

# Alleviating Soil Acidity With Crop Residues

Nguyen V. Hue

**Abstract:** Soil acidity, which is characterized by mainly aluminum (Al) toxicity and often calcium (Ca) deficiency, is a serious constraint for crop production. To separate these two factors and to alleviate the acidity problem using organic materials instead of lime, a greenhouse experiment was conducted on two acid soils of Hawaii. Eight treatments were established: (i) unamended (control); (ii) 4 cmol<sub>c</sub>/kg as Ca(OH)<sub>2</sub>; (iii) 4 cmol<sub>c</sub>/kg as MgO; (iv) 4 cmol<sub>c</sub>/kg as CaSO<sub>4</sub> · 2H<sub>2</sub>O; (v) 10 g/kg ground fresh cowpea (*Vigna unguiculata*) leaves; (vi) 10 g ground, dried, fresh cowpea leaves ashed at 350°C for 4 h and then added to 1 kg soil; (vii) 10 g/kg ground fresh pineapple (*Ananas comosus*) crowns; and (viii) ashed pineapple at rate equivalent to (vii). *Desmodium intortum* cv. greenleaf, which is a tropical forage legume highly sensitive to soil acidity, was used as the test plant. The results indicated that treatments 1 to 4 could distinguish Al toxicity from Ca deficiency in acid soils and that crop residues could be used to alleviate soil acidity; the fresh cowpea amendment was most effective. More specifically, soil pH was raised moderately by crop-residue amendments, yet exchangeable Al was lowered substantially. Furthermore, soil-solution Al was complexed substantially by dissolved oxidizable carbon, particularly by organic acids produced by the crop residues. There was a good correlation between plant growth and the activity of total monomeric hydrolytic species of Al ( $\Sigma\{Al\}$ ). Significant growth reduction would be expected when  $\Sigma\{Al\} > 12.0 \mu M$ .

**Key words:** Acidity, aluminum, calcium, organic complexation.

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Soil acidity is a serious constraint for crop production in many regions of the world (Summer and Noble, 2003). In fact, wherever rainfall exceeds evapotranspiration, bases such as calcium (Ca), magnesium (Mg), and potassium (K) (and salts) are displaced by H<sup>+</sup> (derived from the dissolution of CO<sub>2</sub> in H<sub>2</sub>O). The basic cations are leached from the soil profile, leaving behind materials rich in aluminum (Al) and iron (Fe) oxides, which render the soil acidic and infertile (Hue, 2008). Thus, soil acidity is characterized primarily by toxic levels of Al. Secondary harmful effects of soil acidity include manganese (Mn) toxicity and Ca, Mg, and phosphorus (P) deficiencies.

Soil acidity is traditionally corrected by applications of lime [CaCO<sub>3</sub>, CaMg(CO<sub>3</sub>)<sub>2</sub>, or Ca(OH)<sub>2</sub>], which raises soil pH, precipitates Al, and provides Ca (Adams, 1984). However, liming often is not feasible in developing countries because the cost could exceed the value of the crop(s) being grown. Furthermore, lime may not be available in many developing countries where both cash and transportation may be inadequate (R4D, 2007). Fortunately, recent research has shown that additions of com-

posts, green, or animal manures reduce Al toxicity and increase crop yields (Hue and Amien, 1989; Wong and Swift, 2003; Vieira et al., 2009). It is believed that pH increase and Al chelation by organic molecules released from organic amendments are responsible for such positive growth (Wong and Swift, 2003).

Given the complexity of the soil acidity syndrome and current strong interest in sustainable agriculture and organic farming, the use of crop residues to alleviate soil acidity warrants a detailed investigation. Thus, the objectives of this study were to (i) separate Al phytotoxicity from Ca deficiency in acid soils of Hawaii, (ii) compare liming effects of crop residues with those of Ca(OH)<sub>2</sub>, and (iii) evaluate the growth-enhancing effect of organic amendments beyond their direct nutritional contribution.

## MATERIALS AND METHODS

### Properties of Soils and Crop Residues Used in the Experiment

The two soils used in the experiment were an Andisol (Typic Hydrudand, Kaiwika series) and an Ultisol (Typic Haplohumult, Paaloa series). In preparation for the experiment, the Ultisol was air dried, but the Andisol was kept moist to avoid irreversible changes in soil properties. Both soils were screened through a 4-mm sieve before applying treatments. Selected chemical properties of the soils in their unamended state are listed in Table 1.

Crop residues used as soil organic amendments included cowpea (*Vigna unguiculata*) leaves and shredded pineapple (*Ananas comosus*) crowns. The residues were ground to pass a 0.5-mm sieve before being mixed with the soils. Selected nutrients of the residues are listed in Table 2.

To ensure that Al and/or Ca were the only growth-limiting factors, other nutrients were blanket applied (in mg/kg) as follows: 100 N as NH<sub>4</sub>NO<sub>3</sub>, 50 Mg, 10 Mn, 5 Cu, and 5 Zn as sulfate salts. Phosphorus and K were applied at 400 mg P/kg and 503 mg K/kg as KH<sub>2</sub>PO<sub>4</sub> to the Ultisol and twice those rates to the Andisol to offset its greater capacity for nutrient retention.

### Treatments and Experiment Design

Reagent-grade Ca(OH)<sub>2</sub>, MgO, and CaSO<sub>4</sub> · 2H<sub>2</sub>O were thoroughly mixed with the soils having 2 kg/pot for the Ultisol and 1.5 kg/pot for the Andisol. Such a soil-mass difference was required to attain a comparable soil volume per pot.

