0	566.7 (165)	0.161	4.95

^a Significant differences exist for NO₃-N ($P = 0.0001$), alkalinity ($P = 0.04$), and sum of anions ($P = 0.08$). Values are mean and standard deviation ($n = 3$ /treatment).

(ANOVA $P < 0.05$; Table 1). Soil pH in water under the *Albizia* was 0.33 units lower than under the pure *Eucalyptus*. Soil pH in the mixed stands was bracketed by the pure stands; the 25% *Eucalyptus* plots did not differ from the 75% *Eucalyptus* plots, and neither mixed species plots differed from the pure stands. The dilute salt pH was 0.4–0.5 units lower than that measured in water for all species mixtures.

Exchangeable-titratable acidity was three times greater under *Albizia* than under *Eucalyptus* (Table

1). Exchangeable acidity constituted only 2.8% of total acidity under the pure *Albizia* stands, and only 0.7% of total acidity under the pure *Eucalyptus* stand. From the stepwise titration, $BNC_{6.0}$ was 30% higher in the *Albizia* stands than in the pure *Eucalyptus* stands (Table 1). The $ANC_{4.0}$ decreased with increasing *Albizia* in the treatment mixtures. The 20% difference in ANC from the pure *Eucalyptus* to the pure *Albizia* treatment corresponded with percent base saturation for the surface soil (Table 2).

The relationship between base saturation and pH

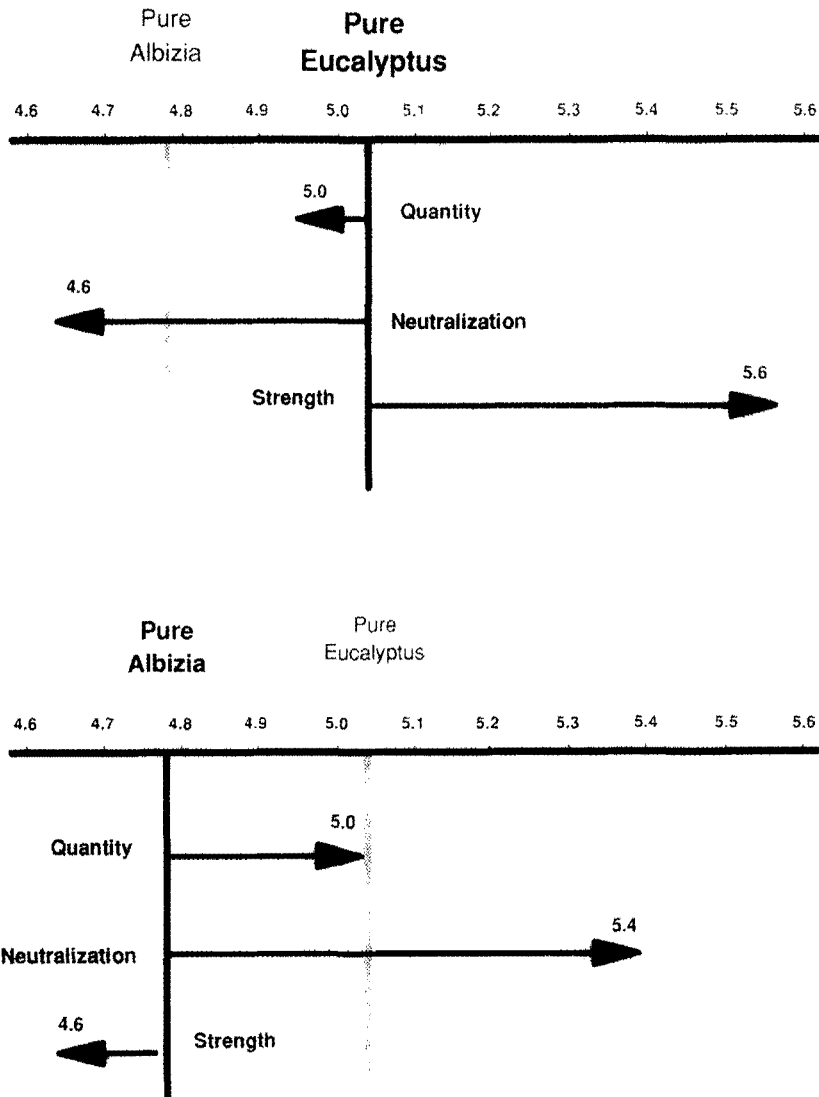


Fig. 3. Expected soil pH of pure *Eucalyptus* (top) and pure *Albizia* (bottom) when single equilibrium factors are adjusted to match other species.

for the four species mixtures was strong for both soil pH in water and in weak salt solution (Fig. 2). The r^2 of the regression of soil pH and base saturation was 0.73 when measured in water, and 0.90 when measured in 0.01 M CaCl_2 . The connection between base saturation and pH derives from the fact that base saturation is a partial index of acid dissociation. The relation is sometimes used to predict percent base saturation at a given soil pH (Brady, 1984).

