INFORMATION TO USERS

ORGANIC RESIDUES AS LIMING MATERIALS AND SUPPLEMENTARY

NUTRIENT SOURCES FOR ACID SOILS

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ABSTRACT

Soil acidity is a major constraint to successful crop production in many highly weathered tropical soils. While liming of temperate soils causes immediate and favorable changes, tropical soils often react differently. Where lime is expensive, difficult to obtain, or ineffective at economic rates, alternatives or supplemental practices to liming must be sought. Recent research has shown that additions of organic wastes and green manures to acid soils could reduce Al phytotoxicity and increase crop yields.

The "liming effect" of four organic manures (leucaena and cowpea green manure, chicken manure, sewage sludge) was quantified and compared with lime ($CaCO_3$) in a greenhouse experiment. Lime at four different rates (0, ½, 1, 2X exchangeable Al of the unamended soil) and organic manures (20 g kg^{-1} soil) were mixed with two acid soils (Kaneohe series, Humoxic Tropohumult; Paaloa series, Rhodic Kandiudult) and then incubated for 1, 6, and 12 months under greenhouse conditions. Aluminum sensitive legumes (*Sesbania cochinchinensis* and *Desmodium intortum*) were planted as test crops. Results showed that animal manures were more effective than their green manure counterparts as liming materials. In terms of detoxifying Al, increasing soil solution pH, and increasing plant root and shoot dry matter yield, animal manures were comparable to the highest rate of lime application. The liming effect of the organic amendments persisted up to one year after soil incorporation.

To evaluate the persistence (residual) of the liming effect of the organic manures, the same soils were allowed to incubate for another 6 months without any additional amendments and then replanted. Chemical analysis showed that soil acidity effectively decreased while the supply of basic cations increased in the organically amended soils resulting in improved plant height and total dry matter yield of plants. The mechanisms that were responsible for the residual liming effect of the organic amendments were a) their ability to increase and maintain soil pH b) Al-organic matter complexation c) and ameliorative effect of Ca ions on Al toxicity.

A 24-week incubation and leaching study was also conducted to determine the rate of N mineralization and ease of release of Ca, Mg, and K from the organic manures as well as their ability to reduce P sorption. Nitrogen in the animal manures was mineralized faster than that in the green manures. The faster rate of N mineralization in the animal manures could have been due to their lower C:N ratio. On the other hand, the higher lignin and polyphenolic contents of the green manures could have slowed the mineralization of N. The cations were released steadily from the decomposing organic manures during the entire incubation period and followed approximately the order, $K > Mg \geq Ca$. Among the organic amendments, chicken manure was the most effective while leucaena green manure was least effective in reducing P sorption. Animal manures also increased soil P levels better than the green manures.

In the last experiment, the effectiveness of surface-applied animal manures in ameliorating acidity and increasing Ca concentration in a Paaloa subsoil has been compared with lime ($CaCO_3$) and gypsum ($CaSO_4.2H_2O$). The animal manures were more effective than lime and gypsum in increasing Ca and decreasing soil solution Al and Al saturation in the subsoil, particularly below the 15-cm depth. Organic anions were also produced during the decomposition of the animal manures as evidenced by an increase in the soluble C levels of the animal manure treated soils. The movement of Ca down to the subsoil may have been facilitated by the formation of Ca-organic anion chelates which could move easily down the soil profile.

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CHAPTER 1

Introduction

Vast areas of arable lands in the tropics and subtropics are dominated by Oxisols and Ultisols which are generally acidic in reaction. Acid soils limit plant growth due to a combination of factors which include Al and Mn toxicities, and deficiencies of Ca, Mg, P, and Mo (Wright, 1989). Within the soil acidity complex, Al toxicity is probably the most important growth-limiting factor. Plants grown in acid soils are highly susceptible to drought since their roots are confined to thin surface layers, nutrients and water in the subsoil are often inaccessible, resulting in poor crop yields (Foy, 1984).

To correct the problem, application of liming materials (Ca or Mg carbonates) is practiced. Liming improves conditions for plant growth by increasing soil pH (Cassel, 1980), decreasing exchangeable Al (Farina et al., 1980; Friesen et al., 1980) and rendering basic cations more available for plant uptake (Kunishi, 1982). Overliming, however, may have negative effects on plant growth and soil properties especially on the strongly weathered and leached soils of the tropics and subtropics (Carran, 1991). A complex of soil conditions is responsible, including induced micronutrient deficiencies, as well as fixation or immobilization of P at higher pH (Sumner et al., 1978). Excessive lime application can induce Mn and P deficiencies (Foy, 1974; Kamprath, 1970) and decrease Mg content of plants (Grove et al., 1981). More importantly, in developing countries where soil acidity constraints are most widespread and

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severe, liming may not be a practical option to cash-poor farmers because of its cost and availability.

Locally available organic residues have shown promise as alternatives to lime in correcting soil acidity. Significant reduction in both soluble and exchangeable Al has been observed through organic amendments (Hue and Amien, 1989; Kretzschmar et al., 1991; Bessho and Bell, 1992; Hue, 1992). The increase in soil pH and Al complexation by decomposition products of the applied organic materials have been suggested as mechanisms for Al detoxification (Hue and Amien, 1989; Hue, 1992).

Organic materials also have many properties of a desirable fertilizer. Organic N is not readily leached or denitrified and its mineralization rate is dependent on many of the same factors affecting plant growth (Kapland and Estes, 1985). Plant materials, especially legumes, may also be very useful in ameliorating nutrient deficiencies which often occur in highly weathered soils (Bessho and Bell, 1992).

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CHAPTER 2

Literature Review

2.1 Soil acidity and aluminum toxicity

2.1.1 Geographical extent of acid soils

Soil acidity is common in Oxisols and Ultisols. These soils are characterized by low inherent fertility, and generally contain high levels of exchangeable Al and Mn which are toxic to most crop species, but deficient in nutrients like Ca, Mg, P and Mo. Estimates show that approximately 55% of the soils in tropical America, 39% in tropical Africa and 37% in tropical Asia are dominated by Oxisols and Ultisols representing a total area of approximately 1.6 billion hectares (Sanchez and Salinas, 1981). Recognizing the importance of this worldwide agricultural problem, the International Board for Soil Research and Management (IBSRAM, 1985), an international network of soil scientists, has been established.

2.1.2 The role of aluminum in acid soil infertility

Despite the structural role that Al plays in various primary and secondary minerals, it can also adversely affect the soil as a plant root environment. Soluble Al, especially Al^{3+}, is toxic to most plants and reacts readily with soluble phosphates, converting them into relatively insoluble forms unavailable for plant uptake (Evans and Kamprath, 1970). Excess soil Al interferes with the uptake,

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transport, and utilization of essential plant nutrients (Ca, Mg, K, P, and Fe) and may inhibit microbial processes that supply these nutrients to plants (Foy, 1988).

Aluminum toxicity is a complex disorder that is manifested in several ways. Foliar symptoms resemble those of P deficiency (overall stunting and small and dark green leaves with leaftip necrosis) in some species. In others, Al toxicity appears as an induced Ca deficiency characterized by curling of young leaves and collapse of growth points and petioles (Alam and Adams, 1979; Foy, 1983, 1984). Aluminum injured roots are stubby and brittle and the root system as a whole becomes "coralloid" in appearance with reduced fine branching (Foy, 1992).

Aluminum tolerance varies with plant species and even between varieties of the same species. Thus it is not possible to stipulate a general threshold value above which Al phytotoxicity occurs. A concentration of as low as 0.2 mg Al^{3+} L^{-1} in solution greatly reduced root length in soybean (Glycine max) (Alva et al., 1986) whereas it requires 8-9 mg Al^{3+} L^{-1} in solution to cause a significant reduction of total biomass in corn (Zea mays) (Bartlett and Riego, 1972). Trees seem to be less sensitive to high Al concentrations than most agricultural crops (Schier, 1985; Ryan et al., 1986).

2.1.3 Factors affecting aluminum phytotoxicity

Aluminum in soil solution is largely governed by pH and clay minerals. Aluminum toxicity is particularly severe when the soil pH is less than 5.0 but can occur at a higher soil pH when soils are dominated by kaolinite, compared to

soils dominated by vermiculite or montmorillonite (Adams and Lund, 1966). The clay content together with base saturation and pH were found to be important soil factors which gave the best estimate for Al uptake in acid forest soils by *Anemone nemorosa* (Tyler et al., 1987). Aluminum phytotoxicity is also dependent on the soil organic matter content, concentration of other cations, anions and total salts, plant species and their genetic properties (Foy, 1984).

2.2 Chemical behavior of aluminum in acid soils

2.2.1 Forms and occurrence of aluminum

Aluminum constitutes about 7.5% by weight of the earth's crust (Haug, 1984). Aluminum occurs most commonly in the primary minerals (feldspars and mica), in the secondary minerals (phyllosilicates and aluminum hydroxides), and in ores such as bauxite (Huang and Violante, 1986). It forms either octahedral or tetrahedral coordination with oxygen in the Al-bearing minerals and also exists as hydroxy Al interlayers or coatings on the external surfaces of phyllosilicates (Huang and Kozak, 1970; Hsu, 1977). In addition to the alumino-silicate minerals, Al also occurs as: (I) exchangeable ions (ii) sorbed or precipitated hydroxy-Al compounds (iii) organo-mineral complexes and associations (Bache, 1986).

Being a common ion in soil solution, aluminum can enter the structure of iron oxides and replace Fe^{3+}. The interaction of Al with low-molecular weight organic acids, fulvic and humic acids may also lead to the formation of insoluble

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hydroxy-aluminum organic complexes (Kodama and Schnitzer, 1980). In the solution phase, Al also occurs in a number of inorganic monomeric and polymeric forms (Bache, 1986). The level of Al in soil solution is governed by soil pH, amount and type of primary and secondary Al-containing minerals, exchange equilibria with inorganic surfaces and complexation reactions with organic constituents (Bell and Edwards, 1986).

2.2.2 Reactions of aluminum in aqueous media

Protons exuded by plant roots and those arising from root respiration, microbial metabolism, decay of plant and animal residues, pyrite oxidation, acid-generating fertilizers and acid-rain attack Al-bearing minerals and release Al into the soil solution and natural waters (Huang, 1986).

In solutions with pH less than 5, Al exists as the octahedral hexahydrate, $Al(H_2O)_6^{3+}$, often abbreviated as Al^{3+}. As the solution becomes less acid, $Al(H_2O)_6^{3+}$ undergoes successive deprotonations to yield the complexes $Al(OH)^{2+}$ and $Al(OH)_2^+$ and decreases in solubility. Neutral solutions give an $Al(OH)_3$ precipitate that redissolves in basic solutions due to the formation of $Al(OH)_4^-$. At high pH's or elevated OH:Al ratio in solution, polynuclear hydroxy-Al species may form (Macdonald and Martin, 1988).

2.2.3 Complexation reactions of aluminum

Inorganic anions. Aluminum forms complexes with several anions found in soil solution, particularly hydroxyl (OH^-), sulfate (SO_4^{-2}), fluoride (F^-) and phosphate (Lindsay, 1985). Several studies have shown that sulfate and fluoride

complexes of Al are not toxic to plants (Kinraide and Parker, 1987; Cameron et al., 1986; Tanaka et al., 1987).

Simple Aliphatic acids. In soils, biochemical compounds having metal chelating properties such as simple aliphatic acids, polyphenolics, fulvic and humic acids are derived from decomposing plant and animal residues, microbial activity and canopy drip (Pohlman and McColl, 1989; Chen and Stevenson, 1986). High amounts are expected to be produced during periods of intense biological activity, such as following additions of fresh organic residues to the soil. The quantities of these substances in the soil solution vary with time, and their concentrations are proportional to the net effect between production and transformation to other low-molecular weight products and/or polymeric humic substances (Chen and Stevenson, 1986).

Simple aliphatic acids are of special interest because of their ubiquitous nature. Organic acids most effective in forming stable complexes with Al and other metal ions are the di- and tri-carboxylic acids (Chen and Stevenson, 1986). The carboxyl and hydroxyl groups are the principal functional groups involved in the reactions of metal ions with organic acids in soil solution and natural waters (Huang, 1988). McColl and Pohlman (1987) and Pohlman and McColl (1988) identified several organic acids in forest litter and showed that oxalic, malic, gallic, and protocatechuic acids were effective chelators of Al.

Humic and Fulvic Acids. The abilities of humic substances to form stable complexes with Al can be accounted for by their high oxygen-containing

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functional groups which include COOH, phenolic-, enolic-, and aliphatic-OH

groups, and possibly ketonic C=O and ester functional groups. In the natural

state, humic and fulvic acids may also contain attached proteinaceous and

carbohydrate residues which may have some complexing ability. According to

Schnitzer and Khan (1972), the main reaction for the binding of Al is at a COOH-

phenolic OH site, of less importance is with adjacent COOH groups. The binding

of Al by humic substances can occur through water bridges, electrostatic

(coulombic attraction), formation of a coordinate linkage with a single donor

group, and formation of a chelate (ring) complex (Stevenson and Vance, 1989).

Young and Bache (1985) showed that fulvic acids complex Al very

strongly when they are highly dissociated. This occurs at higher pH, and thus

these complexes become increasingly important at pH >5. The authors

produced a speciation model for Al complexing with a fulvic acid of molecular

weight >10,000, 51.9% C and carboxyl content of 3.29 mmol g^{-1}. The model

showed that the proportion of Al complexed is a function of the amount of soluble

organic matter and the degree of dissociation of its carboxylic acids. They

observed that very little organic matter is needed to complex Al at pH 6, but

much more is needed at pH 4.

2.2.4 Concentrations of aluminum in the natural environment

Concentrations of dissolved Al are low in most natural waters due to the

relatively low solubility of natural Al minerals, neutral pH values, and low

concentrations of complexing ligands. A median value of 0.4 μM was reported

by Stum and Morgan (1970) for fresh waters, while Hem (1986) gives a range of 1-10 μM. In soil solutions, data of Kamprath (1978), Curtin and Smillie (1983) and Adams and Moore (1983) indicate that total soluble Al is in the range of 10 - 350 μM.

2.3 Diagnosing aluminum phytotoxicity

2.3.1 Soil pH

The 'master variable' governing Al solubility and mobilization is pH. Soil pH is the most common reference for measuring the degree of soil acidity and estimating lime requirement (Haynes, 1984). A favorable pH range is often chosen as the basis of how much lime must be applied in order to raise soil pH from an initial acid condition to the desired pH value (McLean, 1970). Soil, however, is a multiphase heterogeneous system and the measured pH may vary with soil:solution ratio, salts in solution, electrode position in the suspension, and whether the suspension is stirred or not during the measurement (Adams, 1984; Bache, 1988). In addition, plant species and even crop varieties differ in their tolerance to aluminum toxicity. Thus, a fixed chemical criterion for liming such as soil pH is not always feasible (Van Raij, 1991).

2.3.2 Extractable Al

Hoyt and Nyborg (1972) suggested that $0.01M$ $CaCl_2$ soluble Al was a suitable measure of soluble Al intensity. Bache and Sharp (1976), recommended the use of an Al activity ratio, 2pAl -3p(Ca + Mg), while Conyers et

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al. (1991) suggested the ratio $(Ca^{2+})^{0.5}/(Al^{3+})^{0.33}$ in $0.01M$ $CaCl_2$ equilibrium extracts of soil.

2.3.3 Exchangeable aluminum and aluminum saturation

Exchangeable Al is normally defined as the amount of Al displaced by leaching a soil with an unbuffered salt solution such as $1M$ KCl. Lime requirement based on exchangeable Al has yielded good results for highly weathered soils (Evans and Kamprath, 1970; Reeve and Sumner, 1970a). Reeve and Sumner (1970b) obtained a good correlation between yield of Trudan (*Sorghum sudanense* L. X *Sorghum bicolor* L.) and a measure called exchangeable Al index (EAI) which was the amount of Al extracted in a single 2-minute shaking with $0.2M$ NH_4Cl at a 1:10 soil/solution ratio. Like pH, however, exchangeable Al does not always well correlate with plant response because of differences in soil mineralogy, surface charge, organic matter content, and other factors.

Another predictor of Al toxicity is the percentage of the cation exchange capacity (CEC) occupied by Al (Farina and Channon, 1980; Kamprath and Foy, 1985). This Al saturation is determined by displacing soil Al with $1M$ KCl or other neutral, unbuffered salt and expressing the Al as a percentage of the $1M$ NH_4OAc CEC at pH 7.0 [KCl-Al÷ KCl-Al + NH_4OAc-(Ca+Mg+K+Na)]. Evans and Kamprath (1970) found that when Al saturation reached 60%, Al in soil solution was generally greater than 1 mg L^{-1}, and this relationship was fairly constant for kaolinitic, mixed, and montmorillonitic mineralogies. Fox (1979) reported a 28%

Al saturation as a critical level for corn production on two Ultisols in Pennsylvania. Cochrane et al (1980) recommended lime requirements be calculated from equations incorporating Al saturation for a given soil and the required Al saturation for the crop to be grown.

2.3.4 Soil solution aluminum and activity

The soil solution is the environment with which plant roots are in close contact. Thus, soil solution Al is often believed to be a more direct measurement of the conditions to which a plant responds. Several studies have shown that soil solution Al^{3+} concentration is related to plant growth but is not as closely related to plant response as Al^{3+} activity (Adams and Moore, 1983; Evans and Kamprath, 1970). The activity of an ion is thought to be a better measure of availability than its concentration (Sparks, 1984). In accordance with this assumption, Al toxicity symptoms on roots of several cultivated crops have been found to be closely related to Al^{+3} ion activity in solution . Adams and Lund (1966) used Al^{3+} activity to correlate Al toxicity to cotton roots and found that toxicity increased progressively as Al activity exceeded a minimum of 1.5 μM (pAl = 5.82). In a nutrient solution study on coffee seedlings, Pavan and Bingham (1982) found that the critical value for 10% root growth reduction was an Al^{3+} activity of 12 μM (pAl = 4.92). In soils this value was much lower (4.0 μM, pAl = 5.40) as measured in a saturated soil extract (Pavan et al., 1982). Blamey et al. (1983) and Alva et al. (1986a, 1986c) demonstrated that the sum of the activities of monomeric Al species best described tap root growth reduction in

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soybean (*Glycine max* (L) Merr.). In another study where pH levels were

adjusted, strong correlations between root growth and activities of either $AlOH^{2+}$

or $Al(OH)_2^+$ were observed with soybean, subterranean clover (*Trifolium*

subterraneaum L.), alfalfa (*Medicago sativa*), and sunflower (*Helianthus annus*

L.) (Alva et al., 1986b).

2.3.5 Aluminum speciation

The soil chemical properties mentioned above have not always proved to

be reliable indicators of Al toxicity over a wide range of soils. Thus, current

methods are focussed on determining the toxic components of soil solution Al

that best predicts phytotoxicity.

Different forms of Al in soil solution have been separated based on the

rate of reaction between a complexing agent (8-hydroxyquinoline, ferron,

aluminon, pyrocatechol violet) and soluble Al (Wright et al., 1987; James et al.,

1983; Bartlett et al., 1987; Kerven et al., 1989). The concentration of reactive Al

depends on time of reaction, concentration of complexing agent, and the relative

affinity of the complexing agents in solution with Al.

Driscoll (1984) developed a fractionation method to separate soluble Al

into acid soluble Al (colloidal polymeric Al and Al-organic complexes), labile

monomeric Al (Al^{3+}, hydroxy Al and Al-inorganic complexes) and non-labile

monomeric Al (monomeric Al-organic complexes). Speciation calculations were

then performed on the reactive Al fractions to obtain activities. Aluminum

fractionations have also been done using filtration or dialysis separation of Al

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components followed by colorimetry to determine reactive Al (Lazerte, 1984). At least one polynuclear hydroxy Al species (Al_{13}) has been shown to be highly toxic in artificial nutrient solutions (Parker et al., 1989). It is doubtful, however, if this species exists in soil solution due to the high affinity of negatively charged soil surfaces for Al polymers (Zelazny and Jardine, 1989).

2.3.6 Short-term bio-assay techniques

Bio-assay techniques using root development of seedlings offer promise as a quick means of identifying soils with potential Al toxicity problems. The seed supplies the nutrients for the short-term (2-4 days) seedling growth and only Al and H^+ toxicity and Ca and B deficiencies limit root elongation (Ritchey et al., 1988; Karr et al., 1984; Wright et al., 1989; Bessho and Bell, 1992). This approach allows the separation of Al effects on root elongation from those of nutrient deficiencies, thus allowing rapid screening of a large number of soils for Al toxicity and to assess Al tolerance among plant genotypes within a species using soils of known Al toxicity.

2.4 Correcting soil acidity through organic matter management

2.4.1 The role of organic matter in soil fertility

Soil organic matter is one of our most important natural resource. From ancient times man has recognized that soil fertility may be maintained or improved by the application of organic residues to the soil (Allison, 1973).

The relationship of soil organic matter to soil productivity can be ascribed to its role as both a source and sink of plant nutrients, its charge properties making it an active site of ion exchange, its ability to improve soil aggregation and water retention, and as a source of energy supporting soil biological activity (Swift and Woomer, 1993). It is likely that the main contribution of organic matter to soil fertility and plant growth is indirect and consists of improving and maintaining a wide number of physical, chemical, nutritional and biological properties of the soil (Senesi, 1989). Some of these indirect effects are:

(a) Soil structure and stability are of crucial importance in maintaining soil fertility. The loss of stability due to a decrease in soil organic matter content as a consequence of intensive agricultural practices, often results in soil erosion which washes away the nutrient-rich topsoil. By aggregation, soil organic matter maintains large pores in the soil, ensuring adequate drainage and aeration. It makes clay more porous and enables better root penetration, leading to enhanced root growth (Pera et al., 1983).

(b) Soil organic matter acts as a reservoir for plant nutrients and preventing leaching of these elements. This is possible because of the large cation exchange capacity (CEC) of organic matter, which can be in excess of 300 cmol kg^{-1} humus (Simpson, 1983). It has been estimated that 20 to 70% of the CEC of many soils is directly related to the soil organic matter (Stevenson, 1982). Soil organic matter can also form stable complexes with metals, thus

influencing their availability to plants and microorganisms (Stevenson and

Ardakani, 1972).

(c) The capacity of soil organic matter to buffer soils against drastic pH

changes is well established. This property arises mainly from the interaction of

humic substances and clays producing colloidal complexes which possess

negative charges and hold cations such as H^+, Al^{3+}, Fe^{3+}. Thus, the resistance to

pH changes is minimal in sandy soils but high in soils which have substantial

CEC (Hodges, 1992).

(d) Degradation and detoxification of fungicides, herbicides and

insecticides are governed in part by their interaction with soil organic matter

(Kahn, 1978). Biodegradation in the presence of soil organic matter has been

reported for DDT, heptachlor, and endrin (Castro and Yoshida, 1974) while non-

biological decomposition was observed for 3-amino-triazole (Crosby, 1970) and

slow conversion of aldrin to dieldrin (Kaufman, 1970).

(e) Humic substances impart a dark coloration to the soil which facilitates

warming and is particularly important for plant growth and yield in temperate

regions of the world (Senesi, 1989).

2.4.2 Sources of soil organic matter

Organic matter in soil is derived from soil biomass, and it consists of both

living and dead organic materials. It is often classified into two broad categories:

humic substances and non-humic substances (Tan, 1986). The non-humified

materials include substances and biochemicals released from plant, animal and

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microbial tissue decomposition in their original or slightly modified form. These include carbohydrates, amino acids, proteins, lipids, nucleic acids, lignins, hormones and a variety of organic acids. They tend to have low molecular weights and are relatively unstable (Tan, 1994). Following the addition of crop residues, animal manures, and other easily decomposable materials, high amounts of non-humic substances would be expected because of intense biological activity (Chen and Stevenson, 1986). The humified materials are products that have been synthesized from the non-humic substances by a process called humification (Tan, 1994). They have high molecular weights and are relatively stable and consist of a group of complex substances which are often divided into three operationally defined fractions (fulvic acid, humic acid and humin) based on their solubility in acid or base (Schnitzer, 1982).

2.4.3 Ameliorating aluminum toxicity through organic matter management

As early as the 1930's, there were studies which reported that the addition of organic matter to soil could reduce Al toxicity (Mattson and Hester, 1933; Hester, 1935). This was later confirmed by several studies demonstrating a considerable reduction in soluble and exchangeable Al by organic residue applications to very acid soils (Brogan, 1967; Hoyt and Turner, 1975). Evans and Kamprath (1970) observed that less Al was present in solution at any given pH as the organic matter content of the soil increased. In addition, the critical Al concentration, above which Al phytotoxicity occurs, increases with increasing soil

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organic matter content (Adams and Hathcock 1984). The incorporation of ground coffee leaves and pangola grass (*Digitaria decumbens Sent*) to a strongly acid soil of Puerto Rico significantly reduced exchangeable Al and enhanced growth of sorghum (Wahab and Lugo-Lopez, 1980). Other plant residues like alfalfa (*Medicago sativa*) meal (Hoyt and Turner, 1975), wheat (*Triticum aestivum*) straw (Ahmad and Tan, 1986), cowpea (*Vigna unguiculata*) and leucaena (*Leucaena leucocephala*) leaves (Hue and Amien, 1989) applied to Al toxic soils reduced Al toxicity and increased the yield of plants grown in them. Bessho and Bell (1993) applied ground leaves of a tree legume (*Calliandra calothyrsus*) and straw hay of barley (*Hordeum vulgare L.*) to an Al-toxic Ultisol and observed significant decrease in the concentration of monomeric Al in soil solution and greatly increased root length of mung bean.

