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ALUMINUM DETOXIFICATION WITH GREEN MANURES[1]

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ABSTRACT

A greenhouse experiment was conducted to evaluate "liming" potential of different green manures. Ground leafy materials of cowpea (*Vigna unguiculata*), leucaena (*Leucaena leucocephala*) and guinea grass (*Panicum maximum*) were added at 0, 5, 10 and 20 g/kg to an Ultisol having a soil-water pH 4.0, KCl-extractable Al = 7.6 $cmol_c$/kg, Al saturation = 50% and soil-solution Al = 2.2 mM. Treatments with $Ca(OH)_2$ were established for comparison. *Sesbania cochinchinensis*, an Al-sensitive tree legume, was grown for 4 weeks as a test crop. Biomass production and chemical composition of the soil indicated that (i) cowpea and leucaena were more effective than guinea grass in detoxifying Al; for example, the additions of 10 g manure per kg soil were equivalent to 1.8 cmol(OH)/kg for guinea grass, 3.4 for cowpea and 4.2 for leucaena (at least on a short-term basis), (ii) reduction of soluble Al at increased pH as a result of manure additions was the major mechanism for Al detoxification, and (iii) complexation of soluble Al by organic molecules also contributed to the detoxification.

INTRODUCTION

Aluminum (Al) phytotoxicity is a nearly universal factor of soil acidity which seriously limits productivity of many soils around the world. Conventional amendments (e.g., $CaCO_3$ or $MgCO_3$) are relatively expensive and may not be available in many developing countries where neither cash nor transportation is adequate. Alternatives using locally available resources must be sought.

Recent research has shown that the addition of green manures to acid soils reduces Al phytotoxicity and increases crop yields.[3,4,5] Complexation of soil solution Al by decomposition products, particularly low-molecular-weight organic acids, of the added residues has been implicated as a major mechanism for Al detoxification.[6,7] Additionally, freshly added organic materials can also reduce soluble Al by adsorbing it on their surface[3] and/or precipitating Al when soil pH is increased as a result of (i) intense microbial activities[4,8] or (ii) ligand exchange reactions between OH^- and organic anions.[9] Regardless of the mechanism(s) involved and its presumably short-lived (as compared to $CaCO_3$) nature, the Al detoxifying effect of green manures still could give young seedlings the needed time to establish, become more competitive with weeds and/or more tolerant of soil acidity.

The primary objective of this study was to evaluate the Al detoxifying potential of different organic residues which were incorporated into a strongly acid Ultisol. The second objective was to identify possible processes responsible for this Al detoxification.

MATERIALS AND METHODS

Properties of Soil, Manures, and Amendments.

A highly weathered strongly acid Ultisol (Humoxic Tropohumult, Kaneche Series), which had a soil-water pH of 4.0, KCl-extractable Al of 7.6 $cmol_c$/kg, Al saturation of 50% and soil solution Al of 2.2 mM, was used in a greenhouse experiment for Al detoxification. Green manures consisted of ground leafy materials of cowpea (*Vigna*

Table 1. Nutrient values of the green manures used in the liming experiment.

Green manure	N	P	K	Ca	Mg
	<----------------		%	------------------>	
Cowpea	3.60	0.41	3.45	1.54	0.37
Guinea grass	0.85	0.12	1.60	0.57	0.25
Leucaena	3.81	0.16	1.72	1.05	0.32

unguiculata), guinea grass (*Panicum maximum*) and leucaena (*Leucaena leucocephala*). These plant species were selected because they widely grow in the tropics and cowpea, in particular, is known for its acid tolerance. Table 1 lists some nutritional values of the manures.

Treatments included conventional lime as $Ca(OH)_2$ at 0, 1.8, 3.6 and 7.2 cmol(OH)/kg and manures at 0, 5, 10 and 20 g/kg for each source. To ensure that Al toxicity was the sole factor limiting growth, basal fertilizers were added to all treatments at (in mg/kg) 140 N, 200 Ca, 310 P, 390 K, 48 Mg and 64 S. Each treatment was replicated three times, and the experiment had a completcly randomized design.