When the full index of acid quantity was used for comparison to acid neutralization (the term: $\text{ANC}/(\text{ANC} + \text{BNC})$), the r^2 increased to 0.91 for water pH and 0.99 for dilute salt pH.

The closer correspondence between acid neutralization and dilute salt pH compared to water pH illustrates the impact of soil solution ionic strength on soil pH (Fig. 2). Electrolytes in soil solution allow greater release of acid cations from exchange

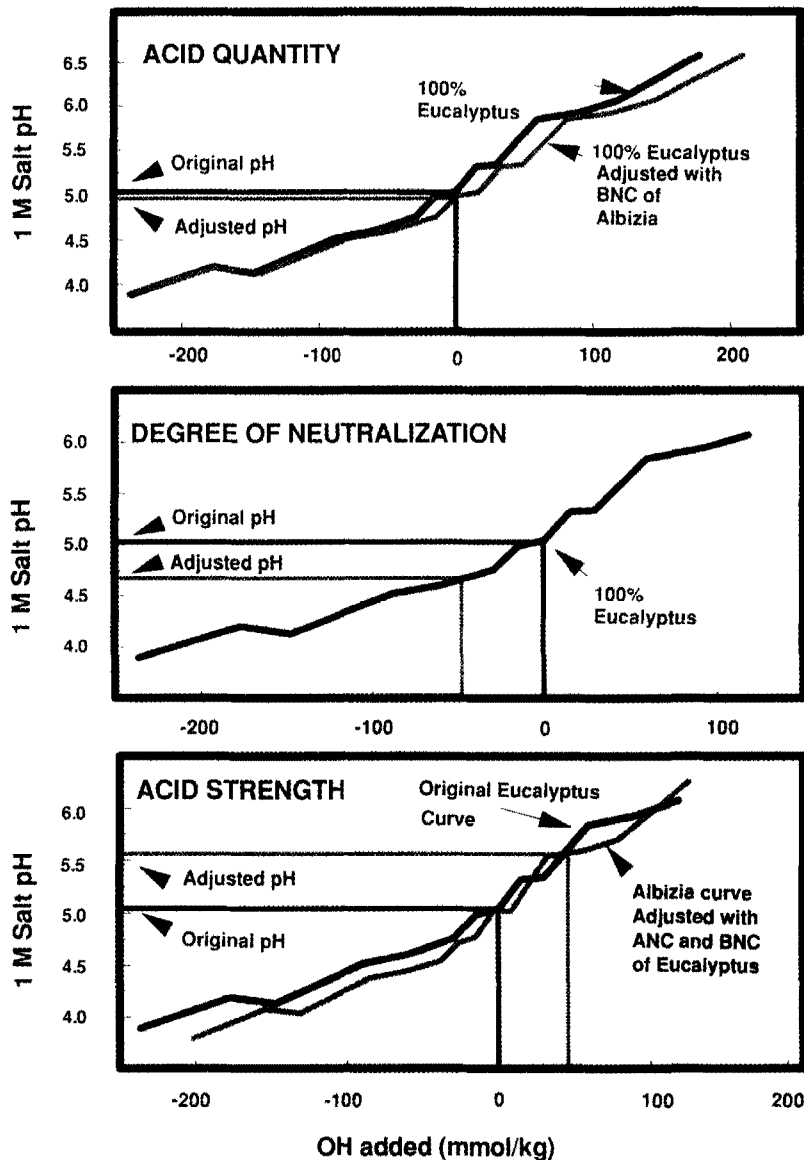


Fig. 4. Pure *Eucalyptus* titration curve adjusted with the acid quantity, degree of neutralization, and acid strength of pure *Albizia*.

sites; soil pH is depressed by high ionic strength (Reuss and Johnson, 1986; Richter et al., 1988). The difference between soil pH in dilute salt and water indicates the magnitude of the impact of ionic strength. In the two mixed stands, where degree of neutralization was nearly equal, the higher ionic strength of the soil from the 25% *Eucalyptus* plots (Table 3) displaced greater concentrations of H^+ into solution, lowering soil pH. Soil solution ionic strength was higher (ANOVA $P = 0.08$) in the pure *Albizia* stands (Table 3). Higher ionic strength resulted from NO_3^- levels that were nearly ten times greater in the pure *Albizia* and the 25% *Eucalyptus* stands than in the pure *Eucalyptus* dominated stands. The difference in concentration of water soluble anions between pure stands was $166 \text{ mmol}_c \text{ kg}^{-1}$. Of this charge, the increase in H^+ balanced only 0.04% ($0.66 \text{ mmol}_c \text{ kg}^{-1}$), but this difference decreased pH by 0.23 units.