Chicken manure and sewage sludge showed similar ameliorative effect on Al toxicity and increased forage yield of an Al-sensitive legume, *Desmodium intortum* (Hue, 1990). Ragland and Boonpuckdee (1986) reported a reduction in Al toxicity with an increase in the yield of rice (*Oryza sativa*) after the application of cattle and poultry manures.

It is believed that Al ions are detoxified by interactions with organic matter and its decomposed by-products in the form of complexation, coagulation, chelation and peptization reactions (Mortenson, 1963 ; Bartlett and Riego, 1972; Cabrera and Talibudeen, 1977). The complexes are formed by one or more bonds between Al and the complexing molecule forming Al-organo chelates or

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complexes which would either not be absorbed by roots or taken up by plants

without adverse effects on growth and yield.

2.4.4 Aluminum detoxification by organic acids.

The decomposition of organic materials applied to soil leads to the

production of various substances such as hormones, organic acids, amino acids,

fulvic acids and other biochemicals. Organic acids, for example, may be

released into the soil from plant canopy drip or as root exudates during the

plant's life cycle, whereas others are products of the oxidative degradation of

organic matter from plant, animal or microbial origin (Inoue and Huang, 1984).

Lactic, oxalic, malic, and citric acid have been shown to occur at 10^{-6} - 10^{-5} $\underline{M}$

concentrations in soil solution (Vedy and Bruckert, 1979). Although organic

acids are generally believed to have short-lived existence in soils (Wang et al.,

1967), they are however constantly being introduced to soils and associated

environments through natural vegetation and farming and are also present in

microbial metabolites in natural environments (Stevenson, 1967; Rao and

Mikkelsen, 1977).

Organic acids of the citric acid cycle are effective chelating agents of trace

metals (Martell, 1975) and are able to reduce Al toxicity without actually reducing

its total concentration (Bartlett and Riego, 1972). Hue et al. (1986) using cotton

root elongation rates as a bioassay of Al toxicity, demonstrated that naturally

occuring organic acids such as citric, oxalic, and malic acid are effective in

alleviating Al toxicity in forest soils. Shuman et al. (1991) using sorghum grown

in nutrient solutions with Al confirmed the ameliorative effects of citric and oxalic acid on Al toxicity. In contrast, Suthipradit et al. (1990) found fulvic acid to be effective against Al inhibition of the taproot of soybean, cowpea, and green gram, but not oxalic and malic acid. The chelating ability of the organic acids appears to increase with concentration. Likewise, the proximity of hydroxyl and carboxylic groups within the molecule is in the same order as their ability to form Al-organic complexes (Hue, 1986). Organic acids like uric, protocatechuic, gallic, and phthalic acid were identified by high performance liquid chromatography (HPLC) to be present in the soil solution during the decomposition of applied organic materials (Hansen, 1988; Hue and Amien, 1989; Hue, 1992).

2.5 Organic residues as supplementary sources of essential plant nutrients

Returning organic residues to the field is an age-old agricultural practice to increase organic matter content of the soil and to supply plant nutrients to the growing crop. The benefits of applying bulky organic materials to improve soil fertility have been well documented throughout the history of agricultural crop production (Avnimelech, 1986).

Sewage sludge and other municipal wastes can benefit soil organic matter relationships in the overall soil-plant-water biosphere and serves as a source of plant nutrients, particularly N and P (Coker and Carlton-Smith, 1986; Metzger and Yaron, 1987; Smith et al., 1989). Cooke (1972) reported that 25 tons per

hectare of farmyard manure could supply a first year crop with about 40 kg N, 20 kg P and 80 kg K.

2.5.1 Nutrient composition of organic residues

Crop residues. The nutrient content of crop residues is variable and depends on the age and type of plant material. In a nitrogen mineralization experiment, Palm and Sanchez (1991) reported a range of 2.37 to 3.94% for the N content of the leaves of ten leguminous trees and shrubs. In a similar study using seven leguminous trees, Oglesby (1990) reported a range of 2.07 to 4.99% N for leafy parts and 0.35 to 1.70% N for twigs. The P content of green manures ranges from 0.20 to 0.34%, K from 1.48 to 2.44%, Ca from 1.04 to 1.89%, and Mg from 0.27 to 1.73% (Yadvinder-Singh et al., 1992).

Animal wastes. Animal wastes also vary considerably in chemical composition due to the type and amount of feed used and also the methods of collection, storage, handling, and treatment of the wastes. The typical nutrient composition of chicken manure on a dry-weight basis are 3.7- 8.8% N, 1.2 - 2.9% P, 1.2 - 2.7% K, 5.2 - 14.9% Ca and 0.6 - 1.3% Mg (Overcash et al., 1983). As with other organic wastes, the elemental composition of poultry manures vary widely as a function of type of poultry, diet and dietary supplements, litter type, and handling and storage operations (Sims and Wolf, 1994).

Sewage sludge. The solid by-product of domestic and/or industrial waste-water treatment plants is termed sewage sludge. As might be expected, the nutrient composition of sludge varies from one treatment plant to another,

depending on the nature of treatment the sewage receives and on the degree to

which the organic material is allowed to digest. In a survey of sewage sludge

composition, Sommers (1977) reported the following ranges for both aerobic and

anaerobic digested sludges: 2.0 - 4.0% N, 1.2 - 3.0% P, 0.02 - 2.64% K, 0.1-

25.0% Ca, and 0.03 - 1.97% Mg. In particular, the concentrations of Ca, Mg, Fe,

and Al vary widely because these elements may be added to sludges in the form

of alum, lime, or other constituents to facilitate sludge settling and dewatering

(Kurihara, 1985; Sommers, 1977).

2.5.2 Mineralization of nitrogen and rate of nutrient release from organic residues

The rate of nutrient release from organic residues added to soils depends

on the system's properties such as types of organic material, chemical

composition of the residue, C/N ratio, and various soil environmental factors

such as moisture, temperature, aeration, and pH (Fu et al., 1987). A stabilized

organic material, well balanced in nutrients, i.e., with low C/N, C/P, and C/S

ratios, will support a slow but steady nutrient release, while fresh, labile

materials, where these ratios are high may cause a limitation of growth of

microbial population which can retard or even disrupt transformation and release

of nutrients.

As with other chemical and biochemical transformations in soils,

mineralization of N and other nutrients from organic wastes is a microbially

mediated process which is dependent on chemical and physical properties of the

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material itself as well as that of the soil receiving it (Broadbent, 1986). Douglas and Magdoff (1991) reported a wide range of the amounts of N mineralized from various organic residues. They observed highest net mineralization from uncomposted sewage sludge (4.3 to 30.0 g kg^{-1}) followed by uncomposted manures (-2.6 to 11.0 g kg^{-1}) and composted blend of animal and plant residues (-0.1 to 5.8 g kg^{-1}). Chae and Tabatabai (1986) likewise found wide variations in the mineralization of N in soils amended with various sludges, animal manures, and plant materials. Expressed as percentage of total organic N added to soils, N mineralization ranged from 1 - 58% for sewage sludge, 13 - 67% for animal manures, 3% for soybean, and 97% for alfalfa after 28 weeks of aerobic incubation. Magdoff and Amadon (1980) reported that up to 55% of the organic-N in sludge mineralized in the first year of application. For a ^{15}N-labeled sludge, 40 % of the N was mineralized in a 16-week incubation study (Terry et al., 1981). King (1973) reported that 60 % of the sludge-applied N was made available after an 18-week incubation.

As for green manures, decomposition and release of N generally proceeds rapidly during the first few weeks followed by a much slower phase thereafter, under both aerobic and anaerobic conditions (Yadvinder-Singh et al., 1992). Fox et al. (1990) reported N release rates from 11% to 47% after 12-week incubation of the leaves of six leguminous species. Tian et al. (1992) using leaves of herbaceous and woody species, reported N release rates of -12% (N immobilization) to 40% (N mineralization) after 7 weeks of soil incubation. Palm

and Sanchez (1991) using leaflets of ten tropical legumes incubated for 8 weeks

in an acid soil, found the amount of N mineralized ranged from -20 % to 46 %.

Khind et al. (1987) observed significant increases in water-scluble Ca and

Mg with green manuring of flooded soils. Tian et al. (1992) and Budelman

(1988) reported rapid release of K, Ca, and Mg in leguminous leaf mulches.

Swift et al. (1981) noted slow release of Ca and Mg in forest litter fall.

2.6 Reducing phosphorus sorption through organic residue application

Acid soils contain considerable amounts of Al and Fe oxides. In these

soils, added P becomes tightly adsorbed on the surfaces of Al- and Fe- oxides,

rendering it unavailable to plants. Mechanisms related to reduced P availability

include adsorption of $H_2PO_4^-$ to Fe-oxide mineral surfaces and precipitation of

$H_2PO_4^-$ with Fe ionic solution species (Chu et al., 1962). Orthophosphate

adsorption may also occur as mono- or binuclear covalent bonding of oxygen

atoms to Fe minerals (Hingston et al., 1980).

2.6.1 Management strategies for reducing phosphorus sorption

The application of inorganic P fertilizers, phosphate rocks and soil

amendments such as liming materials and $CaSiO_3$ are the most common

management strategies adopted by farmers in order to correct the P deficiency

problem (Sanchez and Uehara, 1980).

Previous studies suggest that decomposition products from organic

residues could increase P availability, hence, improve crop yield on high

phosphorus fixing tropical soils. Humic and fulvic acids bind covalently to Fe

mineral surfaces and reduce net positive charge (Moshi et al., 1974). Utilizing

^{32}P tracer techniques, Bhat and Bouyer (1968) observed increased P uptake

from fertilizer and soil P by plants grown in soils with Fe hydroxides that had

been pretreated with organic matter before P fertilization. Sharpley and Smith

(1989) also observed an enhanced availability of inorganic P when various soils

were amended with alfalfa, corn, oat, and wheat crop residues. The authors

suggested that blocking and reduction of the charge potential of P adsorption

sites by decomposition products of the applied organic residues accounted for

the increased P availability.

Bumaya and Naylor (1988) incubated a high P-sorbing Andept with three

kinds of plant residues for a period of 12 weeks. Their results demonstrated that

extractable P increased and P sorption decreased when the P content of the

plant residue exceeded 0.1%.

Decreased P sorption is also attributed to organic acids (produced from

organic residue decomposition) which form stable complexes with soluble Al and

Fe or with sesquioxide surface sites (Olsen et al., 1970). Easterwood and

Sartain (1990) added dried ground clover to a Typic Paleudult from Florida and

obtained substantial increases in P uptake and Bray 2 extractable P levels.

They suggested that organic acids from the clover decomposition bound to

$Fe(OH)_3$ surfaces and were able to complex Lewis acid cations thus increasing

phosphorus availability.

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Other workers reported that increased P sorption is a result of microbial assimilation and/or exchange of P for hydroxyl groups at the surface of some organic molecules resulting from the decomposition of applied organic residues (Harter, 1969; Sen Gupta, 1969; Field et al., 1985).

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CHAPTER 3

Liming effect of organic manures applied to acid soils as measured by soil chemical composition and plant response

3.1 Abstract

A 1-year incubation study was conducted in the greenhouse to quantify the "liming effects" of various organic amendments applied to strongly acid soils as compared to $CaCO_3$. Two Al-toxic soils (Kaneohe series, Humoxic Tropohumult; and Paaloa series, Rhodic Kandiudult) from Oahu, Hawaii were used. The Paaloa soil had an initial pH of 4.0 and solution Al of 58 μM while the Kaneohe soil had a pH of 4.2 and solution Al of 99 μM. Treatments included lime (as $CaCO_3$) at 0, ½, 1, and 2X the exchangeable Al of the unamended soils and 20 g kg^{-1} each of cowpea, leucaena, chicken manure and sewage sludge. The two soils were mixed with lime or organic residues and incubated at greenhouse conditions for 1, 6, and 12 months prior to planting of the indicator crops. Aluminum-sensitive plants *Desmodium intortum* and *Sesbania cochinchinensis,* were grown in the Paaloa and Kaneohe soil, respectively. Shoot and root dry weights, plant tissue chemical composition, and soil chemical properties were measured to assess the liming effectiveness of the various organic residues.

Results indicated that the organic amendments were effective liming materials. Animal manures at 20 g kg^{-1} were as effective as the highest rate of

lime in detoxifying Al, increasing soil solution pH, and improving plant dry matter

yield. Green manures, although less effective than their animal manure

counterparts, were comparable to the lower rates of lime in their liming

effectiveness. Shoot Ca was positively correlated and shoot Al and Mn

concentrations were negatively correlated with shoot dry matter yield. Plant Mg

had no significant relationship with shoot yield. Generally, there were no

differences between the same organic amendments across incubation periods.

This indicates that the effects were similar irrespective of incubation time and

that the liming effects persisted at least one year after soil incorporation.

3.2 Introduction

Organic matter in soils can reduce Al toxicity. Substantial reduction in

the concentration of soluble and exchangeable Al in acid soils can be achieved

through organic amendments (Hargrove and Thomas, 1982; Hue et al., 1986).

Thus, applications of organic residues to Al-toxic soils improve crop yield

(Hargrove and Thomas, 1981; Ahmad and Tan, 1986; Tan and Binger, 1986;

Hue and Amien, 1989). The mechanisms suggested for Al detoxification

include: a) precipitation of Al as soil pH increases (Hue, 1992; Hansen et al.,

1989) and b) complexation of Al by decomposition products of organic residues

(Hue et al., 1986; Bessho and Bell, 1993).

The objectives of this investigation were:

1. To determine whether organic residues could be used to detoxify aluminum in acid soils.

2. To compare the effect of incubation on the effectiveness of various organic residues with that of lime ($CaCO_3$) in correcting soil acidity.

3.3 Materials and methods

The liming effect of the organic residues was assessed by measuring plant shoot and root dry matter production, and changes in chemical properties of both the solution and solid phases of the soils.

3.3.1 Soils and organic residues

Two strongly acid Ultisols (Paaloa series, Rhodic Kandiudult; and Kaneohe series, Humoxic Tropohumult) from the island of Oahu, Hawaii were selected for the study. Soil samples used for the study were collected 40 cm below the surface soil. Table 3.1 lists some of the relevant chemical properties of the two soils in their unamended states. The initial phase of the study involved incubation of the two soils with four rates of lime using reagent grade $CaCO_3$ at 0, ½, 1 and 2X the exchangeable Al concentration of the unamended soil and four different organic manures (chicken manure, sewage sludge, and ground leafy materials of cowpea and leucaena). Since the two soils differ in their initial exchangeable Al, the exact rates of lime applied to the Paaloa soil were 0, 0.90, 1.82 and 3.64 g kg $^{-1}$ while 0, 1.78, 3.56, and 7.11 g kg $^{-1}$ were

applied to the Kaneohe soil. The organic residues were sun dried inside the greenhouse to less than 5% moisture content and then ground to pass a 20-mesh screen. The organic residues were applied at the rate of 20 g kg^{-1} dry soil. Total plant nutrient values of the organic residues are presented in Table 3.2.

Table 3.1 Selected chemical properties of the two acid soils in their unamended states.

Soil property	Paaloa soil	Kaneohe soil
pH (1:2;soil:H_2O)	4.0	4.2
pH (1:2;soil:0.03 M KCl)	3.5	3.8
Soil solution EC (dS m^{-1})	0.6	0.5
Organic C (%)	1.8	0.4
Exch. cations ($cmol_c$ kg^{-1})		
Ca	0.04	0.14
Mg	0.21	3.93
K	0.08	0.34
Na	0.26	0.53
KCl extractable -Al ($cmol_c$ kg^{-1})	3.64	7.11
Ca + Mg saturation (%)	5.84	33.8
Al saturation (%)	86.0	59.0
Soil solution Ca (mg L^{-1})	4.4	1.6
Soil solution Mg (mg L^{-1})	2.8	4.0
Soil solution Al (μM)	57.8	98.5
Extractable P (mg kg^{-1})	6.1	3.0

The lime and organic residues were mixed thoroughly with each soil and put in plastic pots containing 2.5 kg each of dry soil. The soils were wetted to field capacity and the pots were then laid out inside the greenhouse.

There were three periods of incubation of the lime and organic residues, consisting of 1, 6 and 12 months prior to planting of the test crops. During the incubation period, the soils in the pots were subjected to alternate wetting and drying and periodic mixing in order to facilitate lime reaction and decomposition

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Table 3.2 Total plant nutrient composition of the organic residues used in the greenhouse experiment.

Organic material	N	P	K	Ca	Mg	Na	Mn	Zn
	<----------------------------------%---------------------------->						<-- mg kg^{-1}-->	
Chicken manure	3.02	2.29	1.92	14.5	0.98	0.47	860	385
Cowpea	4.12	0.39	3.30	1.83	0.44	0.12	589	50
Leucaena	3.86	0.14	1.29	2.21	0.77	0.10	141	29
Sludge	2.22	1.69	0.12	19.6	1.18	0.18	232	255

of the organic residues in the soils. Periodically, the pots within each block of treatments were also rearranged to minimize environmental effects inside the greenhouse. In order to ensure that nutrient deficiencies did not confound plant response to the various treatments, the following blanket applications of nutrients (in mg kg^{-1}) were applied: 56 N, 80 Ca, 200 P, 250 K, 24 Mg, 32 S, and 5 Cu, Fe, Zn and Mn to the Paaloa soil; and 140 N, 200 Ca, 310 P, 350K, 48 Mg, 64 S and 5 Cu, Fe and Zn as SO$_4$ salts to the Kaneohe soil.

After the last incubation period of 12 months, Sesbania cochinchinensis and Desmodium intortum (both Al-sensitive plants) were planted. Sesbania was grown in the Kaneohe soil while Desmodium was planted in the Paaloa soil. Four seedlings each were initially sown in each pot after which they were thinned to two when the plants had already established vigor (1 week after transplanting).

3.3.2 Laboratory analyses

Plant tissue analyses. Six weeks after planting, the plants were cut at the soil surface, dried at 70°C for 48 hours in the oven, and weighed for the measurement of shoot dry weight. Roots were also washed free of adhering soil, dried, and the weight added to that of plant tops to represent total dry matter yield. Dried plant tops were ground to pass a 30-mesh screen. Sub-samples from the ground plant tissues were ashed in a muffle furnace at 500°C for 3-4 hours until the ash had turned grayish-white. The ash was oxidized with $1M$ HNO_3 and the residue was dissolved in $0.1M$ HCl. This solution was used for the analyses of K, Na, Mn, Zn, Ca, and Mg by flame atomic absorption spectrophotometry (Perkin Elmer, Model 3030B). Plant tissue Al was measured colorimetrically by the pyrocatechol violet method (Wilson, 1984).

Soil solution collection and analyses. Soil solutions used for the analyses of soil solution pH, electrical conductivity, and total soluble Al were collected by centrifugation (Adams et al., 1980). In this method, approximately 250 g of moist soil sample (wetted to field-water-holding capacity) were put into a modified plastic Buchner funnel lined with a Whatman no. 42 filter paper and centrifuged at 500g for 30 minutes. The soil solution collected in a polyethylene cup was analyzed immediately for soil solution pH in order to minimize significant losses of CO_2. The soil solutions were then kept refrigerated at 4°C for later chemical analyses. Analyses were done within five days after collection

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of the soil solutions. Total Al concentration in the soil solutions were determined colorimetrically by the pyrocatechol violet method (Kerven et al., 1989).

Soil extraction procedures and chemical analyses. Exchangeable basic cations, Ca^{2+}, Mg^{2+}, K^+, and Na^+ were extracted with $1M$ NH_4OAc at pH 7.0 as follows. Four grams of air-dried soil sample was mixed with 20 mL of NH_4OAc solution in a 50-mL polyethylene centrifuge tube. The mixture was shaken for 30 minutes in an end to end shaker and then centrifuged for 10 minutes at 10,000 rpm. The extract was poured through a filter paper and collected in 50-mL volumetric flasks. The extraction procedure was repeated and the extracts were combined and brought to volume with the extracting solution. The extracts were then used for the determination of the above cations using flame atomic absorption spectrometry.

Exchangeable Al was determined by mixing 5 g soil with 30 mL of $1M$ KCl solution. The mixture was shaken for 30 minutes, then centrifuged at 10,000 rpm for 10 minutes. The extraction procedure was repeated and the filtered extracts obtained from the centrifugation were combined and made to 100-mL final volume with the KCl solution. Aluminum in the extract was determined by the pyrocatechol violet colorimetric method.

3.3.3 Statistical analyses

The data obtained were statistically analyzed using PC-SAS for analysis of variance (ANOVA). Differences between means of the same treatment across incubation periods and treatment means within each incubation period

were evaluated by the Waller-Duncan K-ratio T test at the 5% level of significance (SAS Institute, Inc., 1985).

3.4 Results and discussion

3.4.1 Effect of lime and organic amendments on selected chemical properties of the soil solution

3.4.1.1 Soil solution pH

Liming acid soils improves the conditions for plant growth by raising soil pH and lowering acidity (Cassel, 1980). As lime dissolves in soil solution, Ca replaces Al on the exchange sites and the CO_3^{2-} anion from lime reacts with H^+ ions, increasing pH. Table 3.3 shows soil solution pH of the two soils at different periods of incubation as affected by liming and organic manure application.

As expected, soil solution pH of both soils applied with lime increased dramatically. Within the same incubation period, soil solution pH of both soils increased significantly for every increment of lime added. Application of organic manures also increased soil solution pH. The animal manures effectively raised soil solution pH for all incubation periods relative to the unamended controls; pH values were above 5.5 in both soils. In fact, these values were even higher than those from soils receiving lime equal to the exchangeable Al concentration of the unamended soil (L-1X) treatments. The animal manures (chicken manure and sewage sludge) were also more effective in raising soil solution pH at any

Table 3.3 Soil solution pH of the two acid soils as affected by lime and organic amendments at different periods of incubation.

Treatments	Kaneohe soil			Paaloa soil		
	1 mo	6 mo	12 mo	1 mo	6 mo	12 mo
	<————————————— Soil solution pH —————————————>					
Control	4.04e[†]	4.18f	4.02f	4.26f	4.15e	3.98g
Lime-½ X	4.32d	4.50e	4.40e	4.64e	4.66cd	4.99d
Lime-1X	4.92c	5.12d	5.01c	4.90de	4.71c	5.18c
Lime-2X	5.68b	6.10b	6.33a	6.28a	6.18a	6.28a
Cowpea	4.38d	4.53e	4.69d	5.26c	4.76c	4.51f
Ch. manure	5.57b	5.68c	6.15b	5.84b	5.89b	6.00b
Leucaena	4.45d	4.47e	4.71d	5.09cd	4.51d	4.80e
Sludge	5.95a	6.33a	6.24ab	6.12ab	6.08a	6.15a
	MSD(0.05)[‡]= 0.18			*MSD(0.05)[‡]= 0.22*		

[†] means within a column and soil followed by the same letter are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.

[‡] minimum significant difference between the same treatment across different incubation periods.

given incubation period as compared to the green manures (cowpea and leucaena). Although green manure application did not raise soil solution pH as high as the animal manures, such pH increases were significantly higher than their corresponding controls.

Increases in soil solution pH after additions of plant or animal residues as amendments to acid soils had been reported by Ritchie and Dolling (1985), Hue and Amien (1989), Hue (1992), and Bessho and Bell (1993). Possible reasons cited for pH increases include: a) the release of NH_3 due to intense microbial activity during the decomposition of the added organic materials, b) the production of OH^- ions by the dissolution of solid Mn and Fe oxides in reduced conditions or by the ligand exchange of terminal OH of Al or Fe-hydroxy oxides

by organic anions (Hue and Amien, 1989), and c) OH⁻ release by the

decomposing manures themselves (Pocknee and Sumner, 1994).

3.4.1.2 Electrical conductivity

Both lime and organic amendments increased electrical conductivity of

the soil solution (Table 3.4). Electrical conductivity values of soils to which

organic manures were applied were twice as high of the control soils

and significantly higher than those of the lime treatments. Mineralization of

readily decomposable organic residues would release large amount of ions into

the soil solution and increase EC (Yadvinder-Singh et al., 1992).

Table 3.4 Electrical conductivity (EC) of the soil solution as affected by lime and organic amendments at different periods of incubation.

Treatment	Kaneohe soil			Paaloa soil		
	1 mo	6 mo	12 mo	1 mo	6 mo	12 mo
	<--------------------------------- dS m⁻¹ --------------------------------->					
Control	1.55d†	1.7d	1.6c	1.1d	1.15e	1.0e
Lime-½x	1.8d	1.75d	1.8c	1.5c	1.7d	1.6d
Lime-1X	1.7d	1.8d	1.85c	1.6c	1.5d	1.7cd
Lime-2X	1.8d	1.87d	1.8c	2.15b	2.0c	1.9bcd
Cowpea	2.4c	2.65c	3.1b	2.3ab	2.2bc	2.2b
Ch.manure	3.75a	3.65a	3.8a	2.7a	2.6a	2.6a
Leucaena	2.6c	3.3b	2.95b	1.6c	1.5d	2.0bc
Sludge	3.3b	3.8a	3.85a	2.4ab	2.35ab	2.55a
	MSD(0.05)‡=0.28			MSD(0.05)‡=0.26		

† means within a column and soil followed by the same letter are not significantly different
  according to the Waller-Duncan K-ratio T test at the 5% level of significance.
‡ minimum significant difference between the same treatment across different incubation periods.