The eight treatments were (i) unamended (control), (ii) 4 cmol<sub>c</sub>/kg as Ca(OH)<sub>2</sub>, (iii) 4 cmol<sub>c</sub>/kg as MgO, (iv) 4 cmol<sub>c</sub>/kg as CaSO<sub>4</sub> · 2H<sub>2</sub>O (gypsum), (v) 10 g/kg ground fresh cowpea, (vi) 10 g/kg of fresh cowpea that was ashed, (vii) 10 g/kg ground fresh pineapple, and (viii) 10 g/kg fresh pineapple that was ashed. The cowpea and pineapple were prepared by ashing ground plant material at 350°C for 4 h.

Treatments 1 through 4 were designed to separate the effects of Al toxicity from Ca deficiency on plant growth. The Ca(OH)<sub>2</sub> treatment would supply Ca and decrease soluble Al with increased soil pH. The MgO treatment would only decrease soluble Al with increased soil pH. The gypsum treatment would only supply Ca, while virtually keeping soil pH and soluble Al

Department of Tropical Plant and Soil Sciences, College of Tropical Agriculture and Human Resources, University of Hawaii at Manoa, Manoa, HI.  
E-mail: nvhue@hawaii.edu  
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**TABLE 1.** Selected Chemical Properties of the Two Hawaiian Soils Used in the Experiment

| Chemical Properties                       | Andisol | Ultisol |
|---|---------|---------|
| Soil pH (1:1 in water)                    | 4.50    | 4.60    |
| Soil-solution pH                          | 4.67    | 4.45    |
| KCl-extractable Al, cmol <sub>c</sub> /kg | 2.20    | 2.78    |
| Al saturation, %                          | 24.86   | 51.80   |
| Ca saturation, %                          | 4.90    | 9.50    |
| eCEC,* cmol <sub>c</sub> /kg              | 8.85    | 4.19    |

\*Effective cation exchange capacity, which is the sum of NH<sub>4</sub>Cl-extractable Ca, Mg, K, Na, and KCl-extractable Al.

eCEC: effective cation exchange capacity.

unchanged. Treatments 5 through 8 were designed to separate the effects of Al complexation by organic molecules in the fresh residues from the direct nutritional contributions that would exist in both fresh and ashed residues.

The experiment was installed in a greenhouse located at Manoa, Hawaii (21°18'18" N and 157°48'37" W). It had a randomized complete block design with three replicates for the Ultisol and four replicates for the Andisol.

The indicator plant was *Desmodium intortum* cv. greenleaf, a tropical forage legume highly sensitive to soil acidity. The seeds were germinated in a mixture of perlite and peat moss and grown for 10 days, after which four seedlings were transplanted into each pot. The temperature averaged 28°C during the day and 22°C during the night, and the relative humidity was maintained near 90% relative humidity by regular misting. During the experiment, the plants were watered regularly to avoid water stress. After 45 days of growth, the plants were cut approximately 5 mm above the soil surface. Soil samples were collected immediately before transplanting (from extra soils) and after plant harvest (from pots).

## Soil Sample Collections and Laboratory Analyses

### Soil-Solution Collection

Soil solution was collected by centrifugation method (Adams et al., 1980), in which about 250 g of moist soil (at field-water holding capacity) was placed into a modified Buchner funnel lined with a Whatman no. 42 filter paper and centrifuged at 1,000g for 45 min. An airtight cup was used to receive the soil solution whose pH was immediately measured (to avoid error due to CO<sub>2</sub> loss). Thereafter, the soil solutions were stored in a refrigerator at 4°C for subsequent chemical analyses.

### Exchangeable Cations (Ca, Mg, K, Na, and Al)

Basic cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, sodium [Na<sup>+</sup>]) were extracted with 1 M NH<sub>4</sub>Cl as follows. Two grams of soil sample was placed in a 50-mL centrifuge tube with 20 mL of 1 M NH<sub>4</sub>Cl. The tubes were sealed with rubber stoppers and shaken horizontally for 30 min and then centrifuged at 8,000g for 10 min. The supernatant was filtered through Whatman no. 42 filter paper and collected in a 50-mL volumetric flask. The extraction procedure was repeated, and the combined extract was brought to 50 mL with 1 M NH<sub>4</sub>Cl.

Exchangeable Al was extracted with 1 M KCl as follows. Five grams of soil was placed in a 50-mL centrifuge tube with 30 mL of KCl. The tubes were sealed, shaken for 30 min, and then centrifuged at 8,000g for 10 min. The supernatant was filtered and collected in a 100-mL volumetric flask. The extrac-

tion procedure was repeated twice, and the combined extract was brought to 100 mL with 1 M KCl. Effective cation exchange capacity (CEC) was calculated as the sum of KCl-extracted Al and NH<sub>4</sub>Cl-extracted Ca, Mg, K, and Na.

Soil pH was measured in a 20 g/20 mL soil-water suspension. The suspension was stirred for 1 min and let stand for 30 min before pH was read with a pH meter.

### Chemical Analyses

Soil-solution Al, Ca, Mg, K, and Na were measured with an inductively coupled plasma spectrometer (Hue et al., 2000). Soil-solution organic carbon was determined by the Mn(III)-pyrophosphate method (Bartlett and Ross, 1988). Soil-solution P was measured by the sulfomolybdate/ascorbic acid method (Olsen and Sommers, 1982).