Sesbania cochinchinensis, an Al-sensitive tree legume, was grown for 4 weeks as a test crop (two seedlings per pot containing 1 kg soil). Deionized water was added daily to replace evapo-transpiration loss. Plant dry matter weight and soil chemical composition were used to measure the liming effectiveness of the manures.

<u>Laboratory Analysis.</u>

Soil solution collection. A centrifugation procedure[10] was used to collect soil solutions just prior to planting (1 week after treatment initiation) for chemical characterization. In this method, approximately 250 g of soil at field water holding capacity was packed into a modified plastic Buchner funnel lined with a Whatman no. 42 filter paper. The whole assembly was centrifuged at 1500 *g* for 30 minutes, pH of the soil solution just collected was immediately measured before significant CO_2 might be lost. Thereafter, the soil solution was filtered through a 0.45-um micropore membrane and refrigerated until chemical analysis which was done within 2 days after the solution was collected.

Chemical measurements. Soil solution Al was unusually high ($\geq$ 0.5 m<u>M</u>, even in the treatments receiving high rates of lime or manures); therefore, desirable sensitivity for measurement of total soluble Al was achieved with atomic absorption spectrometry using a nitrous oxide flame.

Exchangeable Al was first extracted with 1 <u>M</u> KCl and then measured by a titrimetric method using dilute NaOH after the addition of KF.[11] Exchangeable Ca was extracted with 1 <u>M</u> NH_4OAc, pH 7.0, then measured with an atomic absorption spectrometer after $LaCl_3$ addition.

Soil solutions of those treatments receiving the highest rate of $Ca(OH)_2$, cowpea or leucaena were also analyzed for oxidizable carbon and low-molecular-weight organic acids. Soluble oxidizable carbon was determined by the Mn(III)-pyrophosphate method.[12] Organic acids were determined with a high pressure liquid chromatograph (HPLC) after purification of the soil solution as follows. One mL of the solution was passed at a flow rate of 0.25 mL/min through a column (0.5 cm i.d.) packed with a 0.5-cm layer of AG 1-X8 anion exchange resin, pH 4.8, in formate form (bed volume of the resin was approximately 0.1 mL). Adsorbed anions were displaced with 3 mL of 6 <u>M</u> formic acid, which was subsequently removed by drying the eluent at 60 °C. The residue was redissolved in 5 m<u>M</u> H_2SO_4 and analyzed for free organic acids with an HPLC using an Aminex HPX-87H size exclusion column and a variable wavelength UV detector.

For high stability and sensitivity, the HPLC was operated under isocratic (constant mobile-phase composition) mode. This requires two determinations per sample, one for aliphatic acids, and another for aromatic acids. The HPLC operating conditions were as follows.

Aliphatic acids. Mobile phase, 5 mM H_2SO_4; flow rate, 0.5 mL/min; column temperature, 25 $\pm$ 2 °C; sample loop, 50 uL; wavelength, 210 nm; and absorbance unit full scale (AUFS), 0.040.

Aromatic acids. Mobile phase, 5 mM H_2SO_4 containing 10% acetonitrile (CH_3CN); flow rate, 0.6 mL/min; column temperature, 50 $\pm$ 1 °C; wavelength, 254 nm; and AUFS, 0.040. A preliminary study had indicated that these operating conditions were necessary to resolve certain aromatic acids that were unresolvable using the settings for aliphatic acids.

Because the analytical column was highly selective in retaining low-molecular-weight organic acids, these acids were quantitatively determined by comparing the retention times and peak areas of soil-solution chromatograms with those of HPLC-grade chemical standards that had undergone the same resin treatment as previously described for the unknowns.

RESULTS AND DISCUSSION

Liming Effectiveness of the Green Manures.

Since Ca was adequately added to all treatments of this Ultisol, the response of *Sesbania cochinchinenesis* to $Ca(OH)_2$ application rates was a strong indication of Al toxicity (Table 2). Biomass production (dry matter weight of shoots and roots) increased exponentially from 0.54 g/pot in the unamended to 5.99 g/pot at the highest lime rate of 7.2 cmol(OH)/kg. In fact, this rate might have been less than adequate for maximum growth (complete Al detoxification) as indicated by a steady and positive increase in the slope of the curve describing shoot dry weight as a function of $Ca(OH)_2$ additions (Fig. 1).