3.4.1.3 Soil solution aluminum

The concentration of total soluble Al is one way of assessing the potential of Al toxicity because Al in solution better reflects conditions on the soil-root interface (Evans and Kamprath, 1970; Awad et al., 1976). A concentration of 1 mg L^{-1} (37μM) or even lower may significantly reduce growth, especially in Al-susceptible plant species. For example, *Leucaena leucocephala* is known to be very sensitive to Al concentrations in the soil solution in excess of 0.4 mg L^{-1} (Lopez et al., 1976).

Table 3.5 presents the concentrations of Al in soil solution in response to lime and organic amendments at different incubation periods. Liming and organic amendments significantly reduced soil solution Al concentrations in both soils. This Al reduction can largely be attributed to Al precipitation as a result of pH increase. In the Kaneohe soil, the lowest lime rate (L-½X) decreased soil solution Al concentration by as much as 80% (average of 19 μM for all incubation periods) as compared to the control (90 μM). As the rate of lime application increased, further reduction in the concentration of soluble Al was observed.

Similar results were also observed with the Paaloa soil. The mean concentration of soluble Al in the unamended soils across all three incubation periods was approximately 60 μM. This Al concentration was significantly reduced to 18.5 μM (average of 3 incubation periods) in the L-½X treatment corresponding to a 70% reduction relative to the control. Soil solution Al

Table 3.5 Soil solution aluminum concentration of the two soils as affected by lime and organic amendments at different periods of incubation.

Treatment	Kaneohe soil			Paaloa soil		
	1 mo	6 mo	12 mo	1 mo	6 mo	12 mo
	<------------------------------- μM ------------------------------->					
Control	95.4a[†]	96.9a	90.6a	61.8a	58.2a	59.5a
Lime-½x	18.9c	20.4d	17.7cd	15.4bc	20.9bcd	19.3bcd
Lime-1X	16.5cd	14.2e	13.0de	13.1bc	17.2cd	18.5bcde
Lime-2X	13.3d	12.6e	8.7e	11.3c	16.9cd	13.1cde
Cowpea	25.1b	27.4b	21.9bc	17.8b	22.4bc	20.1bc
Ch.manure	20.4c	21.2cd	14.6d	14.7bc	13.9d	12.8de
Leucaena	28.2b	25.9bc	23.5b	18.2b	24.4b	20.8b
Sludge	14.2d	13.8e	13.4de	15.4bc	13.9d	11.6e
	MSD(0.05)[‡]=4.46			*MSD(0.05)[‡]=5.98*		

† means within a column and soil followed by the same letter are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.
‡ minimum significant difference between the same treatment across different incubation periods.

concentration decreased further with increased rates of lime but differences between lime treatments were not significant.

Soil solution Al concentrations in the organically amended soils were also significantly reduced. In the Kaneohe soil, total soluble Al concentrations in the green manure treated soils were reduced to one-third that of the control for all incubation periods. Soluble Al concentrations in the animal manure treatments were not significantly different from soils in the highest lime treatment (2X).

Concentrations of soil solution Al in the Paaloa soil that received animal manures were similar to those that received the highest rate of lime (2X). Soils

that received green manures reduced soil Al concentrations to levels similar to the lowest rate ($\frac{1}{2}$X) of lime application. Although the green manures did not reduce soil solution Al concentrations as effectively as lime and their animal manure counterparts, such decreases were almost one third of the values observed from the control soils. Across incubation periods for both soils, there were no significant differences between the same treatments.

The above results seem to indicate that in acid soils where the main factor causing infertility is soil solution Al, the regular application of organic manures could greatly minimize the use of expensive liming materials. Significant reduction in the concentration of toxic Al in soil solution through organic matter application has also been reported in several studies (Ahmad and Tan, 1986; Tan and Binger, 1986; Hue and Amien, 1989).

3.4.2 Effect of lime and organic amendments on selected chemical properties of the soil solid phase

3.4.2.1 Exchangeable aluminum

Increased soil solution pH resulting from lime application significantly decreased exchangeable Al (Figures 3.1A and 3.1B), by precipitation as $Al(OH)_3$ (Bohn et al., 1985). Exchangeable Al of the unamended Kaneohe soil ranged from 6.24 to 6.74 $cmol_c$ kg^{-1}. Liming at the lowest rate ($\frac{1}{2}$X) reduced exchangeable Al to 0.40 - 0.92 $cmol_c$ kg^{-1} and 0.07 - 0.15 $cmol_c$ kg^{-1} at the 1X lime rate. Exchangeable Al was virtually zero (<0.01 $cmol_c$ kg^{-1}) at the highest lime rate (2X).
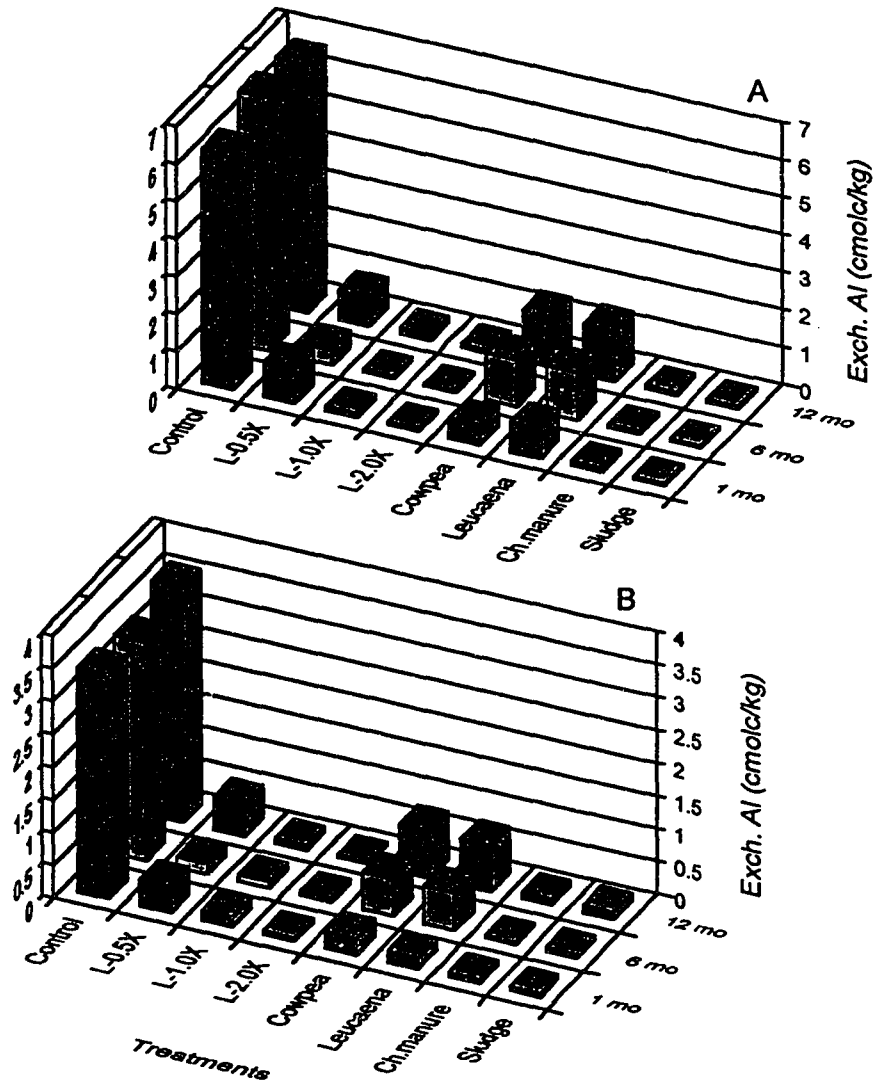
Figure 3.1   Exchangeable Al in the A) Kaneohe and B) Paaloa soil as affected by lime, organic amendments, and period of incubation.

In the Paaloa soil, exchangeable Al of the control soils ranged from 3.33

to 3.57 $cmol_c$ kg^{-1}. At the lowest rate of lime (½X), Al was dramatically reduced

to an average of 0.45 $cmol_c$ kg^{-1} (range of 0.40-0.49 $cmol_c$ kg^{-1}) and further

decreased to only 0.05 $cmol_c$ kg^{-1} at the highest lime rate (2X).

Chicken manure and sewage sludge were likewise very effective in

decreasing exchangeable Al in the 2 soils. These organic amendments reduced

exchangeable Al to levels similar to that observed in the intermediate lime

treatment (1X), even a year after application. Ground cowpea and leucaena

green manures also decreased exchangeable Al, but to a lesser extent than

their animal manure counterparts. The decrease of exchangeable Al in the

organically amended soils was probably a consequence of increased soil pH,

and the chelation of soil Al with the solid organic materials.

3.4.2.2 Aluminum saturation percentage

Aluminum saturation ranged from 50 to 65% of the total effective CEC, in

both the Paaloa and Kaneohe unamended soils (Table 3.6) which strongly

suggest Al phytotoxicity. Growth-limiting Al saturation percentages range from

approximately 20 to 70%, depending on soil type and crop species (Gonzales-

Erico et al., 1979; Sartain and Kamprath., 1977). In fact, an Al saturation of

12% has reportedly reduced the grain yield of corn by as much as 90% in two

acid Ultisols (Fox, 1979). Lime and organic amendments significantly reduced

Al saturation in both soils. The highest lime rate (2X) and animal manure

applications reduced Al saturation in both soils to less than 1% regardless of

Table 3.6 Aluminum saturation percentage of the two acid soils after plant harvest as affected by lime and organic amendments at different periods of incubation.

Treatments	Kaneohe soil			Paaloa soil		
	1 mo	6 mo	12 mo	1 mo	6 mo	12 mo
	<---------------------------------- % ------------------------------------>					
Control	53.2	63.7	63.2	65.0	64.7	66.0
Lime -½X	12.6	6.1	11.9	13.0	5.9	14.3
Lime -1X	1.4	0.9	2.0	4.1	2.9	2.3
Lime -2X	0.7	0.5	0.9	0.9	1.1	0.7
Cowpea	7.8	18.6	20.5	4.3	9.2	11.8
Ch.manure	0.7	0.5	0.6	0.4	0.2	0.6
Leucaena	11.8	18.8	19.8	2.9	9.1	10.7
Sludge	0.9	0.4	0.5	0.5	0.4	0.8

incubation period. The green manures also significantly reduced Al saturation relative to the controls.

In the Kaneohe soil, cowpea application reduced Al saturation to 7.8% after 1 month but gradually increased to 18.6 and 20.5% after 6 and 12 months, respectively. In the leucaena treatments, Al saturation increased from 12% after 1-month incubation to almost 20% after 6 and 12 months. Percent aluminum saturation in the Paaloa soil which received green manures also increased gradually with longer incubation periods.

3.4.2.3 Exchangeable cations and base saturation

Plant nutrients released from the decomposition of the various organic manures applied led to significant increases particularly in the Ca + Mg saturation of the soils. Figures 3.2A and 3.2B show the relative concentrations

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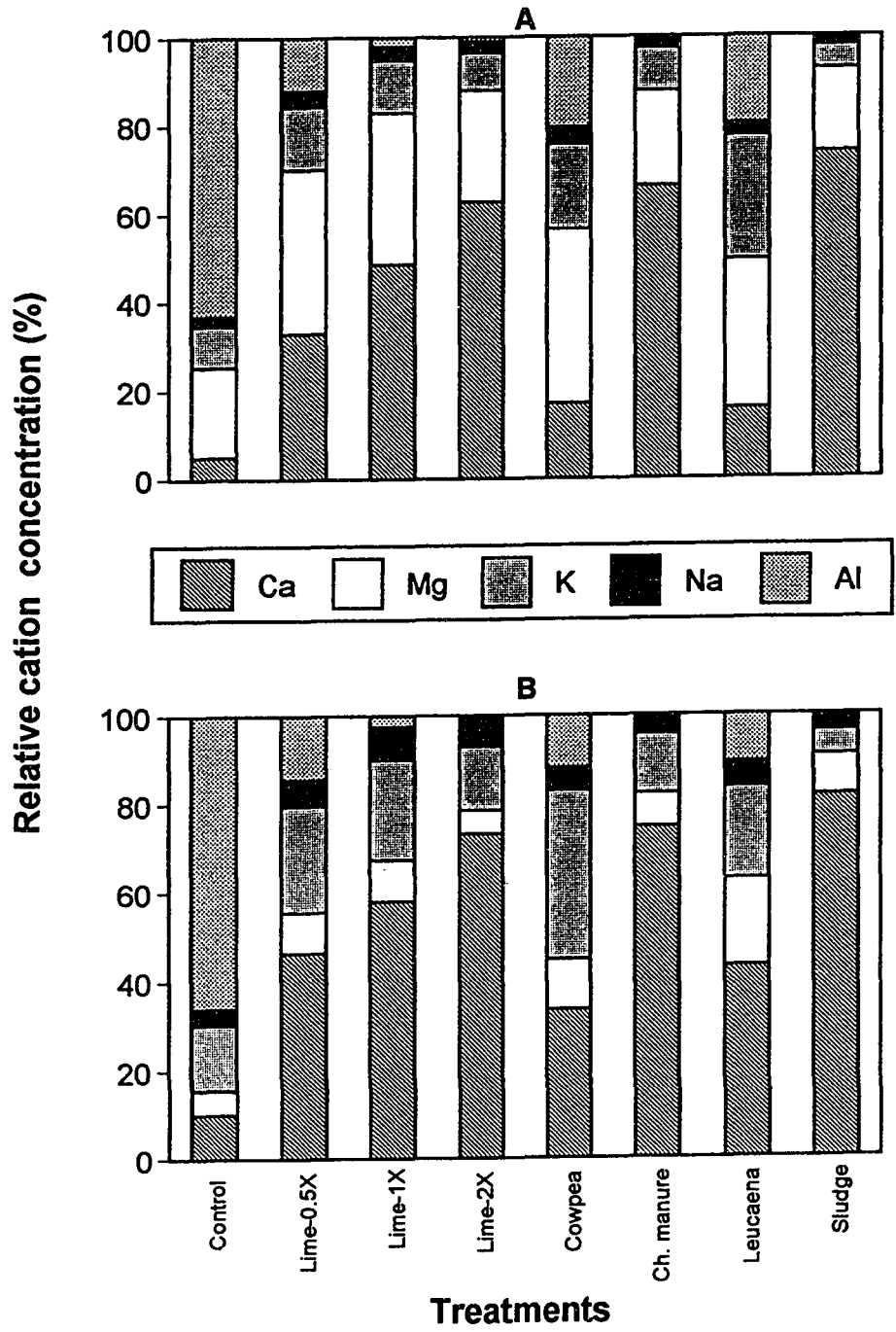
Figure 3.2 Aluminum and cation saturation of A) Kaneohe and B) Paaloa soil as affected by lime and organic amendments after 12 months of incubation.

of exchangeable cations and Al in the soils after 12 months of incubation. The control soils had Ca plus Mg saturation of 25% and 15% for the Kaneohe and Paaloa soils respectively. In the Kaneohe soil, Ca from the applied lime effectively displaced Al from the soil exchange complex. In the lime treated soils, Ca plus Mg accounted for 70 to 88% of exchangeable cations, effectively reducing Al saturation to just 1% in the highest lime treatment, and 12% in the lowest lime treatment.

Calcium saturation in the green manure treatments was similar, and together with Mg they occupied more than 50% of the cation exchange complex, thereby effectively replacing most of the original exchangeable Al in the soil. Even more significant were the concentrations of exchangeable Ca and Mg in the animal manure treated soils. Exchangeable Ca plus Mg percentage was 88% in the chicken manure treatment and 92% in the sludge treatment. These results seem to suggest that nutrients in the organic residues became available for release once they are applied to the soil.

Likewise, in the Paaloa soil, the saturation percentages of Ca + Mg and of Al were 80% and 0.70%, respectively, in the highest lime treatment after 12-month incubation (Figure 3.2B). They were 15% and 66%, respectively, in the unamended soil.

Potassium saturation, on the other hand, decreased with increasing lime application. At the highest lime rate (2X), K saturation percentages dropped close to that of the control soils. The application of cowpea to the Kaneohe soil

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contributed to the highest K saturation of 19% while the leucaena treatment

yielded the highest K saturation of 38% in the Paaloa soil. The lowest K

saturation of 5% was observed from the sludge treatment in both soils. These

differences could be explained by the inherently low K concentration in sludge

(0.12%) versus 3.3% K in cowpea and 1.92% K in leucaena (Table 3.2).

Among exchangeable cations, Na had the lowest saturation percentage.

Percent Na saturation ranged from 2% - 4% in the Kaneohe soil , and 3% - 6%

in the Paaloa soil. These narrow ranges indicate that the various treatments did

not have a large effect on percent Na saturation.

The increase in concentration of exchangeable cations especially Ca,

Mg, and K in the organically amended soils can be attributed to both the

contribution of plant nutrients from the organic manures themselves (Table 3.2)

and increases in pH and EC (Tables 3.3 & 3.4). Increased pH and EC create

additional charges on the variable charge colloids. In the case of lime, the effect

can be ascribed primarily to increased pH and EC (Bessho and Bell, 1993).

3.4.3 Effects of lime and organic amendments on plant growth and chemical composition

3.4.3.1 Root dry matter yield

The initial site where the phytotoxic effect of Al manifests itself is the root

because it is in direct contact with Al in the soil solution (Clarkson, 1965). The

roots of the control plants were detrimentally affected by toxic levels of Al in

solution as reflected by their very low dry weights (Tables 3.7). Roots from the

control plants were thick, brittle, and had very few branching. Root dry weight of

Sesbania grown in the unamended Paaloa soil had a mean of only 0.15 g. Dry

weight of Desmodium roots in the Kaneohe soil was even lower with a mean of

0.11 g (averaged across all incubation periods). As a typical response to liming,

root dry weight of Sesbania dramatically increased from 0.26 g in the ½X lime

rate at the 12-month incubation to 0.65 g at the 2X lime rate for the 1-month

incubation. Root dry weights also increased significantly with organic

amendments. Across incubation periods and organic amendments, root dry

weights ranged from 0.28 g to 0.68 g, a 2- to 4.5-fold increase over the controls.

Table 3.7   Root dry weight of S. cochinchinensis and D. intortum as affected by lime and organic amendments at different incubation periods.

Treatment	Sesbania cochinchinensis[§]			Desmodium intortum[£]		
	1mo	6mo	12mo	1mo	6mo	12mo
	<———————————————— g pot[-1] ————————————————>					
Control	0.15d[†]	0.17c	0.13e	0.13e	0.10e	0.10e
Lime -½X	0.34bc	0.38b	0.26de	0.27d	0.35c	0.26c
Lime -1X	0.48b	0.44ab	0.42bc	0.65b	0.52b	0.56d
Lime -2X	0.65a	0.58a	0.50ab	0.63b	0.69ab	0.73a
Cowpea	0.44bc	0.42ab	0.42bc	0.23d	0.26cd	0.21cd
Ch. manure	0.68a	0.43ab	0.61a	0.57c	0.74ab	0.67ab
Leucaena	0.43bc	0.41b	0.33cd	0.16e	0.17de	0.14de
Sludge	0.29cd	0.45ab	0.28cd	0.70a	0.78a	0.74a
	MSD(0.05)[‡]=0.15			MSD(0.05)[‡] =0.11		

[†] means within a column and soil followed by the same letter are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.
[‡] minimum significant difference between the same treatment across different incubation periods
[§] planted in the Kaneohe soil.
[£] planted in the Paaloa soil.

Highest root dry weights were obtained from the chicken manure treatment. Root dry weight of *Desmodium* in the highest lime treatment increased almost 7-fold compared to the control. Chicken manure and sludge applications also significantly increased root dry weight to levels comparable to those in the 1X and 2X lime treatments. Plants in the green manure treatments nearly tripled their root dry weights over the controls.

3.4.3.2 Shoot dry matter yield

Statistical analyses showed that shoot dry weights of the indicator plants were significantly increased by both lime and organic amendments. Incubation periods, on the other hand did not significantly shoot dry weights of plants between the same treatment (Table 3.8). In both soils, control plants produced the lowest shoot dry weights regardless of incubation period. The highest lime treatment produced the highest shoot dry weight of 3.89 g for *Sesbania* and 3.24 g for *Desmodium*, both obtained at the 6-month incubation period.

Plants grown in the organically amended soils also outyielded their controls. Shoot dry weights of *Sesbania* in the green manure treatments were similar to those in the 1X lime treatment. *Desmodium* plants amended with leucaena or cowpea green manure had shoot dry weights comparable to those of the lowest lime increment (½X). Among the organic amendments, chicken manure produced the highest yields. Shoot dry weight of sludge treated plants were similar to those that received the highest rate of lime (2X).

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Table 3.8 Shoot dry weights of *S. cochinchinensis* and *D. intortum* as affected by lime and organic amendments at different periods of incubation.

Treatment	Sesbania cochinchinensis			Desmodium intortum		
	1mo	6mo	12mo	1mo	6mo	12mo
	<---------------------------- g pot⁻¹ ---------------------------->					
Control	0.51e†	0.55f	0.66c	0.45e	0.51e	0.53e
Lime -½X	2.30c	2.54d	2.29b	1.73bc	1.52d	1.66cd
Lime -1X	3.06b	3.11c	2.56b	2.20b	2.36c	2.08bcd
Lime -2X	3.86a	3.89a	3.27a	3.20a	3.24ab	3.10ab
Cowpea	2.93b	2.98c	2.29b	1.27cd	1.42d	1.23de
Ch. manure	2.97b	3.52b	3.58a	3.29a	3.68a	3.43a
Leucaena	2.93b	2.32d	2.38b	0.72de	1.37d	1.20de
Sludge	1.31d	1.81e	1.15c	2.87a	3.05b	2.29bc

$MSD(0.05)^{\ddagger}=0.44$ $MSD(0.05)^{\ddagger}=0.73$

† means within a column and soil followed by the same letter are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.
‡ minimum significant difference between the same treatment across different incubation periods

Yield increases of *Vigna unguiculata* (soybean) and *Sesbania cochinchinensis* grown in Al-toxic soils were also observed after the application of ground wheat straw (Ahmad and Tan, 1986), and ground leafy materials of cowpea, leucaena, and guinea grass (Hue and Amien, 1989) respectively. In Thailand, the application of cow manure to two acid soils of different fertility status resulted in significantly higher yields of Chinese kale (Vityakon et al., 1988). These results clearly indicate the growth enhancing and liming effect of the organic residues, especially for chicken manure and sewage sludge. Such effects were still evident one year after the initial application to the soil.

3.4.3.3 Relationship between shoot yield and foliar composition

<u>Calcium.</u> Shoot Ca concentrations were lowest in both control plants,

ranging from 0.42% to 0.55% for *Sesbania* and 0.56% to 0.90% in *Desmodium*

(Tables 3.9). Hue (1992) reported that *Desmodium* requires at least 1% Ca in

the shoots for good growth, while Evans and Rotar (1987) found that 0.8 to

1.1% was required for maximum *Sesbania* growth. Liming the soils effectively

Table 3.9 Shoot calcium concentrations of *S. cochinchinensis* and *D. intortum* as affected by lime and organic amendments at different periods of incubation.

Treatment	Sesbania cochinchinensis			Desmodium intortum		
	1mo	6mo	12mo	1mo	6mo	12mo
	<-------------------------------------- % -------------------------------------->					
Control	0.55f[†]	0.46g	0.42e	0.56d	0.90g	0.73g
Lime -½X	1.05e	1.15f	1.38d	1.58c	2.78f	1.38f
Lime -1X	2.18c	1.81d	1.89c	2.56b	2.71c	2.38d
Lime -2X	3.04a	2.68b	2.49a	2.82b	2.89b	3.12b
Cowpea	1.37d	1.19f	1.49d	1.54c	2.54b	1.95e
Ch. manure	2.86b	2.14c	2.19b	3.45a	3.26a	3.65a
Leucaena	1.04e	1.62e	1.44d	1.40c	1.98e	1.39f
Sludge	2.89b	2.92a	2.52a	3.20a	2.82bc	2.79c
	MSD(0.05)[‡]=0.14			*MSD(0.05)[‡] =0.26*		

[†] means within a column and soil followed by the same letter are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.
[‡] minimum significant difference between the same treatment across different incubation periods

increased Ca concentration in the shoots above the adequate level. For

example, shoot Ca concentrations were 2.5 - 3.0% in *Sesbania* grown in the

highest lime treatment. This is 5- to 6-fold higher than the control plants.

Calcium concentrations of *Desmodium* plants which received chicken manure or sewage sludge were comparable or in most cases even higher than those of plants grown in the highest lime treatment. These observations were also true for *Sesbania*. Chemical analysis of the organic residues (Table 3.2) showed that chicken manure and sludge contained 14.5% and 19.5% Ca, respectively, and this Ca could have became available for plant uptake when the organic manures started to decompose. Indeed, a large portion of the total Ca present in the animal manures had been released and converted into soluble form after 24 weeks of incubation (Table 5.6). Cowpea and leucaena treatments also increased Ca concentration in the shoots but to a lesser extent compared to the animal manures and the lime treatments.