Organic acids in the soil solution were purified as follows. A 1-mL aliquot of sample was passed, at a flow rate of 0.25 mL/min, through a column (0.5-mm internal diameter) packed with a 5-mm-thick layer of AG1-X8 anion exchange resin, pH 4.8, in formate form. The eluent was discarded. The column was rinsed with 1 mL H<sub>2</sub>O. The adsorbed organic anions were eluted into small vials by leaching the column with 3 mL of 6 M formic acid. The eluent was dried at 60°C in an oven overnight. Then the residues were redissolved in 1 mL of 5 mM H<sub>2</sub>SO<sub>4</sub> before analysis.

Purified low-molecular-weight organic acids in soil solution were determined with a high-performance liquid chromatograph, using a Bio-Rad (Richmond, CA) Aminex HPX-87H organic acid column. Isocratic mode was used with 5 mM H<sub>2</sub>SO<sub>4</sub> as the mobile phase and a flow rate of 0.5 mL/min. A UV detector was used to measure the absorbance at 210 nm. Ultrapure chemicals of selected organic acids were used as the standards.

### Preparation and Analysis of Plant Tissue Samples

Above-ground plant samples were harvested and washed first with tap water then twice with deionized water before being pat dry. The plant material was dried in an oven at 80°C for 48 h. Dry weight was recorded, and the sample was ground to pass a 0.4-mm sieve. A subsample of 0.20 g was ashed in a muffle furnace at 500°C for 4 h. The ash was dissolved in 3 mL of 1 M HNO<sub>3</sub> and heated slowly until dry. The residue was redissolved

**TABLE 2.** Elemental Composition of Dried Cowpea (*V. unguiculata*) and Pineapple (*A. comosus*) Residues Used in the Acidity Amending Experiment

| Elements | Residues |           |
|----------|----------|-----------|
|          | Cowpea   | Pineapple |
| (g/kg)   |          |           |
| N        | 26.0     | 15.0      |
| P        | 3.1      | 1.3       |
| K        | 37.0     | 53.0      |
| Ca       | 18.2     | 7.3       |
| Mg       | 4.7      | 2.8       |
| Na       | 0.98     | 1.04      |
| (mg/kg)  |          |           |
| Al       | 738      | 1,016     |
| Mn       | 628      | 496       |
| Cu       | 13       | 14        |
| Zn       | 50       | 24        |

in 10 mL of 0.1 M HCl and filtered before being analyzed with an inductively coupled plasma spectrometer.

**Data Analysis**

**Al Activity and Speciation**

The GEOCHEM-EZ program (Shaff et al., 2010) was used to calculate the activities of several Al species. The input data included pH and concentrations (in mM) of Al, Ca, Mg, K, Na, Cl, P, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, dissolved organic carbon (fulvic acids), and soluble organic acids. Although not directly measured in this study, SO<sub>4</sub> values were assigned to be 0.17 mM for the Ultisol and 0.67 mM for the Andisol based on our data from other experiments on the same soils (Hue, unpublished data).

**Statistical Analysis**

Analysis of variance was used to examine the effect of treatments on shoot dry weight and soil properties. Treatment means were separated by the Duncan's multiple-range test (if analysis of variance showed significance). These tasks were performed with SAS version 9.13 software (SAS Institute Inc., Cary, NC). Regression fitting and plotting were performed with Sigma Plot version 10 (SYSTAT software, Inc., Chicago, IL).

**RESULTS AND DISCUSSION**

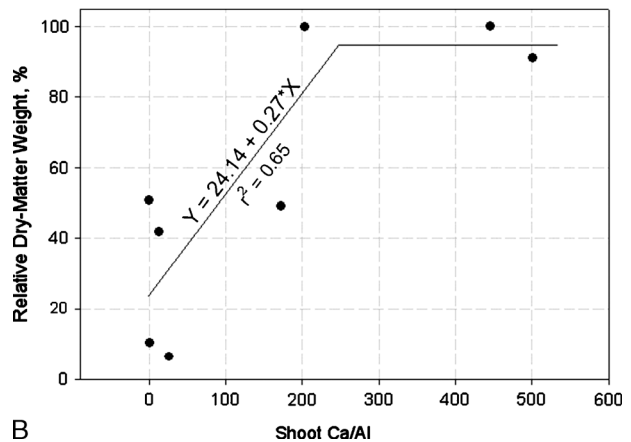
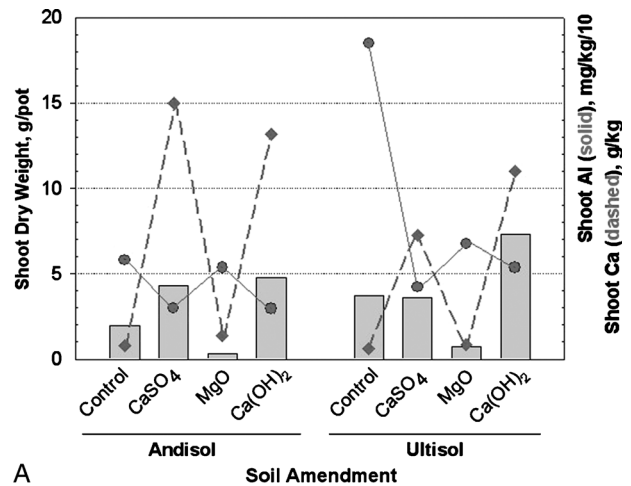
**Al Toxicity Versus Ca Deficiency**

Aluminum phytotoxicity is indicated when plant growth is enhanced by Ca(OH)<sub>2</sub> addition, but unaffected or decreased by CaSO<sub>4</sub> addition. When growth is enhanced equally by CaSO<sub>4</sub> and Ca(OH)<sub>2</sub>, but decreased by MgO addition as compared with the unamended control, soil levels of Ca are insufficient for plant growth. Both Ca deficiency and Al toxicity are indicated when plant growth is enhanced by CaSO<sub>4</sub> and further enhanced by Ca(OH)<sub>2</sub> addition. Based on these criteria, the Andisol was Ca deficient, whereas the Ultisol was marginally Ca deficient and severely Al toxic, as indicated by the shoot dry matter of *D. intortum* (Table 3). In the Andisol, the two Ca treatments resulted in approximately equal amounts of dry matter (4.34 and 4.76 vs. 1.98 g/pot in the control), whereas dry matter production in the MgO treatment was only 0.30 g/pot. The decreased growth in the MgO treatment was probably a result of Ca-Mg imbalances in soil as well as in plant (Adams, 1974).