Using plant growth as a measure of Al detoxification, it is evident that cowpea and leucaena were quite effective as "liming" sources (Table 2). For example, the 5 g cowpea per kg soil yielded

Table 2. Biomass of *Sesbania*, and soil-solution pH, soil-solution Al, exchangeable Al and Ca as functions of lime or green manure additions.

Application rate	Biomass top	Biomass roots	Biomass Total	Soil solution pH	Soil solution Al	Exchangeable Al†	Exchangeable Ca‡
	← g/pot →				mM	← $cmol_c$/kg →	
			$Ca(OH)_2$, cmol(OH)/kg				
0	0.38	0.16	0.54	3.80	2.17	7.55	4.65
1.8	0.92	0.49	1.41	3.90	1.59	5.80	5.45
3.6	1.33	0.92	2.25	4.05	0.73	4.32	7.00
7.2	4.84	1.15	5.99	4.25	0.50	1.92	10.50
			Cowpea, g/kg				
5	1.62	0.62	2.24	3.83	0.73	5.05	4.88
10	2.09	0.85	2.94	4.02	0.67	4.51	4.85
20	4.67	1.72	6.39	4.21	0.58	3.70	4.38
			Guinea grass, g/kg				
5	0.12	0.07	0.19	3.88	2.15	6.97	4.35
10	0.16	0.09	0.25	3.90	2.43	6.17	5.20
20	1.60	0.55	2.15	4.12	0.87	4.17	4.55
			Leucaena, g/kg				
5	0.62	0.30	0.92	3.95	1.89	5.29	4.35
10	3.72	1.51	5.23	4.08	0.93	3.55	4.45
20	5.73	1.58	7.31	4.20	0.58	2.77	4.83

†Extracted with 1 M KCl.
‡Extracted with 1 M NH_4OAc, pH 7.0.

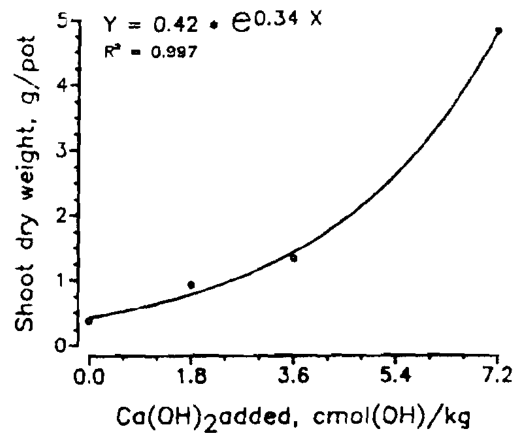


Fig. 1. Shoot dry weight of Sesbania seedlings as a function of $Ca(OH)_2$ added.

2.24 g biomass/pot which was practically identical to 2.25 g/pot produced by the $Ca(OH)_2$ treatment of 3.6 cmol(OH)/kg. The effect of leucaena additions was even more dramatic: while its lowest rate (5 g/kg) was less effective than the corresponding cowpea rate, the other two rates (10 and 20 g/kg) surpassed those of cowpea (and lime) in terms of detoxifying Al (Fig. 2). By contrast, amendments with guinea grass reduced growth at the two lower rates relative to the unamended (Fig. 2). It was not clear as to how this growth reduction actually occured but it is probable that the nutrient-poor grass might have tied up soil nutrients, particularly nitrogen and micronutrients, that would otherwise be available to the sesbania seedlings. The 20 g grass/kg produced a growth increase, but its magnitude was much smaller than those or cowpea or leucaena (Fig. 2).

Possible Processes Responsible for Al Detoxification by the Green Manures.