Calcium concentrations in shoots of both plants were significantly correlated with shoot dry weight (Fig. 3.3A & 3.3B). In *Sesbania*, the linear relationship is described by the equation, $Y = 26.98-5.08X$ $(R^2 = 0.78)$. On the other hand, the relationship of plant tissue Ca to shoot dry matter yield of *Desmodium* is described by the quadratic equation, $Y = -13.9X^2 + 74.8X -10.9$ $(R^2 = 0.81)$. Shoot Ca concentration of 3.5% and 3.0% correspond to 90% shoot relative dry weight for *Sesbania* and *Desmodium* respectively.

Magnesium. The concentration of Mg in *D. intortum* was significantly affected by lime and the various organic amendments (Table 3.10). Shoot Mg was highest in the control plants but decreased as lime increased. Decrease in plant Mg content with liming has also been reported by Grove et al. (1981) and
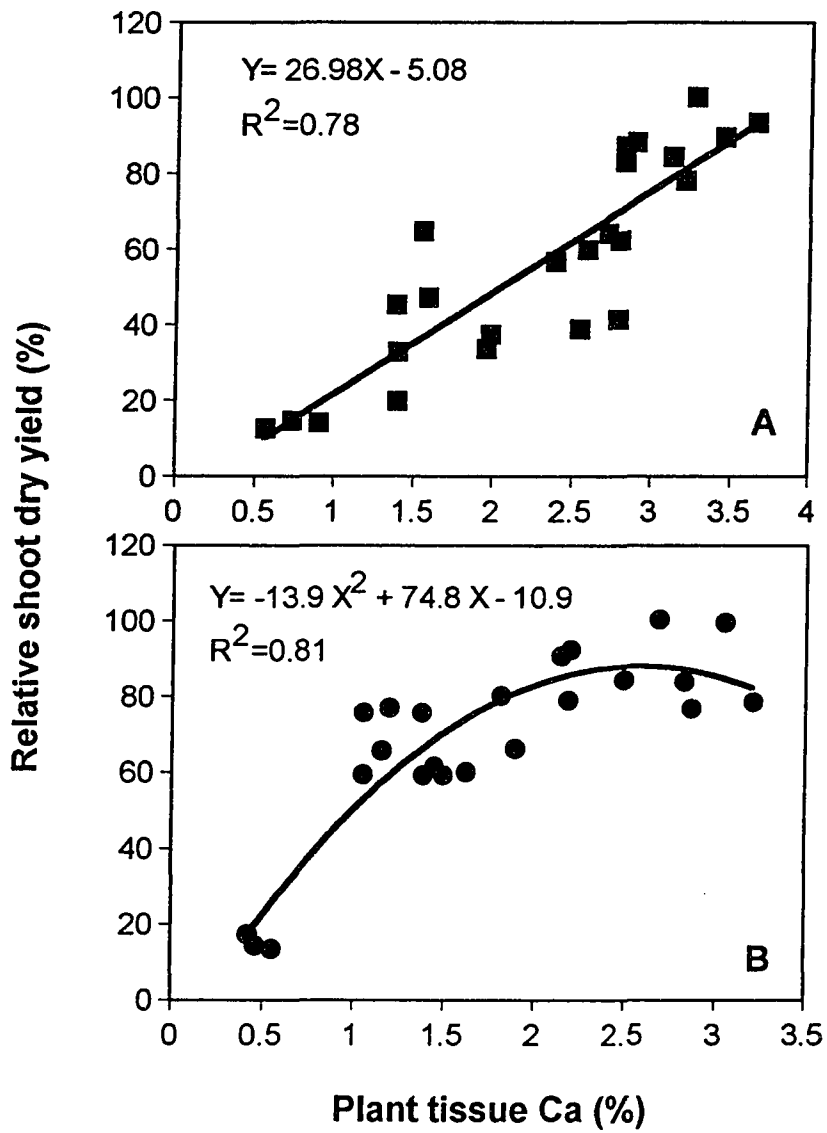
Fig. 3.3 Relationship between shoot Ca concentration and relative shoot dry weight of A) *Sesbania cochinchinensis* and B) *Desmodium intortum*.

Pavan et al. (1984), which could be an antagonistic effect of Ca over Mg when

there is an increase in the supply of Ca. This effect occurred across all

incubation periods. Shoot Mg concentrations of plants in the green manure

treatments were significantly higher than those in the animal manure treatments.

Although the various organic amendments significantly affected shoot Mg

Table 3.10 Shoot magnesium concentrations of *S. cochinchinensis* and *D. intortum* as affected by lime and organic amendments at different periods of incubation.

Treatment	*Sesbania cochinchinensis*			*Desmodium intortum*		
	1mo	6mo	12mo	1mo	6mo	12mo
	<-------------------------------- % -------------------------------->					
Control	0.14d[t]	0.15c	0.13b	0.91e	0.93b	1.05b
Lime -½X	0.21c	0.14c	0.15b	1.01de	1.04a	0.99bc
Lime -1X	0.26b	0.19b	0.27a	1.18cd	0.90b	0.96bc
Lime -2X	0.30a	0.25a	0.25a	0.94e	0.70c	0.85c
Cowpea	0.22c	0.14c	0.13b	1.37bc	1.02a	1.34a
Ch. manure	0.20c	0.16bc	0.16b	1.50b	0.89b	1.23a
Leucaena	0.26ab	0.17bc	0.23a	1.12de	0.94b	0.92bc
Sludge	0.29a	0.26a	0.25a	1.68a	0.91b	0.66d
	MSD(0.05)[‡]=0.04			*MSD(0.05)[‡] =0.16*		

[t] means within a column and soil followed by the same letter are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.
[‡] minimum significant difference between the same treatment across different incubation periods

concentrations, shoot dry weight did not correlate with shoot Mg levels probably

because Mg concentration in the plant tissue was above the critical level

(Figures 3.4A and 3.4B).
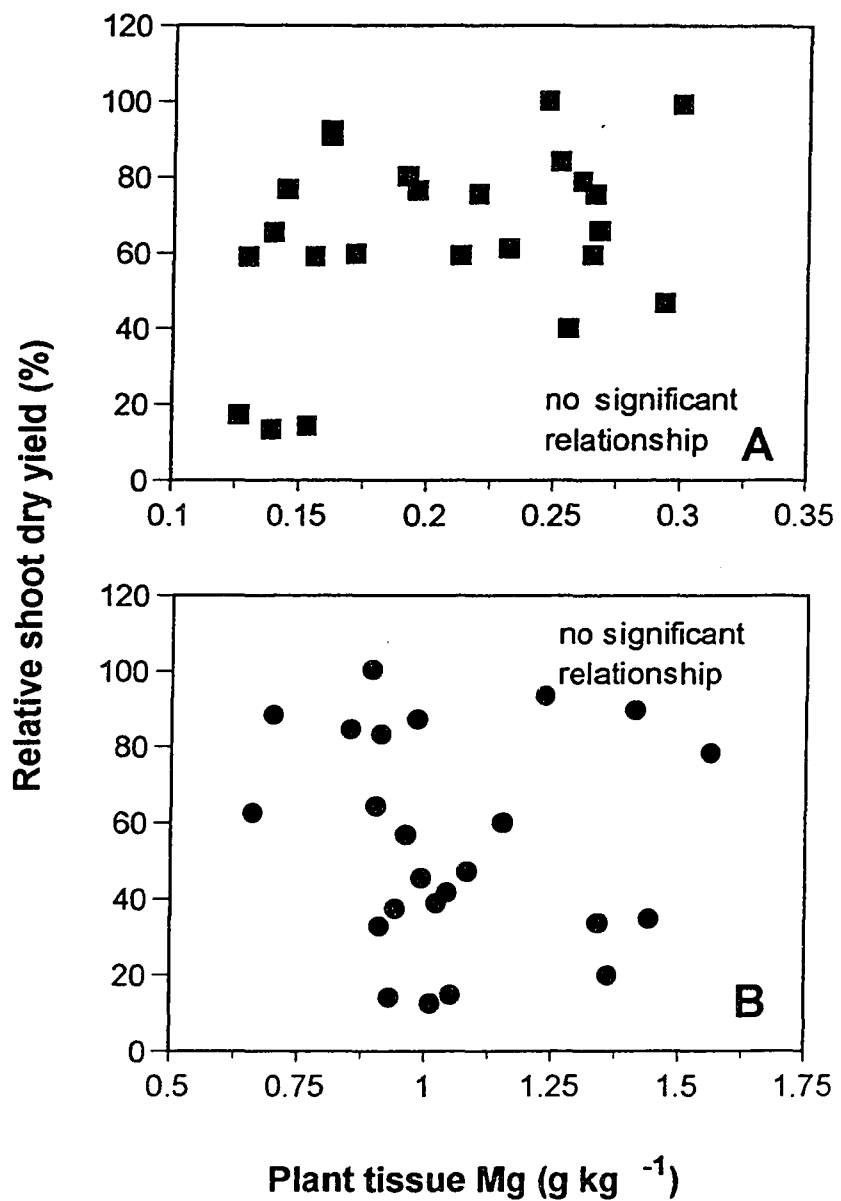
Fig. 3.4 Relationship between plant tissue Mg concentration and relative shoot dry weight of A) *Sesbania cochinchinensis* and B) *Desmodium intortum*.

Aluminum. The control plants had foliar Al concentrations ranging from 309 to 335 mg kg^{-1} in *Sesbania* and 90 to 121 mg kg^{-1} in *Desmodium* (Table 3.11). At the highest lime rate(2X), shoot Al was reduced from 75 to 87 mg kg^{-1} in *Sesbania* and 39 to 57 mg kg^{-1} in *Desmodium* . Shoot Al concentrations in the organic amended treatments were not significantly different from those in the 1X lime treatment.

Table 3.11   Shoot aluminum concentrations of *S. cochinchinensis* and *D. intortum* as affected by lime and organic amendments at different periods of incubation.

Treatment	*Sesbania cochinchinensis*[§]			*Desmodium intortum*[£]		
	1mo	6mo	12mo	1mo	6mo	12mo
	<------------------------------ mg kg^{-1} ------------------------------>					
Control	322a[†]	309a	335e	121a	181a	90a
Lime -½X	221b	255b	259b	69b	74b	61cd
Lime -1X	143cd	174c	169c	66b	60c	56d
Lime -2X	87e	75e	84e	57c	40d	39e
Cowpea	138cd	225b	191c	49de	56c	70bc
Ch. manure	107de	96e	115de	58c	38d	58d
Leucaena	175bc	169c	195c	43e	61c	75b
Sludge	120de	138d	146cd	52cd	44d	55d
	MSD(0.05)[‡]=40.20			*MSD(0.05)[‡] =8.25*		

[†] means within a column and soil followed by the same letter are not significantly different
  according to the Waller-Duncan K-ratio T test at the 5% level of significance.
[‡] minimum significant difference between the same treatment across different incubation periods

Plant tissue Al was negatively correlated with shoot dry matter yield in both plants as described by the exponential equation, $Y = 167.35 * \exp^{-0.007X}$ ($R^2=0.75$) for *Sesbania* and $Y = 159.3 * \exp^{-0.016X}$ ($R^2=0.70$) for *Desmodium*

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(Figures 3.5a & 3.5b). A 10% reduction in shoot dry weight was observed when

plant tissue Al was $\geq$ 89 mg kg^{-1} in *Sesbania* and $\geq$36 mg kg^{-1} in *Desmodium*.

Manganese. Plant tissue Mn of both plants was significantly reduced by

lime and organic amendments (Tables 3.12). The concentration of shoot Mn

consistently decreased with increased lime rate. The animal manures reduced

Table 3.12 Shoot manganese concentrations of *S. cochinchinensis* and *D. intortum* as affected by lime and organic amendments at different periods of incubation.

Treatment	Sesbania cochinchinensis[§]			Desmodium intortum[£]		
	1mo	6mo	12mo	1mo	6mo	12mo
	<————————————— mg kg^{-1} —————————————>					
Control	661a[†]	767a	775a	178a	185a	190
Lime -½X	472b	485b	544b	125b	158b	160
Lime -1X	385c	187e	229e	91de	130c	128
Lime -2X	264d	157e	138f	78e	62f	53
Cowpea	405c	437e	494c	104d	114d	122
Ch. manure	238d	273d	293d	90de	101de	119
Leucaena	462b	496b	484c	118bc	130c	121
Sludge	258d	163e	100g	72e	91e	96
	MSD(0.05)[‡]=35.70			*MSD(0.05)[‡] =8.25*		

[†] means within a column and soil followed by the same letter are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.
[‡] minimum significant difference between the same treatment across different incubation periods
[§] planted in the Kaneohe soil.
[£] planted in the Paaloa soil.

shoot Mn more effectively than green manures. This effect was observed in

both plants across all incubation periods in the two soils. Figures 3.6A and 3.6B

show that plant tissue Mn is negatively related to shoot dry matter yield. Shoot

Mn $\geq$ 96 mg kg^{-1} in Sesbania and $\geq$ 80 mg kg^{-1} in Desmodium reduced shoot dry

weight by 10%.
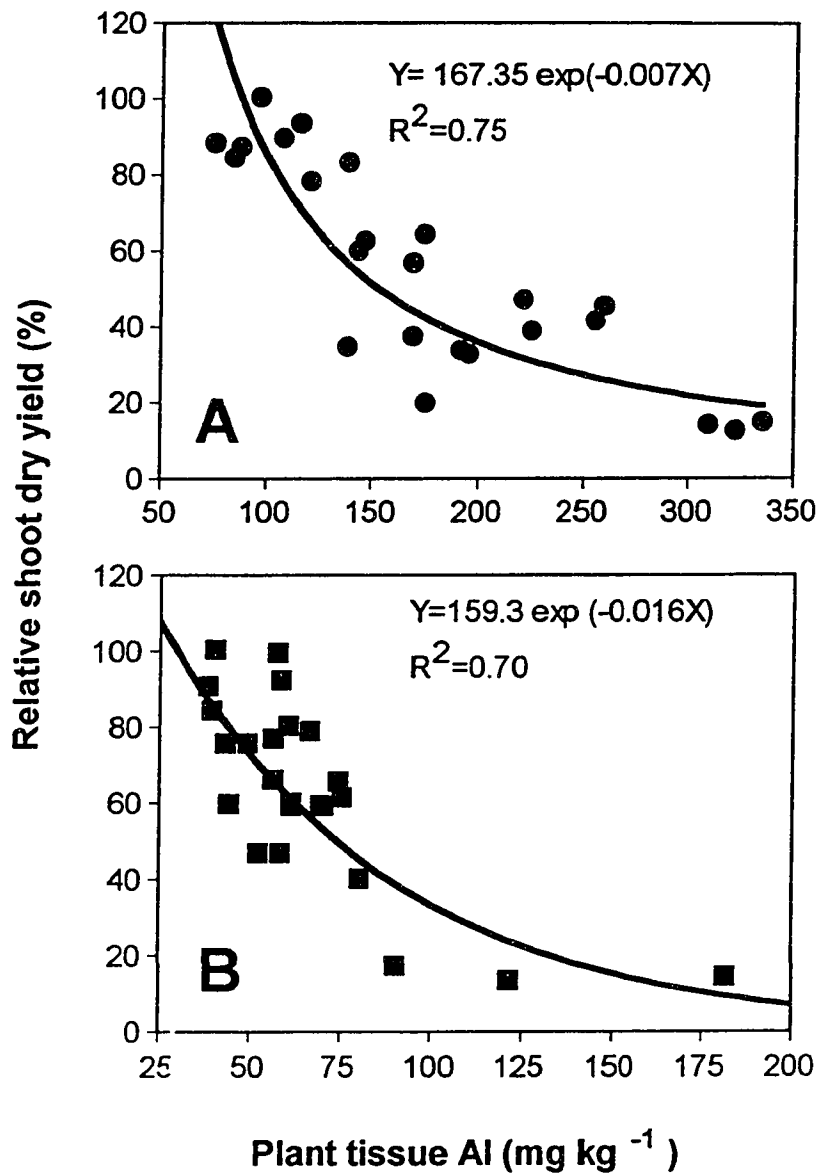
Fig. 3.5 Relationship between plant tissue Al concentration and relative shoot dry matter yield of A) *Sesbania cochinchinensis* and B) *Desmodium intortum*.
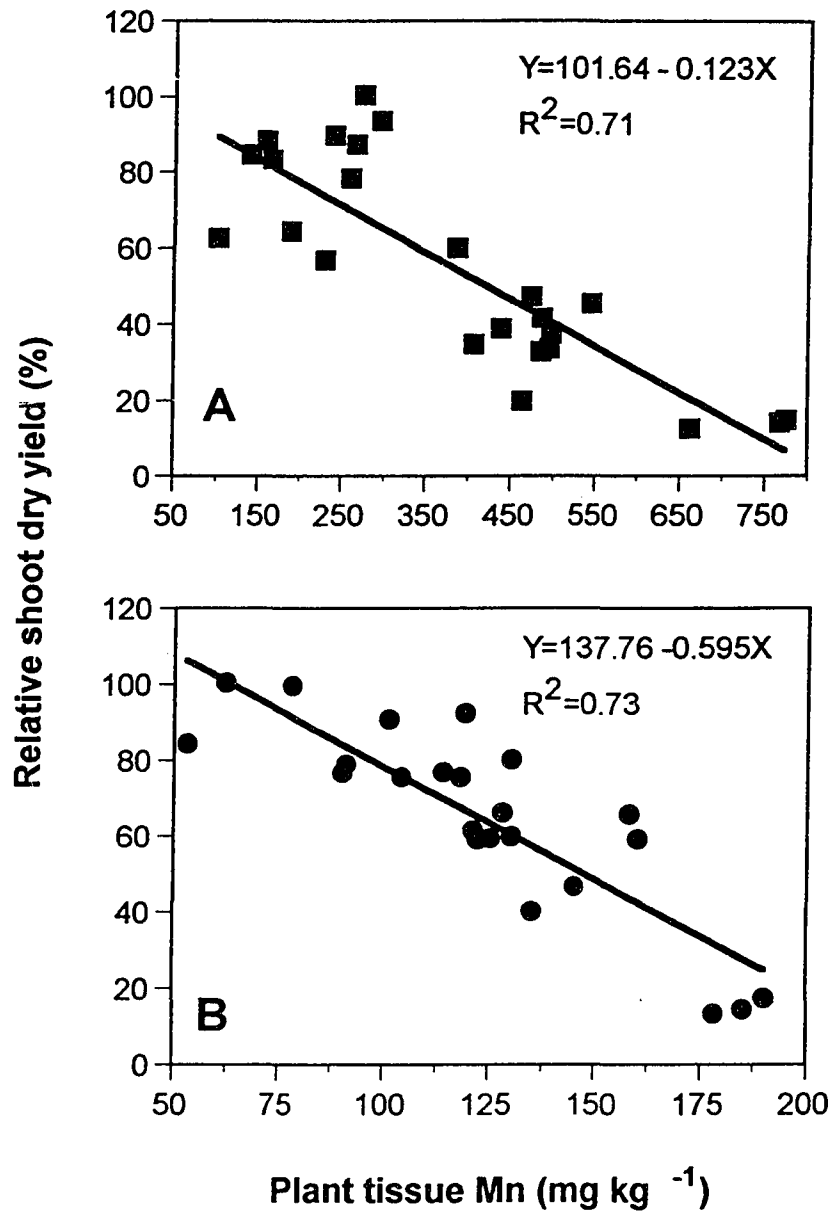
Fig. 3.6 Relationship between plant tissue Mn concentration and relative shoot dry matter yield of A) *Sesbania cochinchinensis* and B) *Desmodium intortum*.

3.5 Summary and conclusions

The liming effectiveness of four different organic manures (cowpea, leucaena, chicken manure, and sewage sludge) were compared with lime ($CaCO_3$) in a greenhouse study using two Al-toxic Ultisols: Paaloa and Kaneohe series. Lime and organic manures were mixed with the soils and allowed to incubate for 1, 6, and 12 months before *Sesbania cochinchinensis* and *Desmodium intortum* (Al-sensitive legumes) were grown for 45 days. Results showed that the organic manures can be used effectively as liming materials for acid soils. In terms of liming efficiency, chicken manure and sewage sludge were more effective than cowpea and leucaena. The animal manures effectively increased soil-solution pH and EC, and significantly reduced the concentrations of soluble and exchangeable Al, while increasing the concentrations of exchangeable Ca and Mg. The green manures had liming effects comparable with the lower rates of lime used in this study.

Shoot and root dry weights of *Desmodium intortum* and *Sesbania cochinchinenses* were significantly increased by both liming and organic amendments. Soil solution pH, total soluble Al, exchangeable Al, Ca, and Mg, as well as foliar concentrations of Al, Ca, and Mn were good parameters in evaluating the liming effectiveness of the organic amendments. Plant tissue Ca $\geq 3.5\%$ for *Sesbania* and $\geq 3.0\%$ for *Desmodium* were necessary to achieve 90% of the relative shoot dry weight of the plants. On the other hand, plant

tissue Al $\geq$ 89 mg kg^{-1} in Sesbania and $\geq$ 36 mg kg^{-1} in *Desmodium* caused a

10% reduction in shoot dry weight.

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CHAPTER 4

Residual liming effect of organic manures

4.1 Abstract

The residual liming effect of organic manure application to strongly acid soils was evaluated in a greenhouse experiment on acid soils that were initially incubated with cowpea, leucaena, chicken manure and sewage sludge for one year and previously planted with *Desmodium intortum* and *Sesbania cochinchinensis*. The organic manures and lime (equivalent to 2X the exchangeable Al of the unamended soil) were allowed to incubate further in the soils for another six months for a total of 18 months before planting.

Soil chemical properties indicated that organic residues, especially animal manures, could be used as soil acidity amendments. Soil-water pH, soil solution pH, and concentrations of soluble Ca, Mg, and K were increased, while concentrations of soil solution and exchangeable Al were effectively reduced 18 months after the application of organic amendments.

Increased plant height and total dry matter yield of *Desmodium intortum* and *Sesbania cochinchinensis* grown on the organically amended soils may be attributed to increased soil pH which resulted in lowered concentration and activity of soluble Al, and increased concentrations of soil solution Ca, Mg and K which were released by the decomposition of the applied organic manures.

Major mechanisms that were responsible for the residual liming effect of the organic manures might be: a) the ability of the organic residues to increase

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and maintain soil pH; b) Al-organic matter complexation; and c) the mitigating

effect of increased soil solution Ca concentration on Al toxicity. Biomass

production and plant height were significantly related to the activity of Al^{3+} and

total monomeric Al activities in both soils.

4.2 Introduction

In acid soils, lime (Ca or Mg carbonates) improves plant growth by

increasing soil pH (Cassel, 1980), decreasing exchangeable Al (Evans and

Kamprath, 1970; Farina et al., 1980), and also providing basic cations for plant

uptake (Kunishi, 1982). Liming, however, may have negative effects on plant

growth and soil properties. Phosphorus and Mn deficiencies can be induced by

excess lime application (Foy, 1974; Kamprath, 1970). More importantly, in the

humid tropics where soil acidity constraints are most widespread, lime and

fertilizers may not be economical for most farmers due to their high costs or may

simply be unavailable.

The use of organic residues whether of plant or animal origin as

"alternative liming materials" to alleviate Al toxicity in acid soils has shown

promise. Organic matter, an eventual product from the decomposition of organic

residues, plays an important role in controlling Al reactivity in soils. When grown

at the same pH, plants from soils high in organic matter do not exhibit the

symptoms of Al toxicity observed in plants grown in soils of low organic matter

(Evans and Kamprath, 1970).

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Although several studies have demonstrated the positive effect of organic amendments in detoxifying Al and improving plant growth (Ahmad and Tan, 1986; Hue and Amien, 1989; Hue, 1992; Bessho and Bell, 1992), information is scarce on the long-term or residual liming effect of organic residue application to strongly acid soils. In view of the above and as a follow-up to the initial greenhouse experiment (Chapter 3), this study was conducted to achieve the following objectives:

1. Determine the persistence of the "liming effect" of organic residues applied to Al-toxic soils in order to optimize the frequency of application.

2. Identify, through chemical analyses, the possible processes responsible for the liming effect of organic manures.

4.3 Materials and methods

4.3.1 Soils and organic amendments

The two soils (Paaloa series and Kaneohe series) used in the initial greenhouse experiment (incubated with the organic manures for 12 months and planted once) were allowed to dry and stand undisturbed in the greenhouse for six more months without any further treatment, and subsequently used for the residual liming-effect experiment.

After the 6-month "fallow period", the same indicator plants used in the earlier greenhouse study were planted, except this time they were rotated to simulate a crop rotation pattern, i.e., Desmodium intortum was grown in the

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Kaneohe soil, and *Sesbania cochinchinensis* in the Paaloa soil. The pot

experiment followed a randomized complete block design with three replications.

The highest lime treatment ($CaCO_3$ equivalent to 2X the KCl extractable-Al of the

unamended soils) was chosen as reference for the various organic amendments.