**TABLE 3.** Shoot Dry Weight (DW) and Chemical Composition of *D. intortum* as Affected by the Four Inorganic Treatments

| Treatment           | Shoot DW | Al      | Ca                   | Mg      | K      | Na     |
|---------------------|----------|---------|----------------------|---------|--------|--------|
|                     | g/pot    | mg/kg   | ← ----- g/kg ----- → |         |        |        |
| <b>Andisol</b>      |          |         |                      |         |        |        |
| Control             | 1.98 b   | 58.2 a  | 0.79 c               | 3.91 b  | 40.8 a | 4.48 b |
| CaSO <sub>4</sub>   | 4.34 a   | 29.9 b  | 15.0 a               | 2.32 c  | 16.2 c | 5.10 a |
| MgO                 | 0.30 c   | 53.7 a  | 1.39 b               | 7.71 a  | 23.5 b | 2.33 c |
| Ca(OH) <sub>2</sub> | 4.76 a   | 29.6 b  | 13.2 a               | 2.23 c  | 22.2 b | 4.05 b |
| <b>Ultisol</b>      |          |         |                      |         |        |        |
| Control             | 3.73 b   | 185.3 a | 0.61 c               | 2.36 b  | 23.0 a | 1.10 c |
| CaSO <sub>4</sub>   | 3.60 b   | 42.2 c  | 7.27 b               | 1.73 c  | 24.6 a | 1.68 b |
| MgO                 | 0.74 c   | 67.5 b  | 0.84 c               | 7.00 a  | 20.3 b | 2.05 a |
| Ca(OH) <sub>2</sub> | 7.34 a   | 53.8 bc | 11.0 a               | 1.91 bc | 24.2 a | 1.68 b |

Numbers followed by the same letter within a column and a soil are not significantly different at the 5% level according to the Duncan's multiple-range test.



**FIG. 1.** Shoot dry weight and Al and Ca concentration of *D. intortum* in different inorganic treatments addressing soil acidity (A), shoot dry weight as a function of shoot Ca/Al ratio (B).

In the Ultisol, only suppression of soluble Al in the Ca(OH)<sub>2</sub> treatment increased yield, whereas dry matter production in the CaSO<sub>4</sub> treatment was not significantly different from the control (although Ca uptake markedly increased). The MgO treatment depressed yield significantly to 0.74 g/pot as compared with 3.73 g/pot in the control, perhaps because of the imbalance between Ca and Mg as previously noted for the Andisol (Table 3).

By plotting dry matter weight and shoot Ca and Al on a same graph (Fig. 1A), it is evident that shoot Al and Ca concentrations were inversely related. Because both Ca and Al seemed to affect plant growth, although to different extents, in the two soils, expressing relative plant growth as a function of Ca/Al ratio could make use of the data from both soils (Fig. 1B). Linear-plateau response model (Schabenberger and Pierce, 2002) applied on such combined data suggests that optimal growth would be attained when Ca/Al is greater than 264 (Fig. 1B). Because Al toxicity was not present in the Andisol, shoot Al in the control treatment (58.2 mg/kg) could be reasonably assumed to be the “critical” level, below which Al is not toxic. Using this Al concentration and the “critical” Ca/Al ratio of 264, the “critical” Ca level can be calculated to be 15.4 g/kg, a level above which Ca deficiency is not likely to occur for *D. intortum*. This value was approximately double the “average”

**TABLE 4.** Soil pH and Exchangeable Cations as Affected by the Inorganic Treatments\*

| Treatment           | pH                  | Al                                | Ca           | Mg      | eCEC    |
|---------------------|---------------------|-----------------------------------|--------------|---------|---------|
|                     |                     | ←-----cmol <sub>c</sub> /kg-----→ |              |         |         |
| Andisol             |                     |                                   |              |         |         |
| Control             | 4.50 b <sup>†</sup> | 2.20 (24.9) <sup>‡</sup> a        | 0.44 (4.9) b | 0.96 bc | 9.18 c  |
| CaSO <sub>4</sub>   | 4.58 b              | 1.59 (17.3) b                     | 4.13 a       | 0.55 c  | 10.04 b |
| MgO                 | 5.42 a              | 0.18 (2.1) c                      | 0.44 b       | 5.68 a  | 11.15 a |
| Ca(OH) <sub>2</sub> | 5.38 a              | 0.18 (2.0) c                      | 4.51 a       | 1.15 b  | 11.61 a |
| Ultisol             |                     |                                   |              |         |         |
| Control             | 4.60 b              | 2.78 (49.9) a                     | 0.46 (8.2) b | 0.45 b  | 5.57 b  |
| CaSO <sub>4</sub>   | 4.45 c              | 2.38 (39.8) b                     | 3.06 a       | 0.24 c  | 5.98 ab |
| MgO                 | 5.36 a              | 0.09 (1.5) c                      | 0.48 b       | 3.56 a  | 6.16 a  |
| Ca(OH) <sub>2</sub> | 5.32 a              | 0.10 (1.6) c                      | 3.07 a       | 0.49 b  | 6.35 a  |

\*Average values of those taken at planting and at harvest.