The growth response of sesbania seedlings to $Ca(OH)_2$ or green manure additions can be attributed primarily to pH increases and

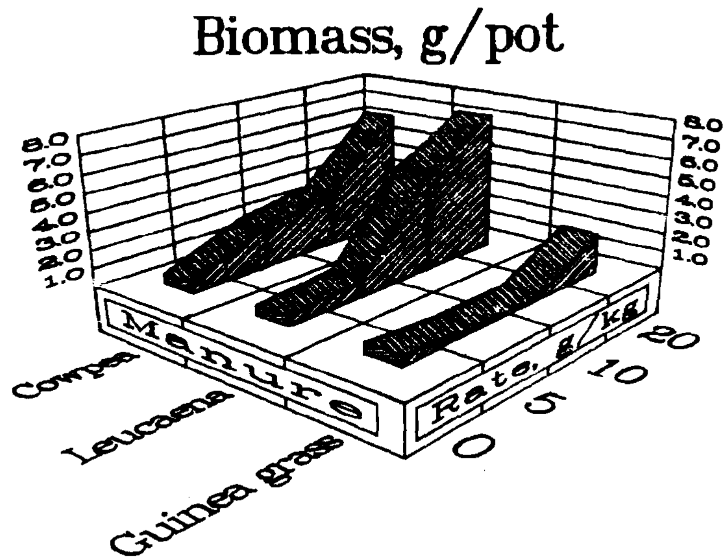


Fig. 2. Biomass production of *Sesbania* seedlings as functions of green manure sources and rates.

consequent decreases in Al, both soluble and exchangeable (Table 2). For example, the highest addition rate of cowpea increased soil solution pH from 3.80 to 4.21 and decreased soluble Al from 2.17 to 0.58 mM. The production of OH^- from $Ca(OH)_2$, which raised soil pH and precipitated Al, was well documented and understood, but the OH-releasing effect of green manure additions was more intriguing. It is possible that (i) a reducing environment was created shortly after green manure additions as a result of intense microbial activities, which in turn dissolved solid Mn and Fe oxides and produced OH^- as proposed by Asghar and Kanehiro,[4] and illustrated below:

$$MnO_2 + 2\ H^+ + 2\ e^- \Longleftrightarrow Mn^{2+} + 2\ OH^-$$

and/or (ii) ligand exchange reactions occurred by which terminal OH's of Al or Fe hydroxy oxides were replaced by organic anions,

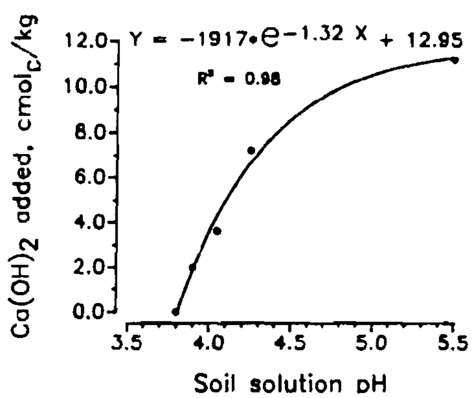
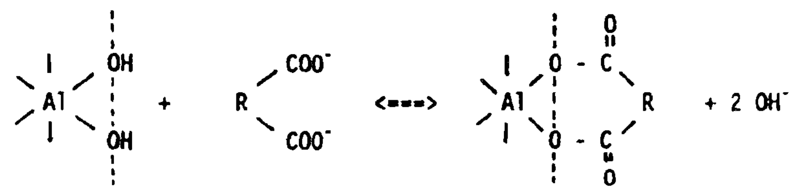


Fig. 3. Relationship between soil-solution pH and amounts of $Ca(OH)_2$ added.

decomposition products of the manures, such as malate, citrate and tartrate. These reactions can be illustrated as follows.[13,14]



Further work is required to elucidate these mechanisms, however.

In term of pH increase, regardless of mechanism(s) involved, a practical application can be made by estimating lime equivalence of the added green manures. A lime titration curve (Fig. 3) was used to estimate that additions of 10 g manure/kg were equivalent to 1.8, 3.4 and 4.2 cmol(OH)/kg for guinea grass, cowpea and leucaena, respectively. In terms of reducing soluble Al, however, cowpea was the most effective and guinea grass the least effective of the manure sources (Fig. 4). This discrepancy suggests that the relationship between pH and soluble Al in manure-amended soils varied significantly with the manure source. In fact, when biomass