Except for the addition of 100 mg P kg^{-1} to the Paaloa soil and 150 mg P kg^{-1} to

the Kaneohe soil (both as KH_2PO_4), no other input was added to the soils. The

indicator plants were grown for six weeks. Plant height was measured at harvest

and plant shoots were cut at the soil surface while roots were carefully washed

and separated from the adhering soil.

4.3.2 Laboratory analysis

Plant tissue analysis. Plant shoots and roots were oven dried at 70°C for

48 hours, and weighed separately for dry matter yield. After drying, the shoots

were ground to pass a 40-mesh sieve. Sub-samples from the ground shoots

were ashed for 3-4 hours at 500 °C for foliar chemical analysis. Total plant tissue

N was determined by the micro-Kjeldahl method. Calcium, Mg, K, Na, Mn, Fe

and Zn were analyzed from a solution of the ashed sample by atomic absorption

spectrophotometry. Plant tissue P was determined from the ash solution by the

sulfo-molybdate ascorbic acid method (Olsen and Somners, 1982).

Soil solution collection and analysis. Soil chemical analysis was done

before planting and after harvest. Collection and analyses of the soil solution

and solid phase were done following the same procedures that were described in

Chapter 3. Soil solution NO_3^- and SO_4^{-2} were analyzed by high pressure liquid

chromatography. Total organic C in the soil solution was determined by the Mn(III)-pyrophosphate method of Bartlett and Ross (1988). Soil organic C was determined by the Walkley-Black method (Black, 1965). Soil P was extracted with $0.5M$ NaHCO$_3$ and measured by the same method used for plant tissue P. Organically bound Al was calculated as the difference between Al extracted with $0.33M$ LaCl$_3$ solution and $1M$ KCl solution.

Analysis of total Al in the soil solution was determined by the pyrocatechol violet method (Kerven et al., 1989). Aluminum activity was estimated using the SOILSOLN program (Wolt, 1989). Total monomeric Al activity was calculated as the sum of monomeric Al species in solution as follows.

$$(Al_T)=(Al^{3+})+ (AlOH^{2+})+ (Al(OH)_2^+)+ (Al(OH)_3^0)+ (Al(OH)_4^-)$$

The speciation program calculates the concentration of ion-pairs, hydrolytic species of Al, metal-organic complexes and free ions by the method of successive iteration. The concentrations (mM) of dissolved organic carbon and the following ions were entered: Ca, Mg, K, Na, Al, P, Cl$^-$, SO$_4^{2-}$, and NO$_3^-$. In addition, soil solution pH and partial pressure of CO$_2$ were also entered in the speciation program.

4.3.3 Statistical analysis

The data obtained were subjected to analysis of variance (ANOVA) using SAS routines, and differences between treatment means for each soil or plant species were evaluated by the Waller-Duncan K-ratio T test at a 5% level of significance (SAS Institute, 1985).

4.4 Results and discussion

4.4.1 Chemical properties of the soils before planting

Table 4.1 presents selected chemical properties of the two soils 18

months after lime and organic amendment application and prior to planting of the

indicator plants. The beneficial effect of lime on soil pH was still evident 18

months after application; soil pH was significantly increased from 4.56 to 6.02

Table 4.1 Soil pH and selected soil solution chemical properties of the two soils, 18 months after lime or organic amendments and prior to the second planting.

Treatments	pH[†]	E.C. (dS m⁻¹)	Ca	Mg	K	Mn	Al (µM)
			<------------- mg L⁻¹ ----------->				
Paaloa soil							
Control	4.56d[‡]	1.1d	33.8f	17.2e	66.0d	11.2a	56.2a
Lime -2X	6.02b	1.9bc	105.6c	9.8f	52.3e	2.4d	2.2c
Cowpea	4.76c	2.2ab	92.3d	37.6b	286.3a	10.6b	10.1b
Leucaena	4.64cd	1.6c	72.2e	39.4a	136.3c	5.7c	4.4c
Ch. manure	6.47a	2.4a	200.1b	33.4d	158.8b	1.4e	3.9c
Sludge	6.50a	2.3a	312.7a	36.0c	50.6e	0.8f	3.1c
Kaneohe soil							
Control	4.36b	1.8d	16.7f	56.4e	33.9d	10.7c	76.4a
Lime -2X	6.34a	1.9d	197.3c	58.1e	16.9f	0.4e	5.9c
Cowpea	4.52b	2.8c	106.9d	177.3a	152.0a	67.5a	20.7b
Leucaena	4.55b	2.7c	61.2e	104.0d	55.3c	32.1b	17.2b
Ch. manure	6.45a	3.2b	343.8b	157.1b	73.1b	4.7d	7.0c
Sludge	6.50a	3.5a	451.2a	152.6c	30.9e	0.5e	2.3c

[†] 1:1 soil:H_2O ratio
[‡] Means followed by the same letter within a column and soil are not significantly according to the Waller-Duncan K ratio T test at the 5% level of significance.

in the Paaloa soil and from 4.36 to 6.34 in the Kaneohe soil. The chicken

manure and sludge treatments maintained soil pH above 6.0 which were even

higher than those of the limed soils. Although pH values of the green manure

amended soils had dropped to below 5.0, these were still higher than the control

soils. Soil solution EC of the organically amended soils were likewise

significantly higher than those of the control and limed soils. Soil solution Ca

concentration was dramatically increased by lime and animal manure

applications. Concentrations of Mg in solution also significantly increased in the

organic residue treated soils as compared to their limed and unamended

counterparts. Except for the sludge treated Paaloa soil, solution K is significantly

higher in all organically amended soils compared to the lime treatments. Soil

solution Al concentration remained significantly lower in the limed and

organically amended soils than in the control soils. Green manure application to

the Kaneohe soil increased Mn concentration in the soil solution. Vega et al.

(1992) also observed an increase in Mn concentration after additions of organic

manures to a manganiferous Oxisol of Hawaii.

4.4.2 Plant growth in response to residual effects of lime and organic amendments

Plant height and dry weights of shoots and roots of the two plants are

presented in Table 4.2. The Al-stressed control plants made little growth, other

than that initially achieved prior to transplanting, as reflected in their very low

yields. Statistical analyses show that shoot and root dry weights were

significantly increased by both inorganic and organic amendments. Shoot dry

weights were dramatically improved by liming; for example, shoot dry weight of

Desmodium dramatically increased from 0.44 g pot^{-1} in the control to 3.89 g pot^{-1}

Table 4.2 Plant growth parameters as affected by lime and organic amendments
18 months after incubation.

Treatments	Shoot dry weight (g pot^{-1})	Root dry weight (g pot^{-1})	Plant height (cm)
	Desmodium intortum (Kaneohe soil)		
Control	0.44c†	0.06e	9.8e
Lime-2X	3.89a	1.12a	27.8cd
Cowpea	3.94a	0.86bc	38.4a
Leucaena	3.57a	0.63d	30.3bc
Ch. manure	4.18a	1.05ab	33.8b
Sludge	2.68b	0.74cd	24.3d
	Sesbania cochinchinensis (Paaloa soil)		
Control	1.23e	0.09d	14.2c
Lime -2X	3.42bc	0.87a	40.3ab
Cowpea	2.67d	0.79ab	34.5b
Leucaena	3.32c	0.50c	38.7ab
Ch. manure	5.24a	0.63bc	46.2a
Sludge	3.94b	0.57c	44.7a

†Means followed by the same letter within a column for each crop are not significantly
different according to the Waller-Duncan K-ratio T test at the 5% level of significance.

in the limed soil. Similarly, shoot dry weight of *Sesbania* increased from 1.23 g

pot^{-1} in the control to 3.42 g pot^{-1} in the lime treatment. Except for plants in the

sludge treatment, shoot dry weights of *Desmodium* in the organically amended

soils were not different from those in the lime treatment. In the case of

Sesbania, only those plants in the cowpea treatment had shoot dry weights

significantly lower than those which received lime. In fact, both plants grown in

soils that received chicken manure produced the highest shoot dry weights.

The increase in root dry weight in response to lime and organic amendments was dramatic. Lime increased root dry weight almost 10-fold and 19-fold for *Sesbania* and *Desmodium,* respectively. The various organic amendments likewise significantly increased root dry weights of both plants over their corresponding controls.

Plant height also improved significantly with lime and organic amendments. *Desmodium* plants that received applications of cowpea, leucaena, and chicken manure were significantly taller than those that received lime. Organically amended *Sesbania* plants were taller (animal manure treatments) or similar (green manure treatments) to those in the lime treatment.

4.4.3 Plant chemical composition

The different treatments also affected chemical composition of plant shoots (Table 4.3). Organic amendments in the Kaneohe soil significantly increased N concentration in *Desmodium* shoots. Plant tissue N ranged from 20.7 to 29.4 g N kg^{-1} in the organically amended soils as compared 19.7 g N kg^{-1} in the lime treatment. The increase in N concentration was even more dramatic in *Sesbania.* Shoot N concentrations of *Sesbania* in the organically amended soils were more than twice (44.3 to 46.7g kg^{-1} N) that of the control plants (20.6 g kg^{-1}) and significantly higher than that of the lime treated plants (28.5 g kg^{-1}).

Shoot P concentrations were significantly increased by both lime and organic amendments compared to the control. As the organic manures

decompose, they release P into the soil solution which became available for plant uptake. For both plants, shoot P concentrations were highest in the sludge treatments.

Potassium concentration of *Desmodium* was lowest in the control (11.2 g kg⁻¹). Liming significantly increased shoot K concentration to 12.1 g kg⁻¹, and organic amendments to 18.9 - 20.4 g kg⁻¹. Organically amended *Sesbania* plants also had significantly higher shoot K than the control and the lime treated plants.

Table 4.3 Plant shoot chemical composition in response to the residual effects of lime and organic amendments 18 months after incubation.

Treatments	N	P	K	Ca	Mg	Fe	Zn
	<----------------g kg⁻¹---------------->					<-mg kg⁻¹->	
Desmodium intortum (**Kaneohe soil**)							
Control	17.1d[†]	1.11c	11.2f	6.1e	8.9b	67d	223a
Lime -2X	19.7c	2.00a	12.1e	13.2b	10.6a	66d	70d
Cowpea	29.4a	2.04a	20.4a	8.7d	10.2a	91c	158b
Leucaena	29.3a	1.98ab	20.2b	10.6c	10.0a	156a	132c
Ch. manure	20.7b	1.84b	19.4c	13.6b	10.9a	113b	73d
Sludge	26.3b	2.07a	18.9d	17.7a	7.5c	125b	68d
Sesbania cochinchinensis (**Paaloa soil**)							
Control	20.6c	1.60c	14.6f	2.9f	1.5c	116bc	136c
Lime -2X	28.5b	1.91b	19.3e	23.0a	2.5b	181a	53d
Cowpea	46.7a	1.98b	21.4d	19.3c	2.4b	132bc	127c
Leucaena	44.1a	1.97b	27.0a	15.0e	1.8c	120bc	219a
Ch. manure	45.9a	2.01b	24.0b	17.6d	2.2b	113c	169b
Sludge	44.3a	2.20a	23.0c	20.4b	3.1a	140b	174b

[†] Means within a column and crop followed by the same letter are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.

Shoot Ca increased with lime and organic amendments, especially in *Desmodium* amended with chicken manure and sludge. This increase in shoot Ca might be related to increased soil solution Ca, which was available for plant uptake as a result of the release of this nutrient from the decomposing organic manures. Shoot Ca concentration in these plants were even higher than those in the lime treatment. Chicken manure and sludge contained 14.5% and 19.6% Ca, respectively (Table 3.2); and 40 to 50% of the Ca in these materials were released after 24 weeks of incubation (Table 5.6).

Shoot Mg concentration in *Desmodium* that received organic amendments (except sludge) compared favorably with that in the lime treatment. On the other hand, *Sesbania* amended with leucaena had only 1.8 g Mg kg^{-1}, nevertheless was higher than the control plants (1.5g Mg kg^{-1}). Plants in the other organic amendments had shoot Mg either similar to or higher than that of the lime treatment.

Shoot Fe in *Desmodium* was not affected by liming but was significantly increased by organic amendments. In *Sesbania*, the highest shoot Fe of 181 mg kg^{-1} was from plants in the lime treatment. Plants from the other treatments ranged from 113 to 140 mg Fe kg^{-1} which were not significantly different from the control. Iron was apparently not a limiting nutrient in all treatments because Fe levels were all within the range of 50-150 mg kg^{-1} believed to be adequate for most plants (Marschner, 1989).

Shoot Zn in *Desmodium* was highest in the control. Plants in the lime and animal manure treatments had tissue Zn levels significantly lower than those in the green manure treatments. No definite trend was observed for Zn in *Sesbania*. The lowest shoot Zn was in the lime treatment while the highest concentrations were from plants that received leucaena.

4.4.4 Shoot dry-matter yield and shoot Al and Mn concentration

Figures 4.1 and 4.2 show the relationships between shoot dry weight and shoot Al and Mn concentration. Figures 4.1a & 4.1b show that an increased Al concentration in shoots was associated with a sharp decrease in shoot dry weight. Applications of lime and organic amendments that led to significant reduction in soil solution Al concentration (Table 4.1), resulted in a depressed uptake of Al to the shoots, thus increasing shoot dry matter.

Shoot Mn concentration also exhibited an inverse relationship with shoot dry weight (Figures 4.2a & 4.2b). For both soils, chicken manure and sewage sludge applications decreased the uptake of Mn more effectively than the cowpea and leucaena green manures.

4.4.5 Soil pH and exchangeable Ca after harvest

To compare the residual liming effect of the organic manures with conventional liming treatment, soil pH and exchangeable Al were measured after plant harvest (Table 4.4). Chicken manure and sewage sludge raised soil pH by nearly 2 units from 4.12 in the Paaloa soil and 4.25 in the Kaneohe soil to higher than 6.0, even 18 months after application. These pH increases led to a

Weight (g/pot)   Al x 100 (mg/ kg)

A

Weight (g/pot)   Al x 10 (mg/kg)

B

Treatments
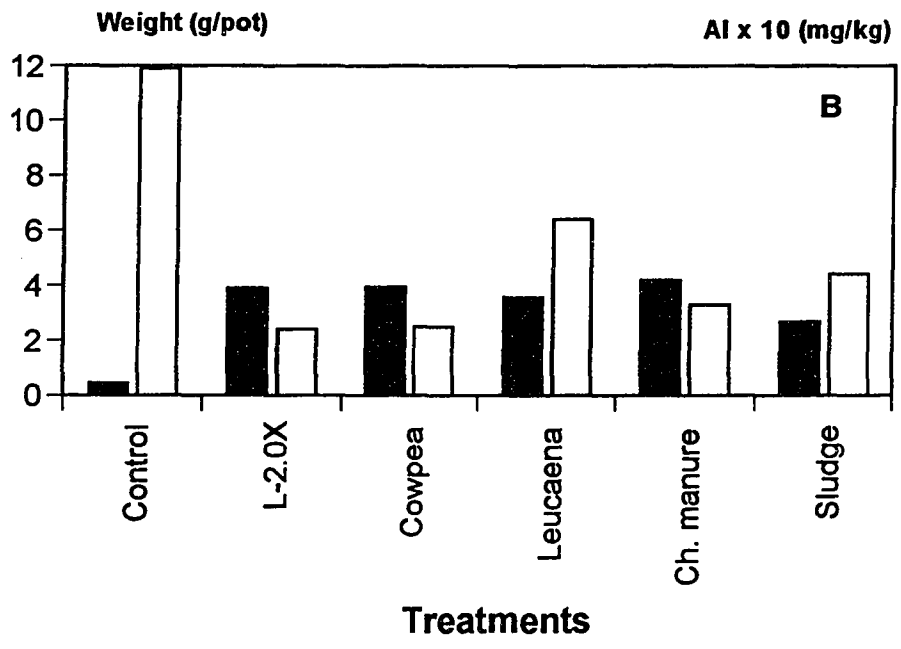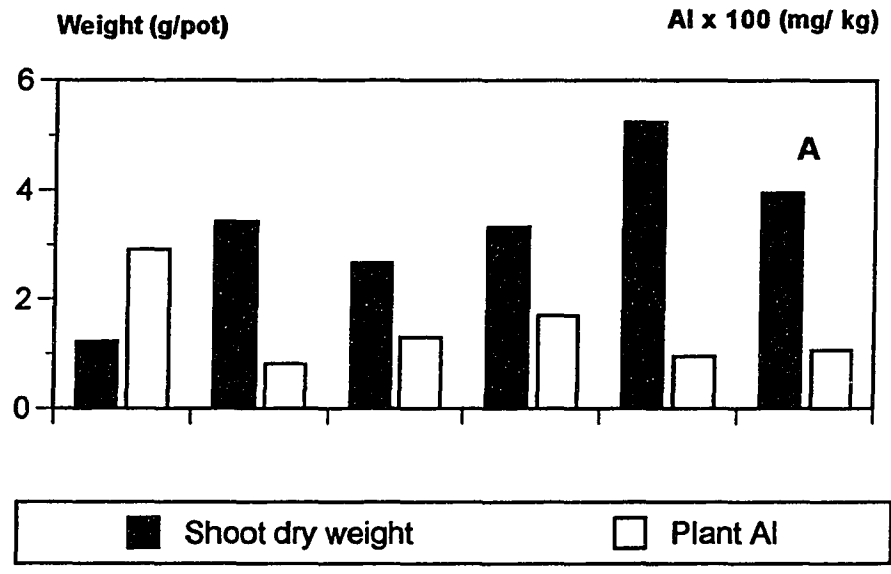
Fig. 4.1 Shoot dry matter yield of A) *Sesbania cochinchinensis* and B) *Desmodium intortum* as affected by plant tissue aluminum.

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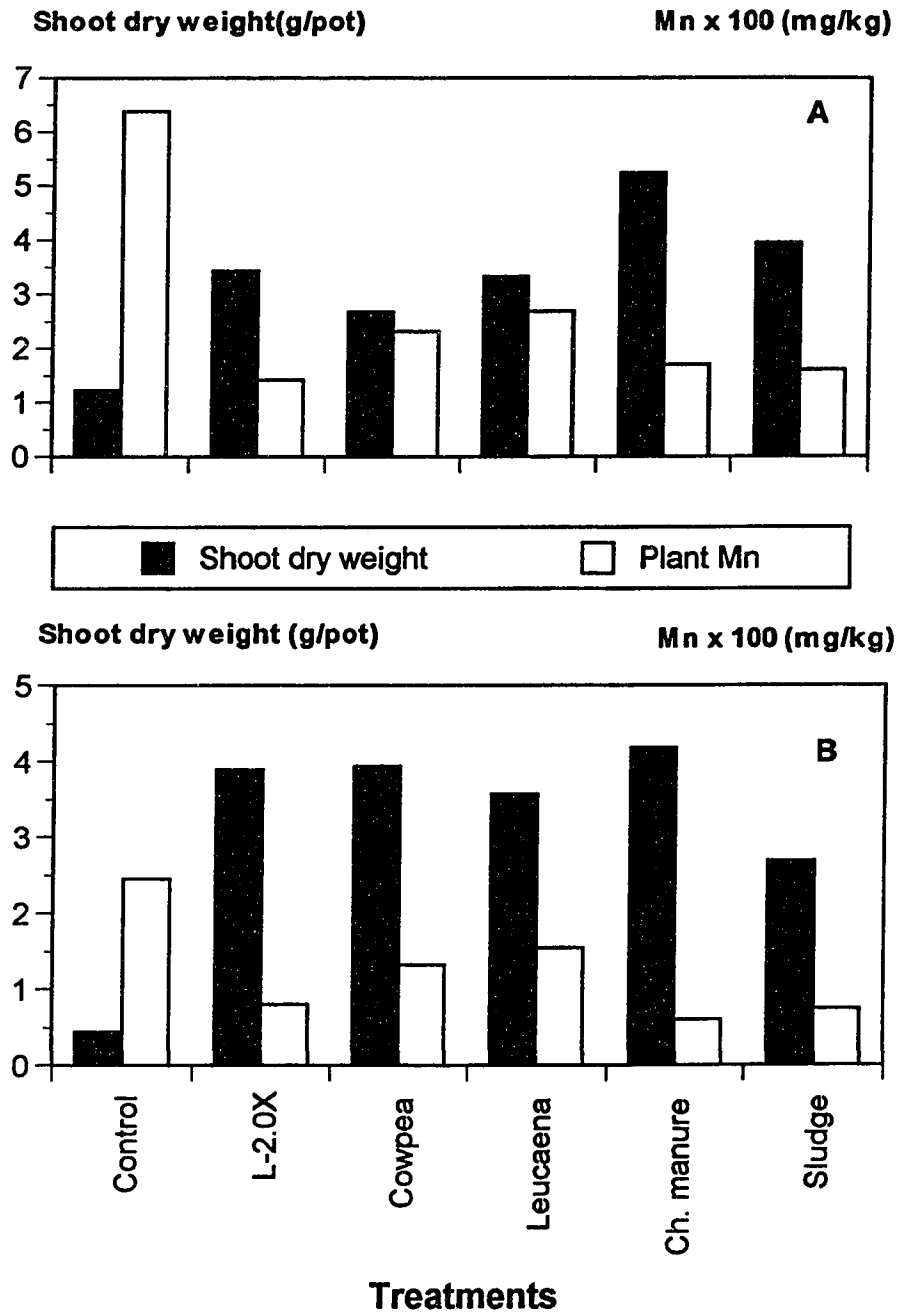
Fig. 4.2 Shoot dry matter yield of A) *Sesbania cochinchinensis* and B) *Desmodium intortum* as affected by plant tissue manganese.

Table 4.4 Soil pH and exchangeable Al concentrations of the two soils after plant harvest as affected by lime and organic amendments.

Treatment	pH	Exch. Al (cmol$_c$ kg^{-1})	pH	Exch. Al (cmol$_c$ kg^{-1})
	Paaloa soil		**Kaneohe soil**	
Control	4.12d[†]	3.71a	4.25d	5.51a
Lime -2X	6.65a	0.01c	6.84a	0.01c
Cowpea	4.95c	0.24b	4.77c	0.75b
Leucaena	4.90c	0.22b	4.81c	0.72b
Ch. manure	6.42ab	0.01c	6.39b	0.04c
Sludge	6.22b	0.01c	6.76a	0.03c

[†] Means followed by the same letter within a column and soil are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.

dramatic reduction in the exchangeable Al which became almost nil. Though less striking, the green manures also increased soil pH significantly over the controls.

4.4.6 Relationship between plant dry matter yield and pH, Al, and Mn in the soil solution.

High concentrations of soluble Al and Mn are two of the most important factors that make acid soils infertile. Table 4.5 presents the concentrations of total soluble Al and Mn in relation to soil solution pH and shoot and root dry weights.

The detrimental effect of high concentrations of total soluble Al in the control soils was clearly reflected in the shoot and root dry weights of both plants. In the unamended soil, *Sesbania* produced only 1.23 g, and *Desmodium*

0.44 g of shoot dry matter. Ismael et al (1993) found a total soluble Al

concentration of > 30 μM to be the critical level for corn grown on two acid soils

in Malaysia. Lime application led to a dramatic decrease in the concentration of

Table 4.5 Dry weights of plant shoot and root in response to soil solution pH and concentrations of soluble Al and Mn.

Treatments	Shoot dry weight (g)	Root dry weight (g)	Sol'n. pH	Soluble Al (μM)	Soluble Mn (mg L^{-1})
Sesbania cochinchinensis (**Paaloa soil**)					
Control	1.23 e[†]	0.10d	4.09	47.4a	14.20a
Lime -2X	3.42bc	0.87a	6.47	4.5c	1.00d
Cowpea	2.67d	0.79ab	4.84	13.0b	10.53b
Leucaena	3.32c	0.50c	4.78	13.3b	6.78c
Ch. manure	5.24a	0.63bc	6.44	4.8c	1.44d
Sludge	3.94b	0.57c	6.36	5.2c	1.97d
Desmodium intortum (**Kaneohe soil**)					
Control	0.44c	0.06c	4.30	88.2a	9.40c
Lime-2.0X	3.89a	1.12a	6.44	2.6e	0.46e
Cowpea	3.94a	0.86ab	4.64	14.8b	56.80a
Leucaena	3.57a	0.63b	4.68	11.8c	35.90b
Ch. manure	4.18a	1.05ab	6.42	6.1d	7.5cd
Sludge	2.68b	0.74b	6.39	6.3d	2.20de

[†] Means followed by the same letter within a column and crop are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.

total soluble Al in both soils, thus increasing shoot dry weight. Liming, reduced

soluble Al concentration to 4.5 μM in the Paaloa soil increased *Sesbania* yield to

3.42 g (almost 3 times the dry weight of the control). The increase was even

more dramatic in *Desmodium* where lime increased plant dry weight nearly 9-fold

over the control.

Organic amendments significantly decreased soluble Al concentrations to

4.5 - 13.3 μM in the Paaloa soil and to 6.1 - 14.8 μM in the Kaneohe soil.

Comparatively, the animal manures were more effective in reducing soil solution

Al than the green manures. Total soluble Al concentration $\geq$ 25 μM in the

Kaneohe soil and $\geq$ 19.5 μM in the Paaloa soil led to a 50% reduction in yields of

Desmodium and Sesbania, respectively (Figures 4.3a and 4.3b).