<sup>†</sup>Numbers followed by the same letter within a column and a soil are not significantly different at the 5% level according to the Duncan's multiple-range test.

<sup>‡</sup>Numbers in the parentheses are the percentage saturation (i.e., 100 \* exch. cation/eCEC).

eCEC: effective cation exchange capacity.

range of 5.8 to 7.4 g/kg reported by Jones et al. (1991), perhaps because plants in this experiment grew fast under favorable moisture and temperature conditions, thereby requiring more Ca.

### Exchangeable Al, Ca, and Mg

As expected, the treatments with Ca(OH)<sub>2</sub> and MgO reduced exchangeable Al from more than 2.0 cmol<sub>c</sub>/kg to less than 0.20 cmol<sub>c</sub>/kg and increased exchangeable Ca and Mg accordingly in both soils (Table 4). More interestingly, the gypsum treatment also reduced exchangeable Al slightly, perhaps because of the specific adsorption of SO<sub>4</sub><sup>2-</sup>, which releases OH<sup>-</sup> into solution as proposed by Hue et al. (1985).

Because the two soils possess different mineralogies and thus significantly different CECs, cation saturation, expressed as a percentage of the effective CEC, would be more appropriately representative of deficiency or toxicity (Miyasaka et al., 2006). Using this metric, severe Al toxicity and moderate Ca deficiency would be expected in the Ultisol where Al saturation exceeded 44.9% (mean of 49.9% and 39.8%) and Ca saturation fell below 8.2% (Table 4). These criteria can be applied to the Andisol as well. With only 4.9% Ca saturation in the control treatment, the Andisol was Ca deficient, yet Al nontoxic for having only 24.9% Al saturation (Table 4).

### Soil-Solution Al, Ca, Mg, and pH

Soil-solution composition is the most direct factor affecting plant growth. Table 5 lists the soil-solution concentration of Al, Ca, Mg, and Ca/Mg ratio as well as pH of the four inorganic treatments (Al activities are also listed).

Although the mechanism of Al toxicity is not fully understood, it is generally believed that inorganic (noncomplexed) Al, specifically Al<sup>3+</sup> and its hydrolytic products (expressed in activity terms), is toxic to plants (Hue et al., 1986; Miyasaka et al., 2006). The Ca(OH)<sub>2</sub> and MgO treatments, which raised soil pH, expectedly reduced Al significantly (Table 5). Because Al was not present at levels toxic to *D. intortum* in the Andisol, an Al activity of 13.0 μM in the control treatment can be considered nontoxic. In contrast, the reduction in shoot dry weights of *D. intortum* when the Al level was 20.3 μM in the CaSO<sub>4</sub> treatment of the Ultisol would indicate a toxic Al level (Table 3). Thus, it can be concluded that the critical Al activity that is toxic for *D. intortum* lies somewhere between 13 and 20 μM, which is similar to the critical Al<sup>3+</sup> levels for cotton (*Gossypium hirsutum*) and wheat (*Triticum aestivum*) (Miyasaka et al., 2006).

Soil-solution Ca was increased with the Ca(OH)<sub>2</sub> and CaSO<sub>4</sub> treatments but decreased slightly by the MgO treatment, probably as a result of pH and CEC increases (Tables 4 and 5). The initial purpose of the MgO treatment was to raise soil pH and precipitate Al. However, shoot dry weight (Table 3) indicated a negative effect of this treatment on *D. intortum* growth. This suggests that Ca might have a specific function that cannot

**TABLE 5.** Soil-Solution pH, Al, Ca, Mg, and Ca/Mg Ratio as Affected by Various Inorganic Treatments\*

| Treatment           | pH                  | Al                 |                   | Ca     | Mg     | Ca/Mg |
|---------------------|---------------------|--------------------|-------------------|--------|--------|-------|
|                     |                     | Conc. <sup>†</sup> | Act. <sup>‡</sup> |        |        |       |
|                     |                     | ←-----μM-----→     |                   |        |        |       |
| Andisol             |                     |                    |                   |        |        |       |
| Control             | 4.57 c <sup>§</sup> | 44.2 a             | 13.0 a            | 0.26 b | 0.19 c | 1.63  |
| CaSO <sub>4</sub>   | 4.36 d              | 44.8 a             | 10.9 a            | 0.65 a | 0.40 b | 1.63  |
| MgO                 | 5.53 b              | 17.8 b             | 3.2 b             | 0.25 b | 0.72 a | 0.34  |
| Ca(OH) <sub>2</sub> | 5.66 a              | 18.0 b             | 2.8 b             | 0.57 a | 0.19 c | 2.68  |
| Ultisol             |                     |                    |                   |        |        |       |
| Control             | 4.45 b              | 62.6 a             | 21.5 a            | 0.21 b | 0.40 b | 0.68  |
| CaSO <sub>4</sub>   | 4.26 c              | 68.3 a             | 20.3 a            | 0.95 a | 0.48 b | 1.98  |
| MgO                 | 5.62 a              | 16.4 b             | 4.2 b             | 0.20 b | 1.64 a | 0.12  |
| Ca(OH) <sub>2</sub> | 5.63 a              | 15.0 b             | 2.1 b             | 0.82 a | 0.24 c | 3.25  |

\*Average values of those taken at planting and at harvest.

<sup>†</sup>Total soluble Al concentration.

<sup>‡</sup>The sum activity of monomeric hydroxy-Al species.

<sup>§</sup>Numbers followed by the same letter within a column and a soil are not significantly different at the 5% level according to Duncan's multiple-range test.