From the curve adjusting routine, the factor responsible for the greatest portion of the difference in pH between *Eucalyptus* and *Albizia* was degree of neutralization (Fig. 3). The ANC of *Albizia* was $45.2 \text{ mmol}_c \text{ kg}^{-1}$ lower than *Eucalyptus* (Fig. 1), so

the pH from the original *Eucalyptus* curve was adjusted by adding -45.2 mmol of OH^- (acid addition), giving a pH of 4.6 if the ANC of the *Eucalyptus* matched that of the *Albizia* (Fig. 4). The comparable adjustment for *Albizia* required a shift of 45.2 mmol of OH^- (upward slide) on the original *Albizia* curve. Depleting the ANC of *Eucalyptus* to the level found in *Albizia* depressed pH by 0.39 units. Adding the equivalent amount of ANC found in *Eucalyptus* to the exchange complex of *Albizia* increased 0.6 pH units from 4.78 to 5.38.

The weaker acid strength of the *Albizia* exchange complex partially balanced its low degree of neutralization and prevented an even larger drop in pH (Fig. 4). After adjusting the *Albizia* system with the acid strength of *Eucalyptus*, the *Albizia* pH would have decreased below the measured 4.78 to a pH of 4.64. Acid quantity of *Albizia* was 9% greater than that found beneath *Eucalyptus*. Adjusting acid quantity decreased the *Eucalyptus* pH by less than a tenth of a pH unit (Fig. 3). Including the smaller BNC of the *Eucalyptus* soil increased *Albizia* pH by 0.24 units. The species difference in sensitivity to change in acid quantity resulted from the greater slope (weaker

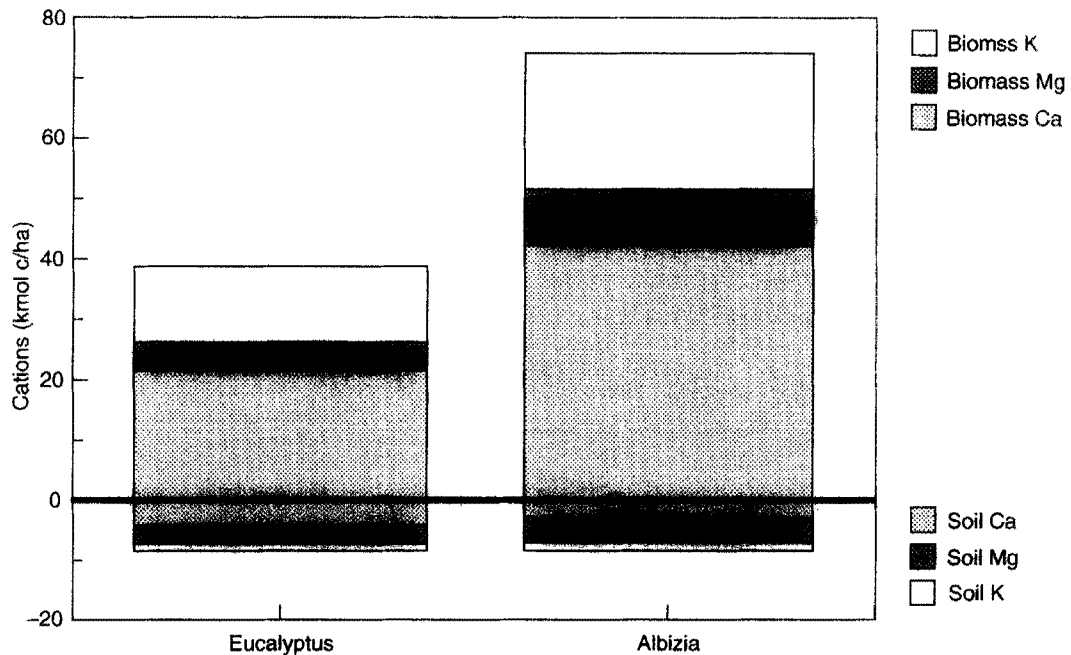


Fig. 5. Exchangeable soil cations (0–0.7m depth; from Rhoades, 1991) and biomass cations in above-ground biomass and forest floor biomass.

buffering) of the titration curve for *Albizia* near its ambient pH.