Soluble Mn concentrations were effectively reduced by lime and animal

manure applications. In contrast, green manure applications seemed to

enhance the release of Mn into the soil solution, especially in the Kaneohe soil.

4.4.7 Activities of soil-solution aluminum as indices of aluminum phytotoxicity

Although Al toxicity clearly limits crop growth in many acid soils,

considerable uncertainty exists in terms of predicting Al phytotoxicity in soils of

varying properties. Soil-solution Al^{3+} concentration has been found to be related

to plant growth (Adams and Moore, 1983; Evans and Kamprath, 1970). In

contrast, Adams and Lund (1966) obtained poor relationships between root

length of cotton and exchangeable Al or Al saturation. When the molar activity of

solution Al^{3+} was chosen as the index, they obtained a better relationship.

Brenes and Pearson (1973) likewise showed that Al activity was a good index of

Al toxicity in corn and sorghum. Noble et al. (1988) demonstrated a high

correlation between relative root length of soybean and Al^{3+} activity. Contrary to

these studies, Adams and Moore (1983) found no relationship between corn
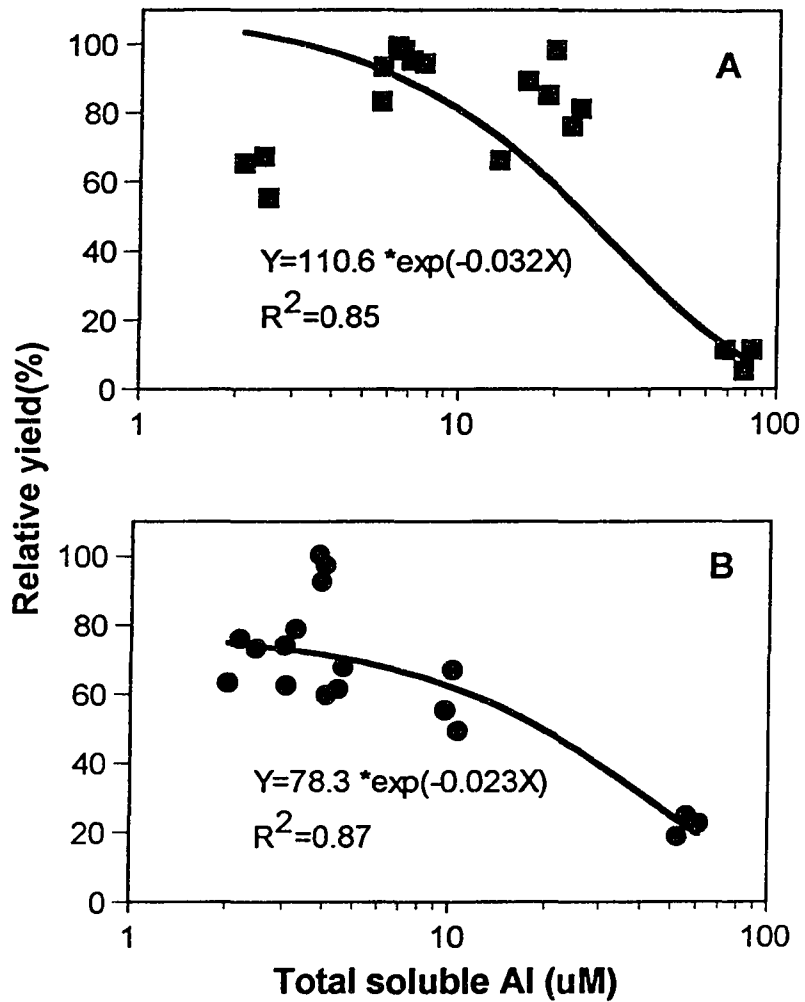
Fig. 4.3 Relationship between total soluble Al concentration and relative yield of A) *Sesbania cochinchinensis* and B) *Desmodium intortum*.

growth and exchangeable Al, Al saturation, and soil solution Al activity in six acid

Ultisols of Alabama.

The mean activities of the various monomeric Al species (Al^{3+}, $AlOH^{2+}$,

$Al(OH)_2^+$, $Al(OH)_3$, and $Al(OH)_4^-$ in the two soils are presented in Table 4.6. In the

Kaneohe soil, total Al activity ranged from 39.44 μM in the control to 1.72 μM in

the chicken manure treatment. The dominant Al species were Al^{3+}, $AlOH^{2+}$, and

$Al(OH)_2^+$ in the control soils and $Al(OH)_2^+$, $Al(OH)_3$ in the lime and organically

amended soils.

Table 4.6 Calculated activities of monomeric Al species in the two soils as affected by lime and organic amendments 18 months after application.

Treatments	(Al^{3+})	$(AlOH^{2+})$	$(Al(OH)_2^+)$	$(Al(OH)_3)$	$(Al(OH)_4)$	$(Al)_{total}$
	<--- μM --->					
Kaneohe soil						
Control	24.6	3.31	11.42	0.08	0.00	39.44
Lime -2X	<0.01	0.01	3.58	0.16	0.05	3.81
Cowpea	1.77	0.34	3.93	2.91	0.08	9.03
Leucaena	2.09	0.31	2.89	3.14	0.28	8.71
Ch.manure	<0.01	0.01	1.69	0.02	0.01	1.72
Sludge	<0.01	0.01	1.76	0.03	0.03	1.84
Paaloa soil						
Control	6.3	2.32	7.79	0.08	<0.01	16.49
Lime -2X	<0.01	<0.01	1.46	0.36	<0.01	1.82
Cowpea	0.38	0.11	2.07	1.53	<0.01	4.09
Leucaena	0.25	0.03	1.48	1.26	0.10	3.12
Ch.manure	<0.01	<0.01	0.99	0.02	0.04	1.05
Sludge	<0.01	<0.01	1.40	0.05	0.04	1.48

In order to obtain a more meaningful interpretation of the relationship between the various Al species in soil solution and plant response, relative dry matter yield and height of the two plant species were regressed against the various Al activity indices. Table 4.7 presents the various equations obtained and their corresponding R^2 values. All treatments were included in the derivation of the regression equations. The critical values represent activity values which correspond to a 50% reduction in plant dry matter yield or height.

Table 4.7 Relationship between plant growth parameters and calculated activities of Al.

Parameter and index	Regression equation	R^2	Critical value[†] (μM)
Sesbania cochinchinensis			
Rel. yield vs (Al^{3+})	$Y = 71.6\ exp^{(-1.63X)}$	0.84**	2.20
Rel. yield vs (Al)$_T$	$Y = 86.4\ exp^{(-0.087X)}$	0.92**	6.20
Rel. height vs (Al^{3+})	$Y = 81.0\ exp^{(-0.047X)}$	0.88**	10.30
Rel. height vs (Al)$_T$	$Y = 89.5\ exp^{(-0.077X)}$	0.93**	7.5
Desmodium intortum			
Rel. yield vs (Al^{3+})	$Y = 87.8\ exp^{(-0.095X)}$	0.95**	5.8
Rel. yield vs(Al)$_T$	$Y = 109.4\ exp^{(-0.062X)}$	0.90**	12.6
Rel, height vs (Al^{3+})	$Y = 76.7\ exp^{(-0.146X)}$	0.88**	3.0
Rel. height vs (Al)$_T$	$Y = 89.6\ exp^{(-0.030X)}$	0.76**	19.5

[†] 50% of relative yield or height
** Significant at $p < 0.01$
( ) = activity of Al species in μM.
(Al)$_T$ = total activity of all monomeric Al species
Y = growth parameter

Among the various Al species, the activity of the mononuclear species (Al^{3+}) and the sum of activity of all monomeric Al species (Al_T), gave the best correlation with relative yield and height for both plants.

4.4.8 Concentrations of Ca, Mg, K and Na in soil solution

Many acid soils are characterized by low concentrations of nutrients

required for optimum plant growth. Concentrations of soil solution Ca, Mg, and K

were lowest in the control soils (Table 4.8). Liming increased soluble Ca but had

little effect on soluble Mg, K, and Na. Organic amendments significantly

increased soluble Ca and Mg over the controls. In fact, the animal manure

treated soils had significantly higher concentration of these nutrients than the

limed soils.

Table 4.8 Concentrations of basic cations in the soil solution at plant harvest as affected by lime and organic amendments.

Treatments	Ca	Mg	K	Na
	<------------------------------ mg L^{-1} ------------------------------>			
Kaneohe soil				
Control	10.4e[†]	31.2d	23.3e	146.5c
Lime -2X	141.3c	3.7d	23.9e	127.3c
Cowpea	71.3d	114.0b	143.3a	246.2a
Leucaena	49.5d	78.6c	62.1c	133.0c
Ch. manure	262.3b	144.3a	76.5b	203.2b
Sludge	282.6a	134.3a	31.9d	150.1c
Paaloa soil				
Control	15.8e	11.6d	42.5d	112.7b
Lime -2X	99.4c	6.2d	39.5d	106.1b
Cowpea	60.2d	18.9c	173.3a	112.0b
Leucaena	54.0d	44.9b	100.5c	124.0b
Ch.manure	190.3b	45.8b	121.3b	179.7a
Sludge	220.3a	68.9a	43.3d	118.3b

[†] Means within a column and soil followed by the same letter are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.

Soil solution K concentrations were also higher in the organically

amended soils than in the control and lime treated soils except for the sludge

amended Paaloa soil. Except for chicken manure in both soils and the cowpea

treatment in the Kaneohe soil, organic amendments had no significant effect on

soil solution Na. Thus, aside from their Al-detoxifying effect (liming effect),

organic amendments can also supply basic cations that are often deficient in

acid soils.

4.4.9 Possible processes responsible for the liming effect of the organic residues

4.4.9.1 Precipitation of Al due to pH increase. Good growth of plants

due to liming can be attributed to lowered concentrations of both soluble and

exchangeable Al as soil pH increases (Hue and Amien, 1989). The dissolution

of lime produces OH^- ions which in turn precipitate Al as $Al(OH)_3$, rendering it

non-toxic or unavailable to plants. Improved plant growth by organic

amendments may be partly explained by their ability to maintain soil pH above

that of the unamended soil. This pH increase may be related to the liming effect

of the organic manures. Using finely ground coral lime as a reference, liming

equivalence was determined by reacting each of the organic manures with $0.5M$

HCl for 30 min. Thereafter, the unreacted acid was titrated to the equivalence

point with standardized NaOH solution. Chicken manure and sludge had higher

liming power than cowpea and leucaena green manures (Figure 4.4).
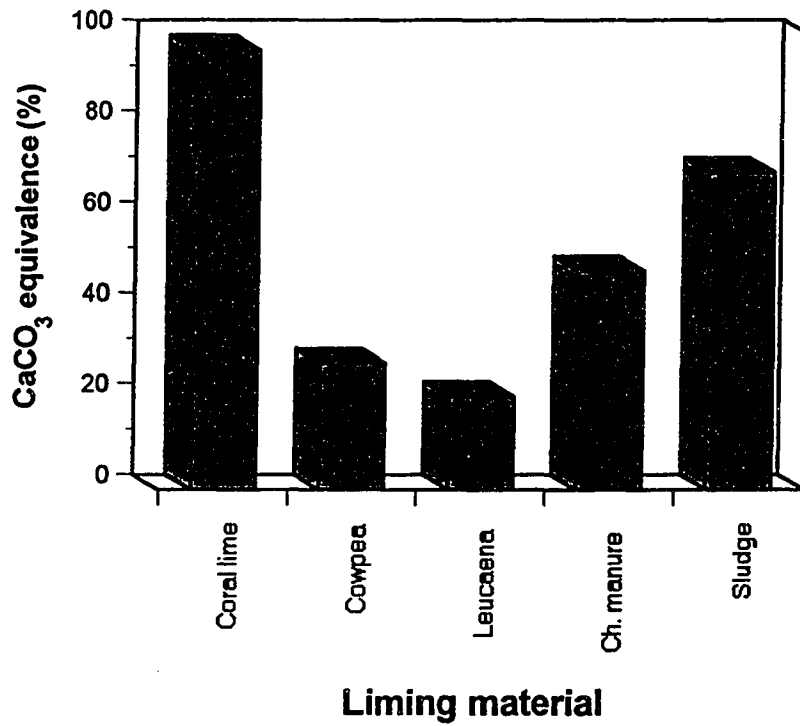
Figure 4.4 Liming equivalence of the organic residues with coral lime as reference.

4.4.9.2 Ameliorative effect of Ca. Increased soil solution Ca could

partly explain the better Al-detoxifying capacity of the animal manure treated

soils. Kinraide and Parker (1987) and Alva et al. (1986) have shown that Ca can

mitigate the deleterious effects of Al because Ca additions increase ionic

strength, and hence also reduce soluble Al^{3+} activity. Hourigan et al (1961)

attributed yield increase due to liming to the presence of more readily plant-

available Ca in soil solution. Materials that release Ca into the soil solution can

alleviate the toxic effects of Al. Figures 4.5a and 4.5b show highly significant

relationship between total plant dry matter yield (combined dry weight of shoot

and root) and soil-solution Ca concentration.

4.4.9.3 Aluminum complexation by biochemicals. Hue and Amien

(1989) speculated that one important mechanism responsible for Al detoxification

in an acid Ultisol amended with green manures was the complexation of soluble

Al by manure-derived organic molecules. Increased concentrations of the

dissolved organic carbon indicates increased concentrations of soil solution

biochemicals (Table 4.9). Dissolved organic carbon (DOC) is composed of a

wide array of organic compounds ranging from short-chain organic acids to large

molecules such as fulvic and humic acid (Thurman, 1985). Dissolved organic C

may influence soil solution acidity, mobility and toxicity of metals, and nutrient

availability (Dalva and Moore, 1991).

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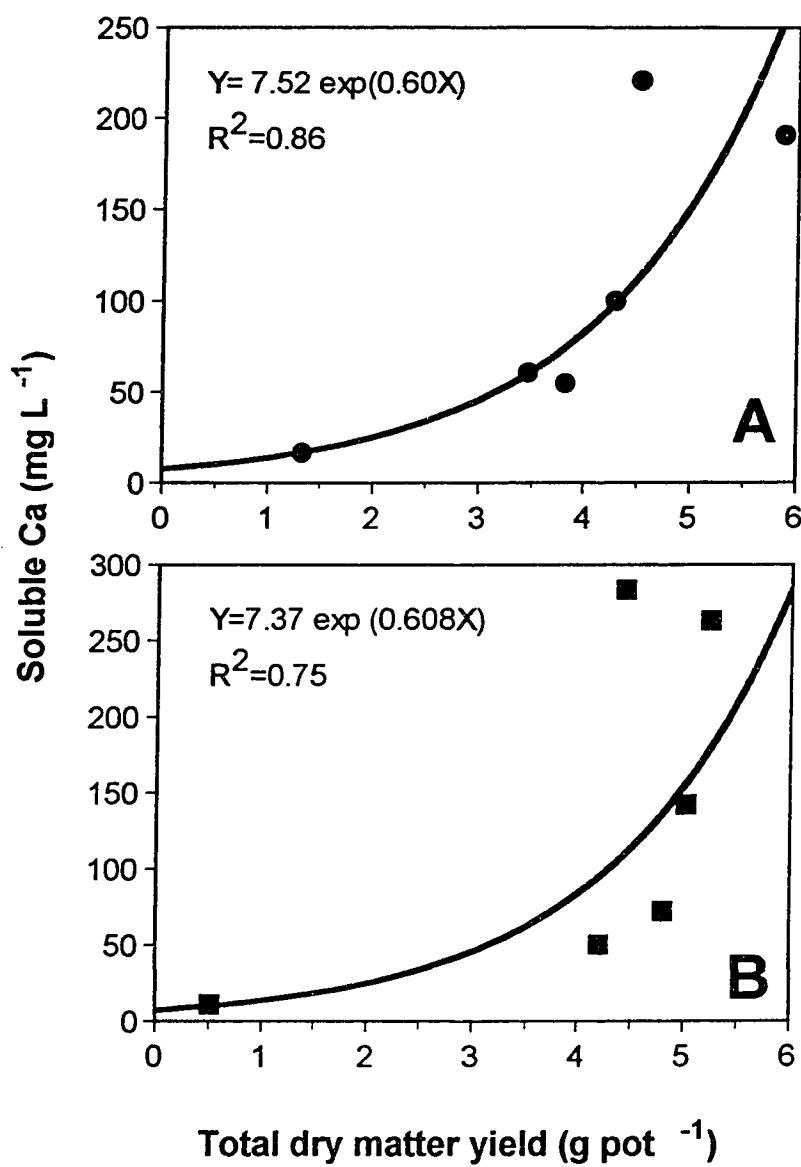
Fig. 4.5 Relationship between total plant dry matter yield of
A) *Sesbania cochinchinensis* and B) *Desmodium intortum* and
concentration of Ca in soil solution.

Organic amendments produced 3.25 - 4.62 m*M* dissolved organic C in the

Kaneohe soil and 6.44 - 7.22 m*M* in the Paaloa soil, which were approximately

twice the concentration of soluble C in the controls.

Total organic C of the organically amended Paaloa soil likewise showed a

significant increase over the control and limed soils. In both soils, lime did not

affect total organic C content, but organic manures understandably did. Soils

amended with the green manures had slightly higher total organic C than those

amended with animal manures . Plant residues which contain lignin and other

biologically recalcitrant materials could have contributed to higher levels of soil

organic C. Several studies have demonstrated that the interactions between soil

Table 4.9 Organic C in soil solution and in the solid phase after harvest in response to lime and organic amendments 18 months after incubation.

Treatments	Soluble C (m*M*)	Total Org.C (%)	Soluble C (m*M*)	Total Org. C (%)
	Kaneohe soil		**Paaloa soil**	
Control	1.21c[†]	1.45c	3.96e	2.50d
Lime -2X	1.72c	1.43c	4.92d	2.47d
Cowpea	4.20ab	1.82a	6.44c	3.15a
Leucaena	3.45ab	1.73ab	7.89a	2.99ab
Ch.manure	3.25b	1.64abc	6.55c	2.84bc
Sludge	4.62a	1.58bc	7.22b	2.75bc

[†] Means within a column and soil followed by the same letter are not significantly different according to the Waller-Duncan K-ratio T test at the 5% level of significance.

organic compounds, such as fulvic and humic acids, with soil minerals play an

important role in immobilizing soil Al and mitigating its harmful effects (Brogan,

1967; Hoyt and Turner, 1975). It is believed that Al ions are detoxified by

interactions with organic matter and its decomposition by-products via

complexation, coagulation, chelation and peptization reactions (Mortenson, 1963; Bartlett and Riego, 1972; Cabrera and Talibudeen, 1977).

4.4.8.4 Binding of Al by soil organic matter. Acid soils that are rich in native organic matter or amended with large quantities of organic residues, have low Al^{3+} concentrations in soil solution and permit good growth of crops under conditions where toxicities would otherwise occur. Results of studies conducted at various pH levels, Al concentrations, and amounts of organic amendments have indicated that lower exchangeable Al, decreased Al toxicity, and better plant growth are achieved with an increase in the amount of organic residue added (Hoyt and Turner, 1975; Kretzschmar et al., 1991; Bessho and Bell, 1992).

It is believed that humic and fulvic acids could form stable complexes with Al due to their high content of oxygen-containing functional groups. Coordinate linkages with a single donor group and formation of chelate (ring) complexes represent the predominant form of complexed Al in environments where humic substances are abundant (Vance, 1989).

Table 4.10 compares the amount of Al extracted by $LaCl_3$ with that extracted with KCl. The difference in the amounts of Al extracted by the two solutions could be attributed mostly to organically bound Al.

The organically amended soils had significantly higher levels of soil Al when 0.33M $LaCl_3$ was used as the extractant. It is generally considered that KCl removes mostly exchangeable Al while $LaCl_3$ or $CuCl_2$ solutions remove Al

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from Al-hydroxy interlayers, organically bound Al, and recently precipitated Al in

addition to exchangeable Al (Oates and Kamprath, 1983). Aluminum

complexed by organic matter is not readily exchangeable (Hargrove and

Thomas, 1981, 1982) and is non-phytotoxic (Bartlett and Riego, 1972).

Table 4.10 Soil Al extracted by $1M$ KCl and $0.33M$ LaCl$_3$ solution.

Treatment	Kaneohe soil		Paaloa soil	
	$1M$ KCl	$0.33M$ LaCl$_3$	$1M$ KCl	$0.33M$ LaCl$_3$
	<————————————— cmol$_c$ kg^{-1} —————————————>			
Control	5.51a[†]	5.57a	3.71a	3.83a
Lime -2X	0.01c	0.04e	0.01c	0.05e
Cowpea	0.75b	1.01b	0.24b	0.48b
Leucaena	0.72b	0.89c	0.22b	0.43b
Ch. manure	0.04c	0.15d	0.01c	0.22d
Sludge	0.03c	0.16d	0.01c	0.29c

[†] Means within a column and soil followed by the same letter are not significantly
different according to the Waller-Duncan K-ratio T test at the 5% level of significance.

4.5 Summary and conclusions

The residual liming effects of cowpea and leucaena green manures,

chicken manure and sewage sludge were evaluated against CaCO$_3$ applied to

two acid soils that were incubated for 18 months after application. Crop

response and soil chemical properties suggest that the residual liming effect of

the organic manures lasted at least 18 months after their application. Animal

manures were more effective than green manures in increasing soil pH and

decreasing the total concentration and activity of soil solution Al and

concentration of soluble Mn. Shoot dry matter yields and heights of plants grown

in the organically amended soils were comparable to those obtained from the limed soils. Organic amendments significantly increased concentrations of cations such as Ca, Mg, K, and Na in the soil solution, which are beneficial to plant growth in acid soils. Liming effects of the organic manures could be explained by the following mechanisms: a) they increase soil pH and precipitate Al, b) they supply cations, specifically Ca upon decomposition, and c) they detoxify Al through complexation with soluble organic molecules and the solid organic matter.

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CHAPTER 5

Nitrogen mineralization, phosphorus sorption, and nutrient release patterns of organic manures applied to strongly acid soils

5.1 Abstract

Application of organic residues is a well known agricultural practice for maintaining soil nutrient levels and ameliorating soil properties to sustain crop production. This is particularly true in many developing countries where fertilizer use is limited due to high prices or unavailability. The rate of N mineralization and release of Ca, Mg, and K from cowpea and leucaena green manures, chicken manure, and sewage sludge were investigated in an incubation experiment in the laboratory. Two acid soils, Kaneohe series (Humoxic Tropohumult) and Paaloa series (Rhodic Kandiudult) were used. Organic amendments at a rate of 20 g kg^{-1} were mixed with the two soils, packed in leaching columns and incubated moist at room temperature. Leaching with deionized water was repeated every 2 weeks for a total of 24 weeks. Leachates were analyzed for NO_3-N and Ca, Mg, and K. The ability of these organic manures to reduce P sorption and increase P availability in the Paaloa soil was also studied.

Nitrogen in chicken manure and sewage sludge mineralized faster than that in cowpea and leucaena green manures. The animal manures released 60.0 to 72.8% of their total N content as compared to 41.2 to 51.6% of the green

manures. The faster release rate of N in the animal manures could have been due to their lower C:N ratio compared to the green manures. The slower rate of N mineralization in the plant materials may be explained by their high contents of lignin and polyphenolics which are known to retard the decomposition of plant tissues, and thus nutrient release. All the organic manures exhibited positive N mineralization during the entire incubation period.

The release of cations from the organic manures followed the order K > Mg ≥ Ca. After 24 weeks of incubation, 60.1% to 79.2% K, 39.6% to 55.3% Mg, and 38.6 to 51.4% Ca of the organic manures were mineralized. The cations were released steadily from the decomposing materials during the entire incubation period.

The organic amendments also effectively reduced P sorption while increasing the concentration of extractable P in the soil. Chicken manure was most effective while leucaena green manure was least effective in decreasing P sorption. Extractable P was significantly increased by the organic amendments with higher levels observed in the animal manure treated soils.

5.2 Introduction

The increasing energy requirements for production of synthetic fertilizers, and problems associated with alternative disposal methods have led to a renewed interest in the application of organic wastes to agricultural land (FAO Bulletin, 1980).

Organic residues have many properties of an ideal N fertilizer and a supplementary nutrient source for growing plants. Organic N is not readily leached or denitrified and its mineralization rate is dependent on many of the same factors affecting plant growth. Organic manures and crop residues added to soil vary widely in their chemical composition. The C/N ratio ranges from as low as 6.5 in composted chicken manure (Castellanos and Pratt, 1981), 14.4 in leguminous tree prunings (Handayanto et al., 1994), to 78 in wheat straw and 85 in rice straw (Yadvinder-Singh et al., 1988). Before it becomes available to plants, the organic N in manures and crop residues must be mineralized. A knowledge of the N-mineralization patterns as well as the release rate of essential plant nutrients in these residues are necessary for efficient soil and crop management.

Acid soils are often noted for their low phosphate availability (Kamprath, 1967). Common management practices to reduce P fixation include addition of large amounts of P fertilizers and soil amendments such as lime or Ca silicates (Sanchez and Uehara, 1980). The application of organic residues to these soils has demonstrated positive results and thus presents an alternative low-input management practice to alleviate the P problem (Bumaya and Naylor, 1988; Singh and Jones, 1976; Easterwood and Sartain, 1990).