**TABLE 6.** Shoot Dry Weight and Mineral Composition of *D. intortum* Leaves as Affected by the Organic-Soil Amendments [Data of the Control and Ca(OH)<sub>2</sub> Treatments Listed for Comparison]

| Treatment           | Shoot      | Mineral Composition of Leaves |                  |      |      |      |
|---------------------|------------|-------------------------------|------------------|------|------|------|
|                     | Dry Weight | Al                            | Ca               | Mg   | K    | Na   |
|                     | g/pot      | mg/kg                         | ←-----g/kg-----→ |      |      |      |
| <b>Andisol</b>      |            |                               |                  |      |      |      |
| Ashed pineapple     | 3.88 cd*   | 56.1                          | 0.85             | 2.09 | 32.5 | 3.36 |
| Fresh pineapple     | 4.23 cd    | 21.8                          | 1.11             | 2.76 | 23.1 | 1.13 |
| Ashed cowpea        | 5.98 b     | 29.3                          | 2.21             | 2.41 | 25.3 | 3.58 |
| Fresh cowpea        | 6.70 a     | 19.1                          | 3.79             | 3.43 | 29.4 | 1.48 |
| Ca(OH) <sub>2</sub> | 4.67 c     | 29.6                          | 13.2             | 2.23 | 22.2 | 4.05 |
| Control             | 1.98 d     | 58.2                          | 0.79             | 3.91 | 40.8 | 4.48 |
| <b>Ultisol</b>      |            |                               |                  |      |      |      |
| Ashed pineapple     | 5.49 cd    | 140.4                         | 1.37             | 2.17 | 21.1 | 6.63 |
| Fresh pineapple     | 8.31 b     | 63.1                          | 1.67             | 1.93 | 18.5 | 4.10 |
| Ashed cowpea        | 5.95 cd    | 80.7                          | 2.53             | 2.26 | 18.4 | 1.57 |
| Fresh cowpea        | 10.93 a    | 49.5                          | 4.74             | 3.90 | 27.0 | 3.15 |
| Ca(OH) <sub>2</sub> | 7.34 bc    | 53.8                          | 11.0             | 1.91 | 24.2 | 1.68 |
| Control             | 3.73 d     | 185.3                         | 0.61             | 2.36 | 23.0 | 1.10 |

\*Numbers followed by the same letter within a column and a soil are not significantly different at the 5% level according to Duncan's multiple-range test.

be replaced by Mg, or the imbalance between Ca and Mg in soil solution (and in plant) would depress growth (Adams, 1974). Based on shoot dry weight of the Ca(OH)<sub>2</sub> treatment, Andisol, it appears that adequate levels of Ca and Ca/Mg are about 0.6 mM and 3.0, respectively.

**Effects of Crop Residues**

**On Shoot Dry Matter and Nutrient Composition**

Amending either of the acid soils with crop residues increased plant growth significantly relative to the control (Table 6). The results suggest that the benefits of organic amendments are greater than just their direct nutritional contribution. Dry matter production in soils amended with fresh residues was similar to or greater than that produced in the Ca(OH)<sub>2</sub> treatment in both soils, demonstrating their good potential for correcting soil acidity. In fact, Al concentrations in leaves of plants grown in organic treatments (except for the ashed pineapple treatment) were reduced to levels similar to those grown in the Ca(OH)<sub>2</sub> treatment (Table 6). Between the

two residue sources, cowpea was more effective than pineapple in correcting soil acidity. This difference might result from the higher nutrient composition of cowpea (Table 2), from organic acids such as pascidic and citric acids that can detoxify Al (Ishikawa et al., 2002), or from some growth stimulants produced by the decomposition of cowpea (Chen et al., 2004).

In general, the fresh residue treatments produced higher yields than their ashed counterparts, especially in the Al-toxic Ultisol. In the Andisol, however, only the fresh cowpea treatment had significantly higher yield than its ashed counterpart, whereas the pineapple treatment did not. That is perhaps because in the Ca-deficient Andisol, only the cowpea treatments supplied enough Ca (cowpea had 1.82% Ca) to eliminate Ca deficiency, then the Al detoxification minor effect further increased yields. In contrast, Ca supply of the pineapple residue, which had 0.73% Ca, was not sufficient to eliminate Ca deficiency.

Effects of crop-residue amendments were also reflected in mineral composition of leaves (Table 6). For example, leaf Al concentration decreased from 185.3 mg/kg in the control to 49.5 mg/kg in the fresh cowpea treatment in the Ultisol.

**TABLE 7.** Soil pH and Exchangeable Al and Ca as Affected by Crop-Residue Amendments\*

| Treatment           | Andisol             |                                   |        | Ultisol |                                   |        |
|---------------------|---------------------|-----------------------------------|--------|---------|-----------------------------------|--------|
|                     | pH                  | Al                                | Ca     | pH      | Al                                | Ca     |
|                     |                     | ←-----cmol <sub>c</sub> /kg-----→ |        |         | ←-----cmol <sub>c</sub> /kg-----→ |        |
| Ashed pineapple     | 4.92 c <sup>†</sup> | 2.14 a                            | 0.44 b | 4.78 c  | 1.63 b                            | 0.50 b |
| Fresh pineapple     | 5.03 b              | 1.06 b                            | 0.55 b | 5.01 b  | 1.16 b                            | 0.48 b |
| Ashed cowpea        | 4.79 c              | 1.98 a                            | 0.84 b | 4.75 c  | 1.11 b                            | 0.51 b |
| Fresh cowpea        | 5.04 b              | 0.85 b                            | 0.88 b | 5.11 b  | 0.61 c                            | 0.66 b |
| Control             | 4.50 d              | 2.20 a                            | 0.44 b | 4.60 c  | 2.78 a                            | 0.46 b |
| Ca(OH) <sub>2</sub> | 5.38 a              | 0.18 c                            | 4.51 a | 5.32 a  | 0.10 d                            | 3.07 a |

\*Average values of those taken at planting and at harvest. Data for the control and Ca(OH)<sub>2</sub> treatments listed for comparison.