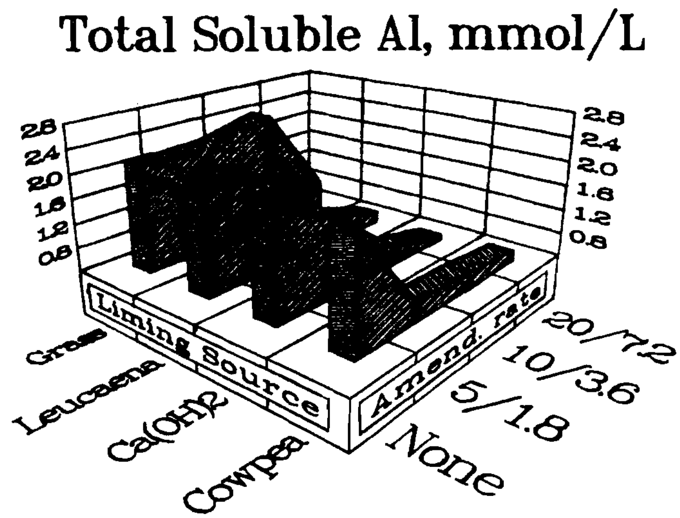


Fig. 4. Total soluble Al relative to rate and source of soil amendments. Manure rates were 0, 5, 10 and 20 g/kg and $Ca(OH)_2$ rates were 0, 1.8, 3.6 and 7.2 cmol(OH)/kg.

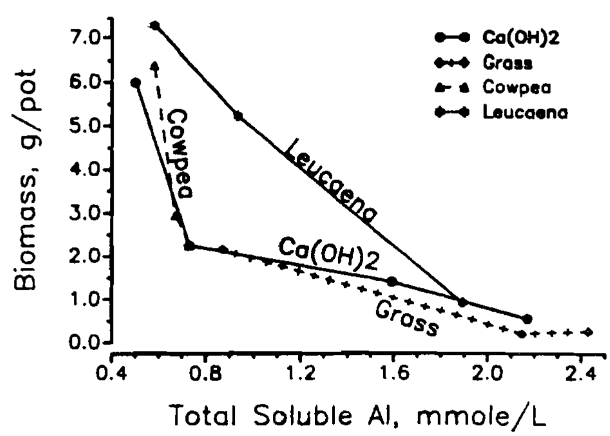


Fig. 5. Biomass production of *Sesbania cochinchinenesis* grown in different Al detoxifying treatments as a function of total soluble Al.

Table 3. Soluble carbon and organic acids in soil solution of selected treatments.

Treatment	Oxidizable C†	Organic acids in soil solution			
		citric	Gallic	Prot‡	Phthalic
	mM	<--------------- uM			-------------->
$Ca(OH)_2$ (7.2 $cmol_c$/kg)	0.8	--§	--	--	0.3
Cowpea, 20 g/kg	8.5	75	1.8	6.2	--
Leucaena (20 g/kg)	4.3	--	3.9	--	--

†Measured by the method of Barlett and Ross.[12]

‡Protocatechuic acid.

§Non detectable. The detection limits (in uM) for citric, gallic, protocatechuic and phthalic were 5, 0.05, 0.05 and 0.02, respectively.

was plotted as a function of total soluble Al, it was clear that sesbania seedlings grew better in the leucaena or cowpea treatments receiving 20 g/kg than in the treatment receiving 7.2 cmol(OH)/kg as $Ca(OH)_2$ even though soluble Al concentrations in the former were greater than in the latter (Fig. 5, three data points with biomass > 5.5 g/pot). This suggests that although total Al concentrations in the soil solution were similar, the forms of soluble Al were probably different among those soils amended with leucaena or cowpea and those with lime, and that these Al species differed significantly in their phytotoxicity.

Soluble carbon data and organic acid concentrations measured by HPLC strongly support these predictions (Table 3). The soil solutions of the leucaena and cowpea treatments contained nearly 5 and 10 times more soluble carbon than the limed soil. Furthermore, several strong Al complexing organic acids, such as citric and gallic, were found in the manure-amended soils. It has been well established that these organically complexed Al species are not phytotoxic.[6,7]

SUMMARY AND CONCLUSIONS

This study demonstrated that (i) green manures can substitute for lime in detoxifying Al (at least on a short-term basis), (ii) liming effectiveness of the manures varied with rate and source, (iii) reduction of soluble Al (by precipitation at increased pH or chelation on organic colloids) resulted from manure additions was the major mechanism of Al detoxification, and (iv) complexation of soluble Al by organic molecules, especially organic acids, also contributed significantly to the Al detoxification.

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