In view of the foregoing, the study was conducted with the following objectives:

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1. Evaluate the N mineralization and nutrient release patterns of organic residues when applied to strongly acid soils.

3. Determine the effect of organic residues in reducing P sorption and increasing P availability in acid soils.

5.3 Materials and methods

5.3.1 Nitrogen mineralization experiment

The different organic materials were thoroughly mixed with 20 grams of air-dried soil to give an equivalent rate of 20 g kg^{-1} dry soil. The organic residue-treated soil was mixed with 20 g of acid-washed silica sand to improve soil aeration during the incubation. Glass leaching tubes (3.5 cm diameter and 9.5 cm length) lined with 5 mm of glass wool pad topped with a thin layer of silica sand were used to retain the final mixture during the incubation period. A second 5-mm glass wool pad was placed on top of the soil mixture in order to avoid dispersion and minimize disturbance of the mixture during leaching. A control using soil-silica sand mixture was also included. Treatments were done in triplicate and arranged in a completely randomized design in the laboratory.

During the incubation period the leaching tubes were covered with a piece of parafilm provided with a single hole at the center for aeration and kept at room temperature (23± 2 °C) in an upright position. Leaching was done by carefully passing 100 ml of deionized water in 5 increments. Every 2 weeks thereafter the leaching process was repeated for a total of 24 weeks. The

moisture content of the columns was periodically adjusted to pre-incubation

conditions by weighing each column every week and readjusting the weight as

necessary by the addition of deionized water.

Leachates obtained at each sampling were analyzed for NO_3-N by the

method involving transnitration of salicylic acid (Vendrell and Zupancic, 1990).

Percentage of organic-N mineralized in the soil was computed as follows:

$$\frac{(\text{N released in} \quad - \quad \text{N released} \atop \text{waste-treated soil} \quad \text{in control})}{\text{Organic nitrogen added in waste material}} \times 100$$

5.3.2 Nutrient release experiment

Leachates obtained from the N mineralization experiment were also

analyzed for concentrations of Ca, Mg, and K in order to assess the rate of

release of these nutrients from the organic materials. Percent nutrient

mineralized was computed using the same formula used for the N mineralization

study.

5.3.3 Estimation of N release constants

The rate constants of N release (k) were estimated using a single

exponential equation, Y=exp(-kt) (Wieder and Lang, 1982); where Y is the

percentage of the original N in the organic residue remained at time t. To

calculate k, linear regression of ln Y versus t was performed. The slope of the

regression line is the k value.

5.3.4 Phosphorus sorption experiment.

The Paaloa soil (Rhodic Kandiudult) was used for the P sorption study.

Selected chemical properties of the soil are presented in Table 5.1. Air-dried

soil samples ground to pass a 2-mm sieve were used for this study. Two

hundred fifty grams of soil were placed in a polyethylene bag and mixed with an

equivalent of 20 g organic residue kg^{-1} soil. An unamended control was included

for comparison. There were three replicates per treatment. The treated soils

were moistened with deionized water to field capacity and

Table 5.1 Selected chemical properties of the Paaloa soil.

Soil property	Concentration
pH (1:2;soil:H$_2$0)	4.0
KCl-Al (cmol$_c$ kg^{-1})	3.64
Exch. cations (cmol$_c$ kg^{-1})	
Ca	0.04
Mg	0.21
K	0.08
Na	0.26
NaHCO$_3$ extractable P (mg kg^{-1})	6.1
Soil solution Ca (mg L^{-1})	4.4
Soil solution Mg (mg L^{-1})	2.8
Soluble Al (μM)	57.8

incubated for 9 weeks in the laboratory at ambient room temperature. Sub-

samples were taken every 3 weeks for the determination of extractable P. Sub-

samples were air-dried, ground to pass a 2-mm sieve and were kept in plastic

bags before analysis.

Phosphorus sorption was investigated after 3 weeks and 9 weeks of

incubation at four initial P levels (0, 20, 40, 60 mg P L^{-1}) using Ca(H$_2$PO$_4$)$_2$.2H$_2$O.

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The sorption method of Fox and Kamprath (1970) was adopted as follows. Exactly 1.00 g sub-sample of the control and treated soils was weighed and then put into a plastic centrifuge tube containing 20 mL of $0.01M$ $CaCl_2$ solution and the four initial levels of P.

The tubes were shaken horizontally for 20 minutes every hour in a reciprocal shaker for 3 days. After the shaking period the tubes were centrifuged at 10,000 rpm for 10 minutes. The concentration of soluble P in the supernatant was analyzed by the molybdate-ascorbic acid method (Olsen and Somners, 1982). The amount of P sorbed and desorbed was calculated as the difference between the initial and final concentrations of P in solution. The P that could not be accounted for in the equilibrium solution (supernatant) was considered as sorbed.

Soil P is determined by extracting 1.0 g of air-dried soil with 20 mL of 0.5 M $NaHCO_3$ solution. The mixture was placed in a centrifuge tube, shaken for 30 minutes, and centrifuged at 10,000 rpm for 10 minutes. Phosphorus in the supernatant is then measured by the molybdate-ascorbic acid method.

5.3.5 Chemical analysis of the organic manures.

Hot-water soluble materials and hemicelluloses were determined by the methods of Harper and Lynch (1981). Lignin was determined by the acid detergent fiber-permanganate method (Van Soest and Wine, 1968). Polyphenols expressed as percent tannic acid equivalent were extracted in hot 50% aqueous methanol and measured with the Folin-Denis method (Quarmby

and Allen, 1989). Ash-free dry weight was determined by ashing samples in a

muffle furnace at 550°C for 3 hours.

5.3.6 Statistical analysis

Analysis of variance and LSD values at the 5% level of significance were

computed using routines of the Statistical Analysis System (SAS Institute, 1985).

5.4 Results and discussion

5.4.1 Chemical composition of organic residues

Table 5.2 presents some chemical properties of the organic materials

used in the study. Hot-water soluble components as well as ash content are

higher in the animal manures than in the green manures. On the other hand,

lignin and hemicellulosic components are expectedly higher in the cowpea and

Table 5.2 Selected chemical components of the organic manures.

Chemical component (%)	Ch. manure	Cowpea	Leucaena	Sludge
Hot-H$_2$O solubles	36.1	17.0	21.1	29.6
Polyphenols	2.4	4.8	5.1	1.9
Hemicelluloses	16.7	24.5	27.6	16.3
Lignin	1.0	5.8	6.6	0.8
Ash	23.3	13.5	10.3	27.6
Carbon	21.4	47.4	46.2	10.9
C:N ratio	7.1	11.5	12.0	4.9

leucaena green manures because these complex compounds are major

components of most plant parts. The green manures had twice as much carbon

content as chicken manure and 4X as much as sludge, making their C:N ratios

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higher. Polyphenols expressed as tannic acid equivalence are also higher in the green manures than their animal manure counterparts.

5.4.2 Rate and pattern of nitrogen mineralization

Figures 5.1A and 5.1B show the amounts of N (as NO_3-N) mineralized from the organic manures in the two soils at bi-weekly intervals during the 24-week incubation period. Nitrogen mineralization from cowpea in the Kaneohe soil was characterized by a sharp increase in the amount of N released from the 2nd to the 4th week followed by a gradual decline up to the end of the incubation. Leucaena N was released steadily from the 2nd week up to the 12th week of incubation followed by a sharp decline in the amount of N released on the 14th and 16th week and then a steady release thereafter. Chicken manure N was continuously mineralized throughout the entire incubation period with the highest amounts observed on the first 6 weeks of incubation. Nitrogen release from sludge was almost linear from the start of incubation through the 8th week then declined gradually towards the end of the incubation period.

In the Paaloa soil, cowpea N mineralized steadily at a gradually declining rate from the 4th week and beyond. On the other hand, leucaena exhibited an almost linear increase in N mineralized in the first 6 weeks followed by gradually declining amount of N released thereafter. Chicken manure exhibited a sharp increase in the amount of N mineralized from the start of incubation up to the 8th week. This was then followed by a steady decrease in the amount of N released until the end of the incubation period. Sludge N was continuously released until

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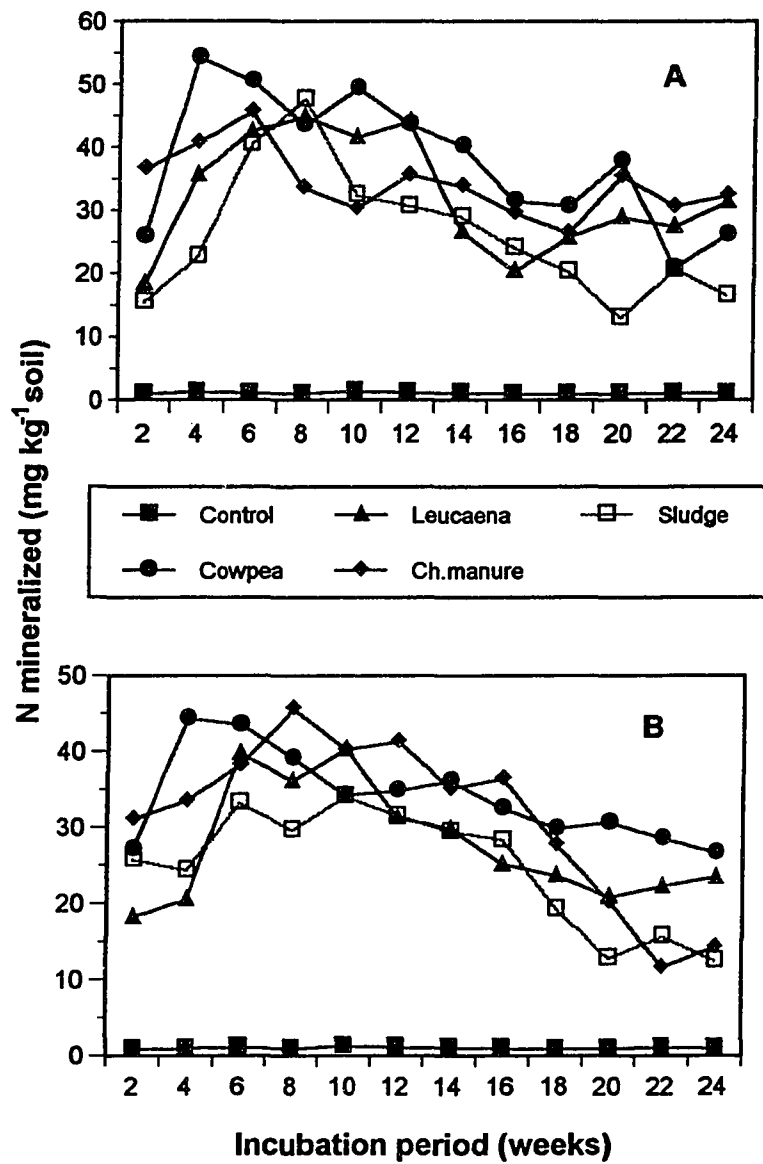
Fig. 5.1 Amounts of N mineralized bi-weekly in A) Kaneohe and B) Paaloa soil treated with organic residues in relation to incubation time.

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the 16th week and then decreased sharply thereafter. In agreement with the

findings of Chae and Tabatabai (1986), the patterns and amount of N

mineralized from the various organic residues were variable, depending on the

type of waste materials and the soil to which the residues were added.

Regardless of soil type, however, all organic manures exhibited net N

mineralization over their corresponding controls during the entire incubation

period.

The total amounts of N mineralized in the organic residue-treated soils

are presented in Table 5.3. In both soils, total N mineralized was highest in the

cowpea treatment and lowest in sludge. In terms of percent N released,

however, 65.1% to 72.8% of the organic N in chicken manure was mineralized

Table 5.3 Total amount of nitrogen mineralized from the organic manures after
24 weeks of incubation under laboratory conditions.

Organic residue	N mineralized in soil specified (mg/kg soil)			
	Kaneohe soil		Paaloa soil	
Control	11.6			12.4
Cowpea	417.4	(49.2)	477.4	(56.4)
Leucaena	330.1	(41.2)	410.6	(51.6)
Chicken manure	405.2	(65.1)	452.2	(72.8)
Sludge	278.1	(60.0)	288.6	(62.2)
LSD(0.05)	14.98	(1.65)	17.56	(1.66)

Figures in parentheses are the amounts of N mineralized in the organic manure treated
soils, expressed as percentage of the net amount of N per total N in the organic manure.

and is highest among all organic manures. The lowest proportion of N

mineralized was from the leucaena treatment which was 41.2% in the Kaneohe

and 51.6% in the Paaloa soil.

Sims (1985) reported that mineralization of organic N in an anaerobically digested sludge was 4 to 48% after 16 weeks of incubation. Parker and Sommers (1983) reported a lower range of 2 to 27% N mineralized in sludge at the same period of incubation. Frankenberger and Abdelmagid (1985) found that only 36% of the original N in cowpea foliage was mineralized after 20 weeks. In a study conducted in Nigeria, Leucaena released almost 25% of its original N after 7 weeks incubation (Tian et al., 1992). These wide differences in the percentage of N mineralized from organic materials are expected because of differences in incubation periods, incubation conditions (soil pH, temperature, moisture content, field versus laboratory) , and on the leaching procedures used by different researchers.

5.4.3 Relationship between nitrogen release rate and chemical composition of organic residues

Table 5.4 shows the calculated N release constants (k) of the different organic manures. The sludge treatment had the highest k value among all the organic manures while Leucaena had the lowest k value for both soils. The higher k values of the animal manures indicates that organic N in these materials are more rapidly mineralized compared to that in the green manures.

Nitrogen release is known to be strongly affected by the chemical composition of the organic residue (Muller et al., 1988). Castellanos and Pratt (1981) observed N release of about 48% from poultry manure (C:N=6.5)

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Table 5 .4 Rate constants for N release (k) of the different
organic manures added to the 2 soils.

Organic manure	Kaneohe	Paaloa
	<————————— week^{-1}—————————>	
Cowpea	0.034	0.028
Leucaena	0.029	0.024
Chicken manure	0.045	0.042
Sludge	0.051	0.046

incubated at 23 °C for 10 weeks. Fig. 5.2 shows a significant inverse linear

relationship between the C:N ratio of the organic manures and the N release rate

constant. Frankenberger and Abdelmagid (1985), and Iritani and Arnold (1960),

working on legumes and vegetable crop residues respectively, also reported

inverse relationships between percent N mineralized and increasing C:N ratio.

Franklin and Abdelmagid (1985) calculated that the critical C:N ratio for N

mineralization was <19, while Black (1968) reported a C:N ratio between 15 and

33. In the present study, the C:N ratios ranged from 4.9 to 12.0 which are far

below the critical C:N ratio reported in the literature. Thus, it is not surprising that

organic manures in this study showed net N mineralization in both soils.

The relatively lower percentage of N mineralized from the green manures

(41.2 % to 56.4 %) compared to the animal manures (60.0 % to 72.8 %) could be

partly explained by their high concentrations of lignin and polyphenolic

constituents (Table 5.5). Melillo et al. (1982) found that a high lignin

concentration reduced the decomposition rate of plant residues and could also

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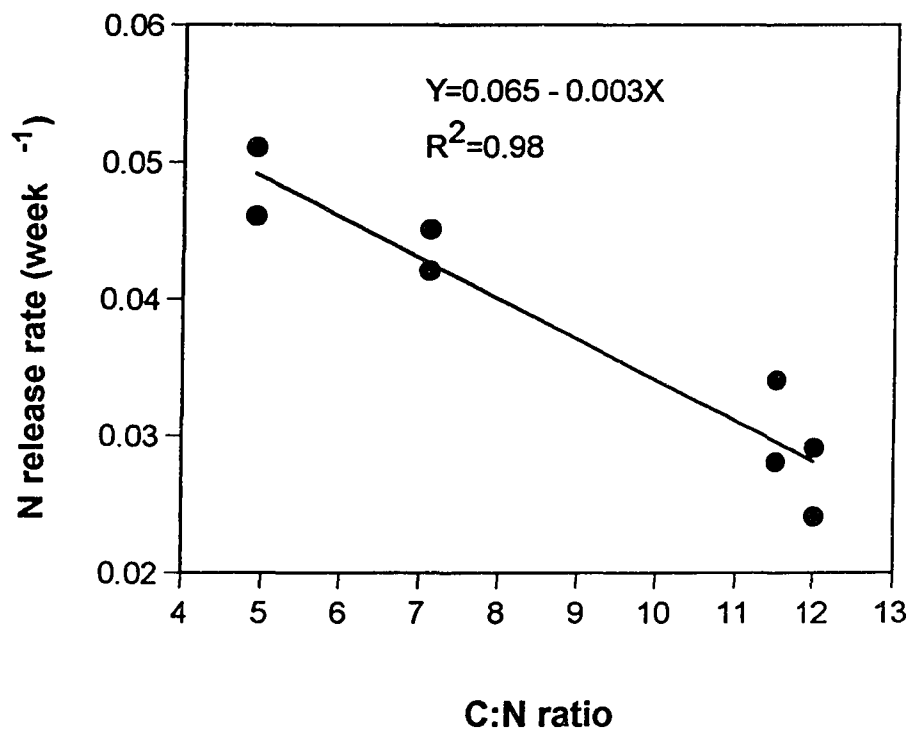
Fig. 5.2 Relationship between N release rate and C:N ratio of the organic manures.

Table 5 . 5 Percent N mineralized after 24 weeks of incubation, in relation to the nitrogen, lignin, and polyphenolic contents of the organic residues.

Organic manure	% N	% Lignin	% PP	% N mineralized in	
				Kaneohe	Paaloa
Cowpea	4.12	5.8	4.8	49.20	56.40
Leucaena	3.86	6.6	5.1	41.21	51.30
Chicken manure	3.02	1.0	2.4	65.12	72.83
Sludge	2.22	0.8	1.9	59.96	60.27

enhanced nutrient immobilization, especially of N. The negative effects of polyphenols on decomposition and nutrient release was reported by Vallis and Jones (1973). Sivapalan et al. (1985) observed that N mineralization was lowered by the presence of polyphenols due to the binding of mineralized N into an insoluble organic compound. Haynes (1986) believed that lignin and polyphenols reduces N release rate because these substances combine with protein and amino acids to form humic polymers that resist decay.

5.4.4 Calcium release

Figures 5.3A and 5.3B show the amounts of Ca released biweekly in the Paaloa and Kaneohe soils treated with organic residues. In the Kaneohe soil, chicken manure and sewage sludge exhibited similar patterns of Ca release, characterized by a gradually declining amount of Ca released from the start of incubation up to the 16th week followed by a steady release towards the end of the incubation period. In the Paaloa soil, the amount of Ca released from the chicken manure declined sharply from the start of incubation until the 8th week

Fig. 5.3 Net amounts of Ca released bi-weekly in A) Kaneohe
and B) Paaloa soil treated with organic residues in relation to
incubation time.

and then followed by a steady release up to the 24th week. Sludge Ca, on the

other hand, was released continuously from the start of incubation up to the 10th

week. After a sharp decline on the 12th week it then followed a release pattern

almost identical to that of chicken manure Ca towards the end of the incubation

period. Calcium from the green manures exhibited a gradual but steady release

during the entire incubation period in both soils.

The total amount of Ca released from each organic manure is presented

in Table 5.6. As expected, the animal manures released higher amounts of the

nutrient because of their higher Ca content compared to their green manure

counterparts.

Table 5.6   Total amount of Ca released from the organic residues after
24 weeks of incubation.

Organic residue	Ca released in soil specified (mg kg^{-1} soil)	
	Kaneohe soil	Paaloa soil
Cowpea	155.5 (40.4)	150.4 (38.6)
Leucaena	229.7 (50.3)	205.0 (44.4)
Ch. manure	1332.4 (45.7)	1499.1 (51.4)
Sludge	1654.8 (42.0)	1645.2 (41.7)
LSD(0.05)	53.5 (2.08)	55.8 (2.37)

Figures in parentheses are the percent of Ca released from the organic manure
treated soils, expressed as net amount of Ca per total Ca in organic manure.

Relative to their original Ca content, however, *Leucaena* had the highest

percentage (50.3%) of Ca released in the Kaneohe soil and chicken manure

(51.4%) in the Paaloa soil. Cowpea had the lowest percentage of Ca released in

both soils. The slow release rate of Ca in green manures may be explained by the role of Ca in plant tissues. In general, plant tissue Ca is not very mobile and tends to lag behind in senescent leaves. It is present as Ca-pectate in the middle lamellae of the cell wall. Another possibility is that Ca is stored as Ca oxalate crystals (Russell, 1988). In either form Ca would not be easily subjected to decomposition and release, especially by the limited soil faunal and microbial populations that prevailed in this study.

5.4.5 Magnesium release

In the Kaneohe soil, Mg from the organic residues was continuously released from the start of the incubation period up to the 12th week and then followed by a steady but smaller amounts of the nutrient released afterwards (Fig.5.4A). On the other hand, chicken manure and cowpea in the Paaloa soil released their Mg in a similar pattern characterized by a gradually declining amount of Mg released as the incubation progressed (Fig. 5.4B). Magnesium from sludge was released continuously at a gradually declining rate from the start until the end of the incubation period. Leucaena showed a variable pattern of Mg release until the 12th week of incubation then it was followed by a small but steady release of the nutrient towards the end.

Table 5.7 shows that the green manures released a significantly higher percentage of their original Mg content into the soil compared to the animal manures. Higher percentages of the Mg content of the organic residues were
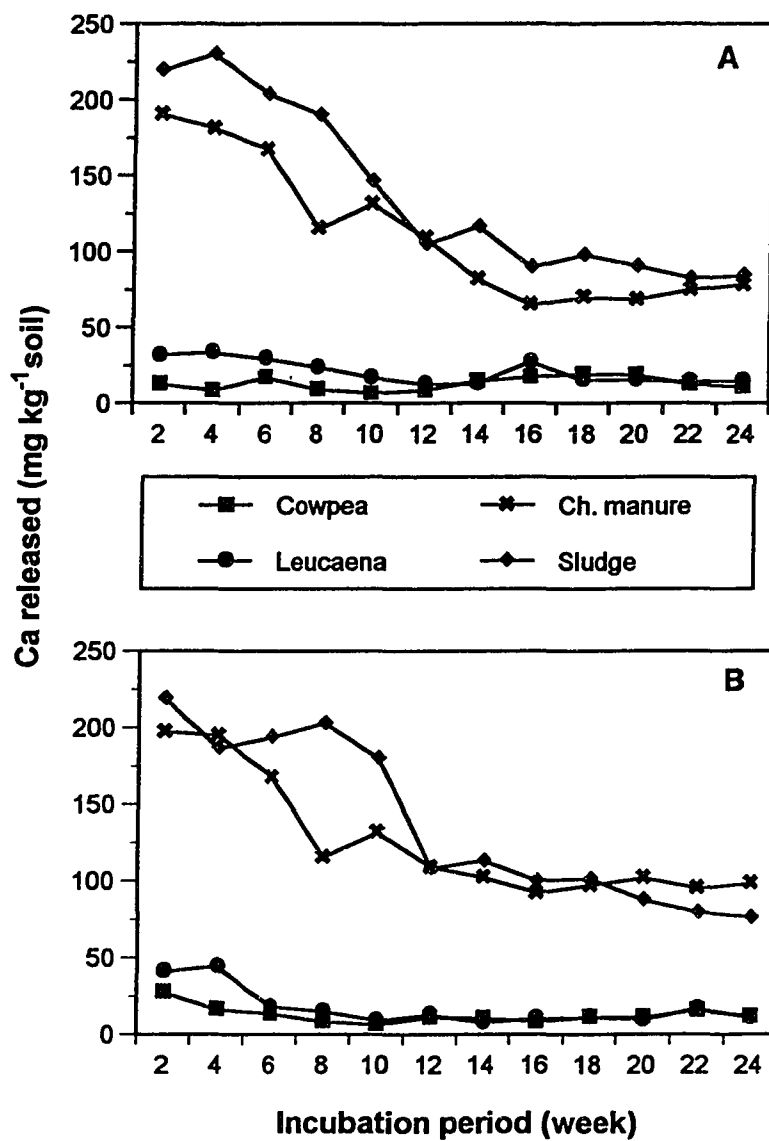
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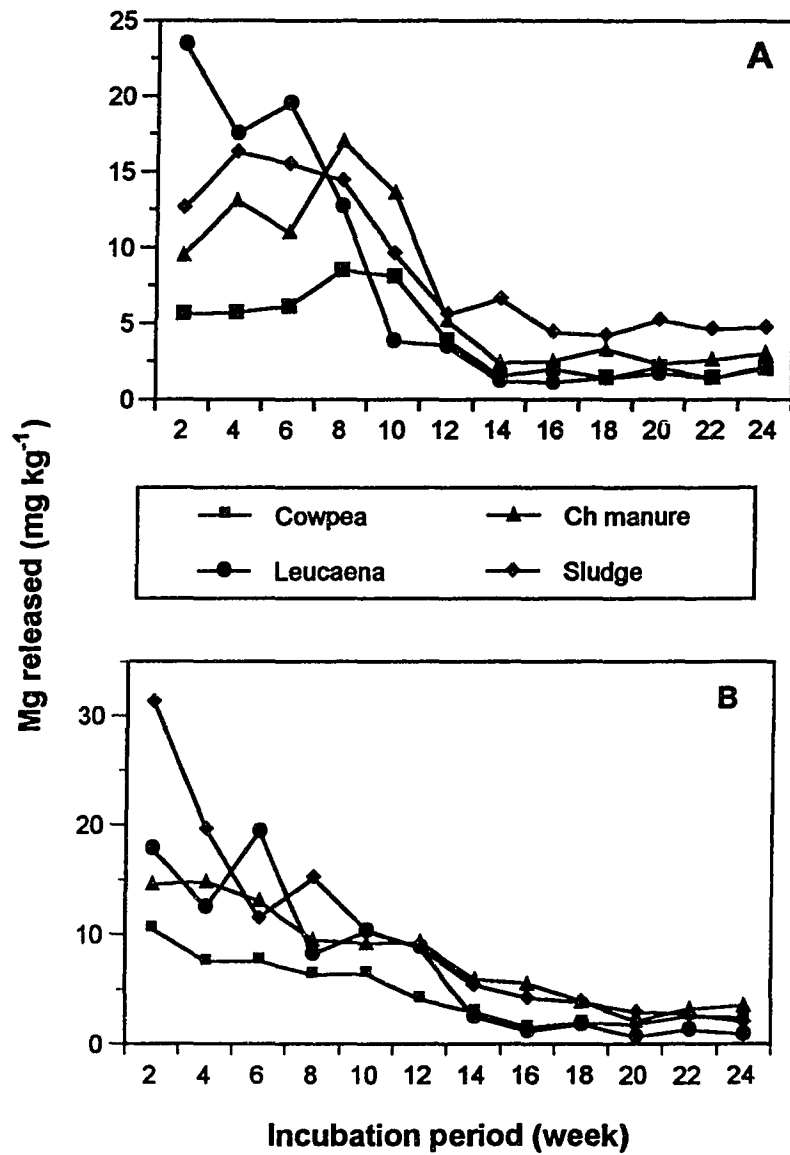
Fig. 5.4 Net amounts of Mg released bi-weekly in A) Kaneohe
and B) Paaloa soil treated with organic residues in relation to
incubation time.

released in the Paaloa soil than in the Kaneohe soil. Tian et al. (1992) and

Budelman (1988) reported fast release of Mg from plant residues. On the

Table 5.7   Total amount of Mg released from the organic residues after 24 weeks of incubation.