<sup>†</sup>Numbers followed by the same letter within a column are not significantly different at 5% level according to Duncan's multiple-range test.

**TABLE 8.** Soil-Solution pH, Total Soluble Al, and Ca as Affected by Crop-Residue Amendments\*

| Treatment           | Andisol             |               |        | Ultisol |               |         |
|---------------------|---------------------|---------------|--------|---------|---------------|---------|
|                     | pH                  | Al            | Ca     | pH      | Al            | Ca      |
|                     |                     | $\mu\text{M}$ | mM     |         | $\mu\text{M}$ | mM      |
| Ashed pineapple     | 5.02 c <sup>†</sup> | 24.7 b        | 0.15 b | 4.95 c  | 20.0 b        | 0.22 c  |
| Fresh pineapple     | 5.53 b              | 19.6 b        | 0.13 b | 5.57 b  | 15.7 b        | 0.20 c  |
| Ashed cowpea        | 4.88 c              | 24.2 b        | 0.28 b | 5.04 c  | 18.9 b        | 0.29 bc |
| Fresh cowpea        | 5.52 b              | 16.6 bc       | 0.23 b | 5.45 b  | 12.3 bc       | 0.37 b  |
| Control             | 4.57 d              | 44.2 a        | 0.26 b | 4.45 d  | 62.6 a        | 0.21 c  |
| Ca(OH) <sub>2</sub> | 5.66 a              | 18.0 b        | 0.57 a | 5.63 a  | 15.0 b        | 0.82 a  |

\*Average values of those taken at planting and at harvest. Data for the control and Ca(OH)<sub>2</sub> treatments listed for comparison.

<sup>†</sup>Numbers followed by the same letter within a column are not significantly different at 5% level according to Duncan's multiple-range test.

Ahmad and Tan (1986) reported a similar decrease when wheat straw was applied to a Bradson soil (Typic Hapludults) of Georgia. Leaf Ca concentrations in the crop-residue treatments, however, were slightly higher than in the control, but markedly lower than in the Ca(OH)<sub>2</sub> treatment. Furthermore, concentrations of leaf Mg, K, and Na in all the organic treatments remained nearly constant and were similar to those in the control.

#### On Soil pH and Exchangeable Al and Ca

Additions of crop residues increased soil pH slightly, and the fresh materials were more effective than their ashed counterparts (Table 7). Such pH increases were probably due to oxides of base cations (i.e., Ca, Mg, K, Na) in the residues (Wong and Swift, 2003) and from the consumption of H<sup>+</sup> by organic anions in the fresh residues. Interestingly, exchangeable Al (as extracted with KCl) was decreased substantially by the

organic treatments. For example, the fresh cowpea treatment lowered exchangeable Al from 2.20 to 0.85 cmol<sub>e</sub>/kg in the Andisol and from 2.78 to 0.61 cmol<sub>e</sub>/kg in the Ultisol. Similar results were reported by Hargrove and Thomas (1981). It is likely that in addition to pH increases that could precipitate Al, functional groups such as COOH and OH carried on the surface of fresh crop residues reacted with soil Al and make Al non-extractable with KCl. Exchangeable Ca was numerically higher in the organic treatments than in the controls, but was not statistically significant (Table 7).

#### On pH, Al, and Ca of the Soil Solution

Similar to soil pH, soil-solution pH was increased from about 4.5 in the control to approximately 5.0 in the ashed residue and 5.5 in the fresh residue treatments (Table 8). More interestingly, there was no difference between the residue treatments (10 g/kg) and the Ca(OH)<sub>2</sub> treatment (4 cmol<sub>e</sub>/kg) in terms of total soluble Al concentrations, which ranged from 15.0 to 24.7  $\mu\text{M}$  (Table 8). For comparison, soil-solution Al was 44.2 and 62.6  $\mu\text{M}$  in the control treatments of the Andisol and Ultisol, respectively. This decreased Al concentration could be explained by the same mechanism that decreased exchangeable Al as previously mentioned. In contrast, the organic amendments did not increase soil-solution Ca significantly relative to the control. Only the Ca(OH)<sub>2</sub> treatment did raise soil-solution Ca to 0.57 mM in the Andisol and 0.82 mM in the Ultisol.

#### On Oxidizable Carbon and Organic Acids in the Soil Solution

Because organic acids can alleviate Al toxicity with citric, oxalic, and tartaric acids being most effective (Hue et al., 1986), these acids and oxidizable organic carbon were measured from the soil solution of all treatments (Table 9). As expected, the fresh residue treatments had much higher soluble organic C than their ashed counterparts and the inorganic treatments. For example, soluble C was 0.11, 0.16, and 2.84 mM in the control,