4. Discussion

Did the lower neutralization of the exchange complex (ANC/(ANC + BNC)) beneath *Albizia* result from the shift of cation nutrients (Ca^{2+} , Mg^{2+} , K^+) from the soil and into tree biomass? The quantity of these cations to a depth of 0.7 m in the soil was only $0.26 \text{ kmol}_c \text{ ha}^{-1}$ less under *Albizia* than *Eucalyptus* (Rhoades, 1991). Tree biomass cation content was $51 \text{ kmol}_c \text{ ha}^{-1}$ greater in the *Albizia* plots. In fact, base cations in biomass of either species totalled from five to eight times the size of the current exchangeable base cation pool in the top 0.7 m of soil (Fig. 5). These results suggest that biomass accumulation has been sustained by a source of nutrient cations without depletion of the exchange complex.

Weathering of soil minerals is a likely source. The total pools of base cations in the surface soil are over ten times greater than the exchangeable cation pools (Rhoades, 1991). One study estimated annual weathering rates for Ca, Mg, and K from volcanic ash in Australia at 1.0, 0.5, and $1.8 \text{ kmol}_c \text{ ha}^{-1}$ respectively (Feller, 1981). Another study, in Hawaii, measured K annual release from minerals at around $8 \text{ kmol}_c \text{ ha}^{-1}$ (Ayers et al., 1947). At these rates, mineral weathering could supply 13, 25, and 50 to 250% of the Ca, Mg, and K content that accumulated in *Albizia* biomass at year 8 without depleting the exchangeable pools. It is also possible that the tree roots are exploiting soil nutrients from the subsoil and recycling them into the upper soil layers.

What role in the changes in these soils was played by the liming (4 years before plantation establishment), and by the early fertilization during the development of these plots? Owing to the extreme leaching on the East coast of Hawaii, the residual effect of liming (with $40 \text{ kmol}_c \text{ ha}^{-1}$) should have been minimal (Mahilum et al., 1960). Cations in fertilizer amendments contributed another $8.5 \text{ kmol}_c \text{ ha}^{-1}$ during early stand development. The impact of nitrogen fertilizer additions on soil acidity depends on the degree to which the N source was leached from the

soil system. Fertilizer and liming treatments may have either buffered soil acidification or accelerated pH decline. The tree species effect on declining soil base status, however, remains the central reason for the differences in soil acidification regardless of the fertilizer regime.

The effect of nitrogen cycling on soil acidification beneath these plantations is uncertain. Our study and other research in these stands has found higher soil NO_3^- and nitrification rates under pure *Albizia* stands (Dunkin, 1989; D. Garcia unpublished data, 1994). Though the nitrification process generates protons and has been shown to lead to acidification (Nambu et al., 1994), neither nitrification or N_2 -fixation result in net acidification unless accompanied by NO_3^- leaching from the soil horizon (Binkley and Richter, 1987). Given the extremely high rainfall regime, leaching of NO_3^- and associated cations may have been substantial enough to contribute to the decline in soil pH. Unfortunately, NO_3^- -N and base cation leaching data are not available for this site. The variable charge dominated exchange complex in these soils adsorbs NO_3^- (Singh and Kanehiro, 1969) thereby limiting leaching related acidification.

5. Summary

Differences in acidification between species resulted from greater depletion of base cations from the exchange complex under the influence of *Albizia*, giving a lower degree of neutralization of the exchange complex. Replacement of base cations by Al and Fe could result from either the loss of base cations from the soil or a shift in selectivity of organic matter exchange sites for multivalent cations. Differences in acid strength moderated the divergence in soil pH beneath the species; the weaker acid strength under *Albizia* prevented a greater drop in pH. Species differences in degree of neutralization and exchangeable base cation content of the soil were small compared with the large differences in the amount of cations stored in biomass. Continued supply of nutrient cations will ultimately control both the extent to which soil pH declines and the level of productivity sustained by current plantations and subsequent rotations.

Acknowledgments

We thank T. Schubert and the BioEnergy Development Corporation for use of their plantations, and X. Zou for help in the field. J. Kettler provided helpful comments on the manuscript. This work was supported by McIntyre–Stennis appropriations to Colorado State University, and by NSF Grant DEB93-06356.

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