**TABLE 9.** Oxidizable C and Organic Acids in Soil Solution as Affected by Crop-Residue Amendments\*

| Treatment                   | Oxidizable Carbon<br>mM | Organic Acids  |        |          | Act.             | Act.                     |
|-----------------------------|-------------------------|----------------|--------|----------|------------------|--------------------------|
|                             |                         | Citric         | Oxalic | Tartaric | Al <sup>3+</sup> | $\Sigma$ Al <sup>†</sup> |
| ←----- $\mu\text{M}$ -----→ |                         |                |        |          |                  |                          |
| Andisol                     |                         |                |        |          |                  |                          |
| Ashed pineapple             | 0.17 b <sup>‡</sup>     | — <sup>§</sup> | —      | —        | 0.50             | 6.80                     |
| Fresh pineapple             | 2.43 a                  | 60             | 16     | 23       | 0.06             | 11.0                     |
| Ashed cowpea                | 0.18 b                  | —              | —      | —        | 1.10             | 8.72                     |
| Fresh cowpea                | 2.50 a                  | 185            | —      | 65       | 0.17             | 3.61                     |
| Control                     | 0.13 b                  | —              | —      | —        | 2.88             | 15.0                     |
| Ca(OH) <sub>2</sub>         | 0.16 b                  | —              | —      | —        | 0.02             | 2.79                     |
| Ultisol                     |                         |                |        |          |                  |                          |
| Ashed pineapple             | 0.20 c                  | —              | —      | —        | 0.17             | 10.1                     |
| Fresh pineapple             | 2.09 b                  | 46             | —      | 32       | 0.02             | 4.68                     |
| Ashed cowpea                | 0.16 c                  | —              | —      | —        | 0.14             | 8.98                     |
| Fresh cowpea                | 2.84 a                  | 132            | —      | 86       | 0.01             | 1.23                     |
| Control                     | 0.11 c                  | —              | —      | —        | 5.41             | 21.5                     |
| Ca(OH) <sub>2</sub>         | 0.10 c                  | —              | —      | —        | 0.01             | 2.23                     |

\*Average values of those taken at planting and at harvest. Data for the control and Ca(OH)<sub>2</sub> treatments listed for comparison.

<sup>†</sup>Total Al hydrolytic species [Al<sup>3+</sup> + Al(OH)<sup>2+</sup> + Al(OH)<sub>2</sub><sup>+</sup> + Al(OH)<sub>3</sub><sup>0</sup> + Al(OH)<sub>4</sub><sup>-</sup>].

<sup>‡</sup>Numbers followed by the same letter within a column are not significantly different at 5% level according to Duncan's multiple-range test.

<sup>§</sup>Non-detectable.

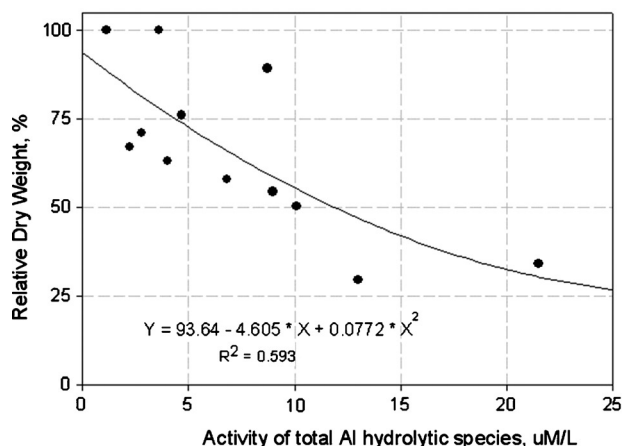


FIG. 2. Relative dry weight of *D. intortum* as a function of soil-solution Al.

ashed cowpea, and fresh cowpea treatments of the Ultisol, respectively (Table 9). The three organic acids studied were found only in the fresh residue treatments, with citric acid being most abundant (range, 46–185  $\mu\text{M}$ ), followed by tartaric acid (range, 23–86  $\mu\text{M}$ ) (Table 9). Oxalic acid (16  $\mu\text{M}$ ) was found only in the fresh pineapple treatment of the Andisol. Using stability constants of Al with organic acids provided by Hue et al. (1986) and the GEOCHEM-EZ software (Shaff et al., 2010), total soluble Al was partitioned into  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3^0$ , and  $\text{Al}(\text{OH})_4^-$ . It is clear that the fresh residue and  $\text{Ca}(\text{OH})_2$  treatments drastically lowered the activity of  $\text{Al}^{3+}$  and total Al hydrolytic species ( $\Sigma\{\text{Al}\}$ ) (Table 9).

By plotting relative dry matter weight of *D. intortum* as a function of the activity of  $\Sigma\{\text{Al}\}$ , it can be stated that a 25% and 50% growth reduction would be expected when  $\Sigma\{\text{Al}\} > 4.9 \mu\text{M}$  and  $> 12 \mu\text{M}$ , respectively (Fig. 2). These values are within the range of 2.1 to 67  $\mu\text{M}$  of  $\Sigma\{\text{Al}\}$  reported for 48 surface soils from Queensland, Australia (Bruce et al., 1989).

In summary, crop residues could be used to alleviate soil acidity. Their effectiveness varied with residue type and mode of preparation (i.e., fresh vs. ashed) and with soil acidity problems (Al toxicity vs. Ca deficiency). More specifically, soil pH was raised moderately by crop-residue amendments, perhaps by the liming effect of basic cations contained in the residues and/or by ligand exchange between terminal OH at the soil surface and organic anions derived from the decomposing residues. Yet, exchangeable Al was lowered substantially, perhaps by reactions with COOH and OH at the surface of the solid organic materials. Furthermore, soil-solution Al was detoxified by complexation with soluble C, particularly organic acids produced by the organic residues. There was a good correlation between plant growth and the activity of total monomeric hydrolytic species of Al ( $\Sigma\{\text{Al}\}$ ). Significant growth reduction would be expected when  $\Sigma\{\text{Al}\} > 12.0 \mu\text{M}$ .

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