Organic residue	Mg mineralized in soil specified (mg/kg soil)	
	Kaneohe	Paaloa
Cowpea	48.0 (45.6)	55.6 (55.3)
Leucaena	79.2 (46.3)	85.4 (50.9)
Ch. manure	85.5 (39.6)	94.5 (44.6)
Sludge	103.7 (40.6)	117.8 (47.0)
LSD(0.05)	5.4 (3.6)	10.7 (7.15)

Figures in parentheses are the percent of Mg released in the organic manure treated soils, expressed as net amount of Mg per total Mg in organic manure.

contrary, Swift et al. (1981) showed a slow release of Mg. Although most plant

tissue Mg is present as a free cation, Mg is a constituent of complex structures

such as chlorophyll and pectins, and thus it may be released slowly from

decomposing organic materials.

5.4.6 Potassium release

Potassium present in cowpea, leucaena, and chicken manure was

released at a gradually declining rate while sludge K was released steadily

during the entire incubation period (Fig. 5.5A & 5.5B). This pattern of release

was observed in both soils. After 24 weeks of incubation, 74.9% and 79.2% of

K in the sludge was released in the Kaneohe and Paaloa soil, respectively.

Cowpea green manure released the least K relative to its K content. In a

decomposition and nutrient release study, using the litterbag method, Tian et al.
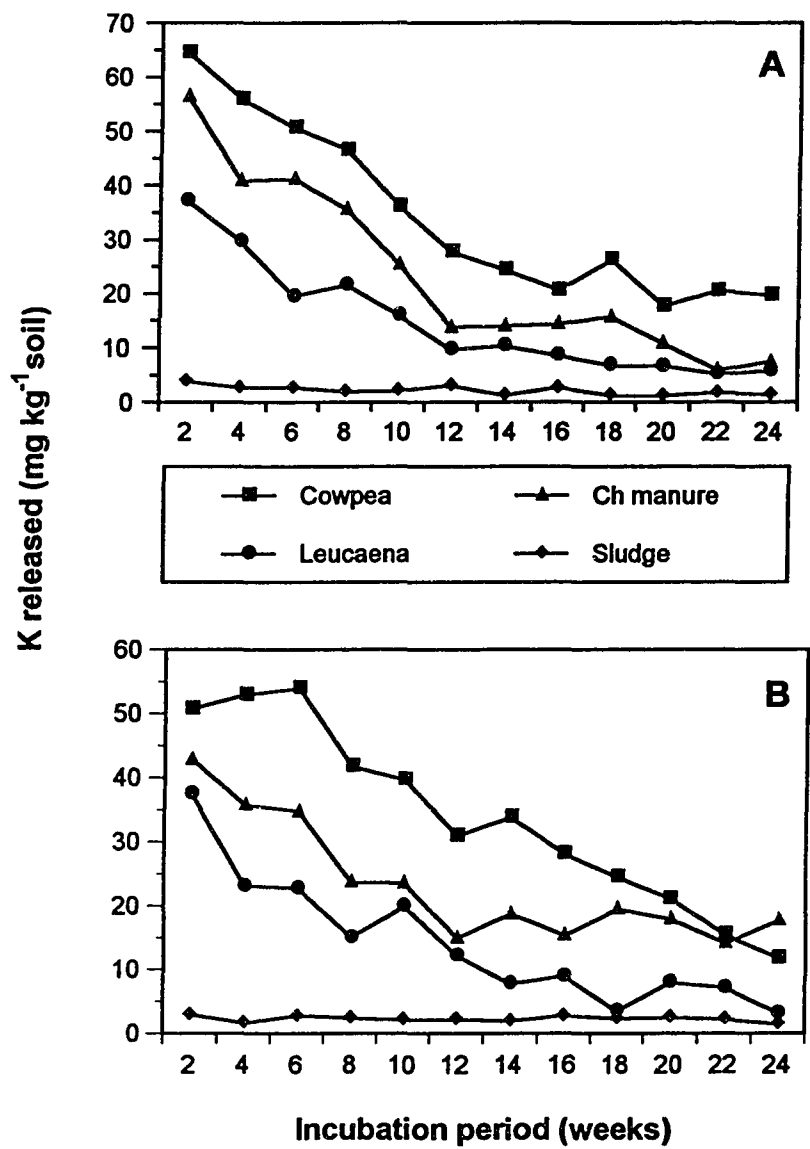
Fig. 5.5 Net amounts of K released bi-weekly in A) Kaneohe
and B) Paaloa soil treated with organic residues in relation to
incubation time.

(1992) observed that leucaena released most of its K after 98 days. Potassium

is present as a cation that freely moves in the cell fluid, taking part in the

synthesis of amino acids and proteins. When cell membranes disintegrate, K is

easily washed out of the organic material. Potassium has also been observed to

leach from living plant leaves (Jordan, 1985).

Table 5.8   Total amount of K released from the organic residues after 24 weeks of incubation.

Organic residue	K mineralized in soil specified (mg kg^{-1} soil)	
	Kaneohe soil	Paaloa soil
Cowpea	410.6 (60.9)	404.3 (60.1)
Leucaena	180.3 (66.7)	168.2 (62.2)
Ch. manure	281.4 (71.2)	278.4 (70.5)
Sludge	26.3 (74.9)	26.7 (79.2)
LSD(0.05)	15.9 (5.92)	11.5 (4.78)

Figures in parentheses are the percent of K mineralized in the organic manure treated soils, expressed as net amount of K per total K in the organic manure.

5.4.7 Effects of organic amendments on P sorption

Phosphorus sorption isotherms as affected by the organic amendments

after a 3-week and 9-week incubation period are presented in Figures 5.6 and

5.7, respectively. The amount of P sorbed decreased in all organically amended

soils as compared to the unamended soil. This effect was observed at all levels

of applied P. Chicken manure caused the greatest reduction in P sorption

especially at the higher levels of P applied. Leucaena was least effective in

reducing P sorption.

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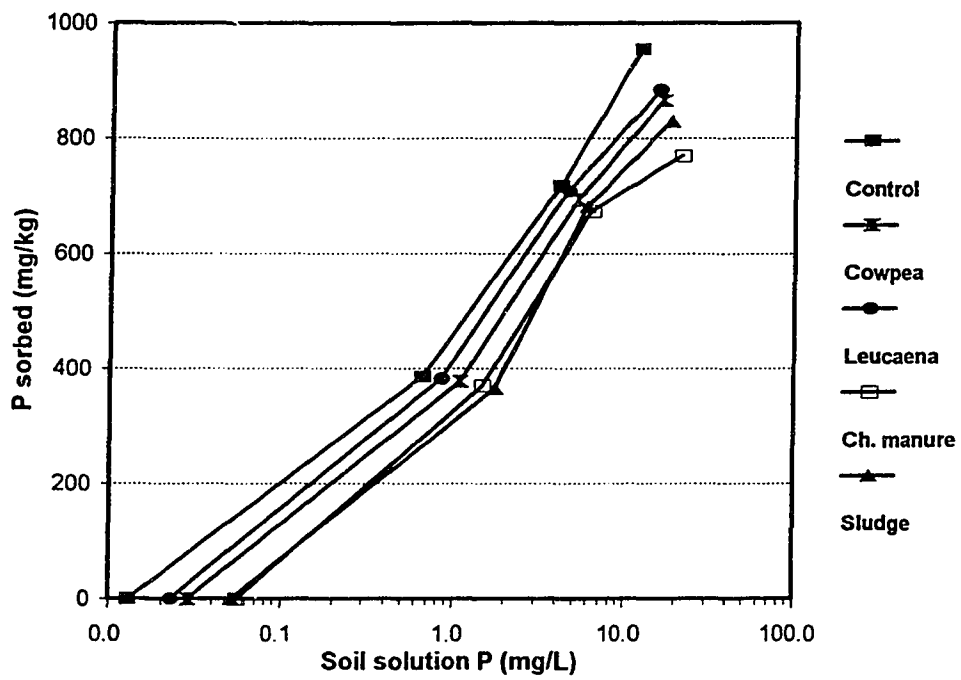
Fig. 5.6   Effects of organic amendments (20 g kg⁻¹)
on P sorption in the Paaloa soil after 3 weeks of incubation.

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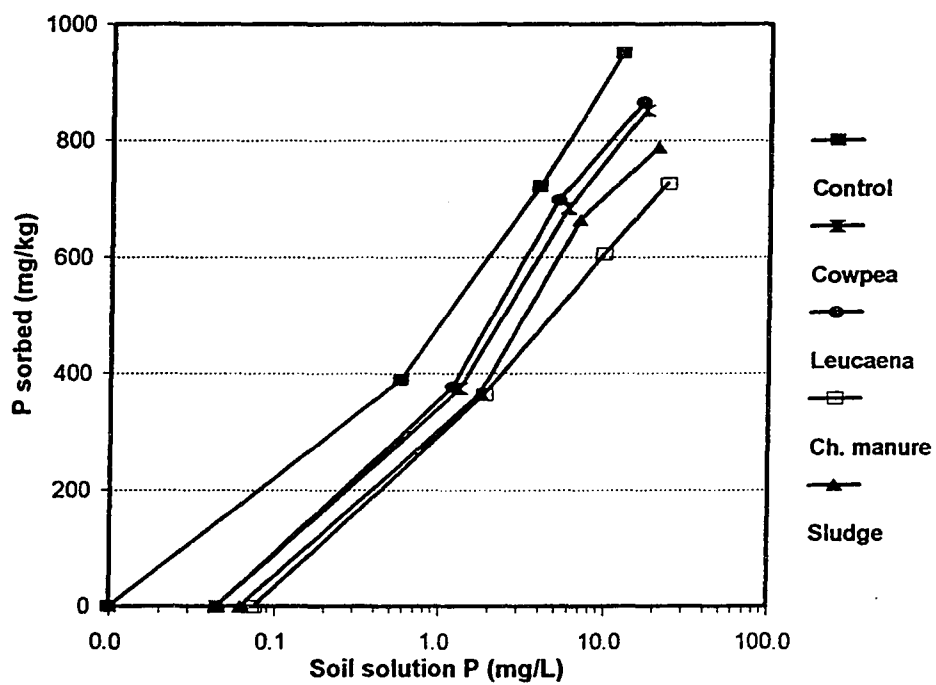
Fig. 5.7 Effects of organic amendments (20 g kg⁻¹)
on P sorption in the Paaloa soil after 9 weeks of incubation.

The concentration of 0.20 mg P L^{-1} is often considered as the critical value

of P in solution for optimum growth of many plants (Fox and Kamprath, 1970).

Using this P concentration as a reference, it can be seen that after 3 weeks of

incubation, the amounts of P sorbed in soils amended with chicken manure,

sludge, cowpea, leucaena, and the control were 130, 140, 195, 220, and 260 mg

kg^{-1} soil, respectively. The corresponding amount of P sorbed in these

treatments decreased to 100, 120, 155, and 165 mg kg^{-1} in the organically

amended soils and increased to 280 mg kg^{-1} soil in the control after 9 weeks of

incubation (Fig. 5.7). The higher concentration of P in solution in the organically

amended soils might be due to release of P from the organic residues as they

decompose in the soil. Hundal et al. (1988) working with a sandy loam soil

under flooded conditions observed a significant reduction in sorbed P with green

manure amended soils. Singh and Jones (1976) reported that organic residues

which contained < 0.3% P, decreased labile P and increased P sorption by soil,

whereas materials that contained P in excess of 0.3% decreased P sorption. In

the present study, only leucaena had a P content less than 0.3% (Table 5.2).

A P sorption study by Scherer and Werner (1992) showed that the

concentration of water soluble P was higher in triple superphosphate (TSP)

combined with farmyard manure (FYM) than that of TSP application alone.

According to these authors, larger amounts of dissolved organic carbon in the

application band of TSP/FYM treatment decreased P adsorption capacity of the

soil. Soil solution analysis results reported in Chapter 4 (Table 4.9) showed that

dissolved organic carbon concentrations in the organically amended soils were significantly higher than in the control. Organic substances produced during the decomposition of organic residues applied to soils could decrease P sorption by either forming stable complexes with Al and Fe, thus eliminating retention sites for P (Sah and Mikkelsen, 1989) or by blocking sorption sites for P through sorption of organic anions. Citrate and oxalate have been shown to decrease P adsorption (He et al., 1990; Kafkafi et al., 1988). Hue (1991) stated that organic acids can be adsorbed by clay minerals, thus competing for P sorption sites. Similar effects have also been observed by other researchers (Sah and Mikkelsen 1986; Singh and Jones, 1976). Consequently, the efficiency of P fertilizers could be increased if they are applied together with organic manures.

5.4.8 Effect of organic amendments on soil extractable (Olsen) P

Phosphorus in acid soils could be tightly adsorbed on the surfaces of Fe- and Al-oxides thus making them unavailable for plant uptake. Previous research has shown that an increase in soil organic matter by organic residue application can minimize P sorption. Table 5.9 shows levels of extractable P in the Paaloa soil after 3, 6, and 9 weeks following organic amendments. Soil extractable P was increased significantly by the organic amendments. Similar to the ability of organic amendments to reduce P sorption, chicken manure increased the level of Olsen P most effectively, while leucaena was the least effective. For example, after 9 weeks of incubation, extractable P was 7.0 mg P kg^{-1} in the

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control and increased significantly to 19.33 and 15.85 mg P kg^{-1} in the chicken

manure and leucaena treatments, respectively.

Yadvinder-Singh et al. (1988) observed that 15% of poultry manure P

was mineralized during the 1st week of incubation in a calcareous sandy loam

under field capacity. The largest amount of Olsen P was observed in soils

Table 5.9   Changes in extractable P (mg kg^{-1}) of the Paaloa soil as affected
by organic amendments and period of incubation.

Treatments	Incubation period (weeks)		
	3	6	9
Control	7.0	7.2	7.0
Cowpea	13.5	16.6	17.0
Leucaena	14.6	15.7	15.8
Ch. manure	18.5	18.9	19.3
Sludge	15.9	16.2	17.2
LSD(0.05)	2.1	1.6	1.1

amended with poultry manure, cattle manure, green manure, and crop residues

in that order. Water soluble P and Olsen P were also found to increase

significantly with the addition of farmyard manure to phosphate fertilizers in a

paddy Ultisol from China (Yang et al., 1994). Thangudu et al. (1981) likewise

reported that available P of an acid soil significantly increased after organic

amendments.

In this study, the increase in P could have also been contributed at least

partially by P from the organic residues themselves. Chicken manure and

sludge contained 2.29% P and 1.69% P, respectively, which are much higher

than the 0.39% P in cowpea and 0.14% P in leucaena. Bumaya and Naylor

(1988), working on a high P-sorbing Andept soil incubated with winter wheat and red clover for 12 weeks, observed an increase in NaAOc-extractable P and a decrease in P sorption when the P content of the plant residues exceeded 0.1%P.

Table 5.10 shows that soil pH has been significantly increased by the application of organic residues. Soil pH also showed a gradual increase as the incubation period progressed.

Table 5.10   Soil pH as affected by organic amendments and incubation period.

Organic manure	Incubation period (weeks)		
	3	6	9
Control	4.18	4.37	4.38
Cowpea	4.70	5.03	5.53
Leucaena	4.57	4.70	4.66
Ch. manure	6.52	6.68	6.78
Sludge	6.45	6.75	7.05
LSD(0.05)	0.17	0.10	0.22

Since P adsorption and desorption by soil clays are highly dependent on pH (He et al., 1990; Nanzyo and Watanabe, 1981), enhanced effects of the organic amendments on P sorption and extractable P may also be related, to some extent, to pH changes in the organically amended soils.

5.5 Summary and conclusions

Both economic and environmental concerns have led to a renewed

interest in the use of organic residues as sources of N and other plant nutrients

in agricultural systems. However, in order to optimize their use as supplemental

fertilizers, their mineralization rate when incorporated into soils needs to be

determined.

Chicken manure, sludge, cowpea and leucaena were incubated for 24

weeks in an acid Ultisol and the mineralization of N and the release of Ca, Mg,

and K were monitored. Results of the study indicated that all the organic

manures showed net N mineralization. Nitrogen in the animal manures was

mineralized faster than in the green manures. Possible reasons for the slower

rate of N mineralization in the green manures could be the higher C:N ratio and

higher concentrations of lignin and polyphenols in leucaena and cowpea.

Potassium was more easily released from the organic manures than Ca and Mg.

The gradual and steady release of nutrients in the decomposing organic

materials suggests that they could be successfully used as supplements to

inorganic fertilizers in supplying nutrients to growing crops.

Organic amendments also effectively reduced P sorption and increased

extractable P. Reduced P sorption may be due to the production of organic

anions during the decomposition of the added organic residues which could

block sorption sites for P. Increased levels of extractable P in the organically

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amended soils may be a direct contribution from the P content of the organic

residues themselves.

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CHAPTER 6

Amelioration of subsoil acidity through surface application

of animal manures

6.1 Abstract

Correcting subsoil acidity requires a decrease in Al concentration along with an increase in Ca in the subsoil. Applications of $CaCO_3$, although effective in correcting surface soil acidity have little effect on subsoil acidity because of its slow downward movement. Surface application of organic residues to acid soils may be an economical alternative. A greenhouse column leaching study was conducted to compare the effects of chicken manure and sewage sludge with gypsum ($CaSO_4.2H_2O$) and lime ($CaCO_3$), surface applied, on reducing subsoil acidity and increasing subsoil Ca concentration in an acidic Paaloa soil (Rhodic Kandiudult). Leaching with the different amendments was done by applying 37.85 cm (1000 mL) of water in 5 days. The soil columns were then cut into 4 equal segments and chemically analyzed.

Results of soil and soil solution analysis showed that surface-applied animal manures can be used successfully to correct subsoil acidity. In terms of increasing soil solution pH, soluble Ca, and decreasing soil solution Al and percent Al saturation in the subsoil, the animal manures were more effective than lime and gypsum, particularly below the 15-cm depth. Soil solution Al and percent Al saturation were reduced more by animal manures than by lime and gypsum at all soil depths. Lime significantly increased soil solution and

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exchangeable Ca concentration only at the 5-15 cm depth while gypsum

effectively moved Ca down the whole soil profile.   Soluble C concentration in the

soil solution was also higher in the animal manure treatments than in the

unamended and inorganically amended soils. The production of organic anions

as the animal manures decomposed may have facilitated the downward

movement of Ca as they form Ca chelates which could move freely down the soil

profile.

6.2 Introduction

Subsoil acidity is a major problem particularly in highly weathered tropical

soils. Poor crop performance is often attributed to excess Al and/or insufficient

Ca in the subsoil. To improve crop yields, lime application is necessary. Liming

is adequate to raise soil pH and neutralize exchangeable Al in the topsoil, but

subsoil acidity remains unaffected. Surface applied lime moves very slowly

down the soil profile, thus has little effect on subsoil Al (Pavan et al., 1982;

Ritchey et al., 1980). Deep incorporation of lime is recommended for best

results (Farina and Channon, 1988; Anderson and Hendrick, 1983) but is difficult

and expensive (Cassel, 1980; Adams et al., 1967). Several studies have shown

that gypsum and phosphogypsum may be used effectively as subsoil acidity

amendments (O'Brien and Sumner, 1988; Matthews and Joost, 1990;

Shamshuddin et al., 1991). Since gypsum does not alter soil pH appreciably,

pH-dependent charge remains unchanged, enabling gypsum to move through

the soil much faster than lime (McCray and Sumner, 1990). Improved crop performance on acid soils with surface-applied gypsum has been attributed to increased exchangeable Ca, decreased exchangeable Al, and increased root density in the subsoil (Farina and Channon, 1988b; Sumner et al., 1986).

Another approach to the amelioration of acid subsoils is the incorporation of organic materials into the soil which may provide chelating ligands for the detoxification of Al (Hue and Amien, 1989; Hue, 1992). Chelation may be a means of mobilizing soil Al and removing it from the root zone. Hern et al. (1982), showed that using EDTA, a synthetic chelating agent, Al was mobilized to a depth of 60 cm in leached soil columns. Wright et al. (1985) also obtained maximum root growth and rooting depth with animal manure treatments. Higher reductions in exchangeable Al and increases in pH were obtained with farmyard manure alone, or in combination with lime, in a field experiment conducted on an acid Alfisol in Zambia (Lungu et al., 1993).

The objective of this study was to evaluate the potential for using surface-applied animal manures as subsoil acidity amendments and to compare their effects with those of gypsum ($CaSO_4.2H_2O$) and lime ($CaCO_3$).

6.3 Materials and methods

6.3.1 Leaching experiment

The soil used in the study was an acidic Ultisol (Rhodic Kandiudult, Paaloa series) with an original pH of 4.45 and KCl-extractable Al of 2.78 $cmol_c$ kg^{-1}. Soil samples were collected from a depth of 40-60 cm.

Soil columns were constructed from rigid polyvinyl chloride (PVC) columns, 50-cm long and 5.8-cm inside diameter. The columns were lined with hard plastic material to allow easy removal of the soil after the leaching experiment. The bottom end was supported with a nylon net which was lined with a 2-mm layer of acid-washed silica sand above a thin layer of glass wool. Each column was packed with 1.5 kg of moist soil (250 g H_2O kg^{-1} dry soil).

The experimental treatments consisted of:

1. Deionized water (control);

2. Lime ($CaCO_3$) at 2.78 g kg^{-1} soil equivalent to 2X the KCl-Al of the unamended soil.

3. Gypsum ($CaSO_4 \cdot 2H_2O$) at 4.80 g kg^{-1} soil which provided the same amount of Ca as the lime treatment.

4. Chicken manure at 20 g kg^{-1} dry soil;

5. Sewage sludge at 20 g kg^{-1} dry soil.

The chicken manure analyzed 3.12% N, 1.89% P, 2.02% K, 1.63% Ca and 0.65% Mg on a dry-weight basis. On the other hand, the sewage sludge (collected from the Kaneohe wastewater treatment plant) contained 4.36% N, 0.65% P, 0.08% K, 2.06% Ca and 0.54% Mg.

The different treatments were carefully mixed with 150 g of soil and placed on the top 5-cm section of the column. After packing, each column was slowly leached with 1.5 L of deionized water to remove free salts. The columns

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were then arranged inside the greenhouse in a completely randomized design with three replications per treatment.

Leaching was done by carefully adding 200 mL of deionized water to the surface of the soil column which was covered with a thin layer of glass wool to aid in the dispersion. Deionized water was applied carefully to avoid ponding on the surface (50 mL/30 min) and was continued until all 200 mL was added. The columns were then covered with parafilm and allowed to drain overnight. Leachate was collected in a plastic cup placed under each column. The leaching process was done for 5 consecutive days until a total of 1.0 L (equivalent "rainfall" of 37.85 cm) had been added. After leaching was completed, the plastic lining containing the soil column was carefully removed from the PVC casing. The top and bottom 5-cm segments of the column were discarded and the remaining soil column was cut into four 10-cm long segments. The soil segments were then air-dried and ground to pass a 1-mm sieve prior to soil and soil solution analyses.

6.3.2 Soil chemical characterization

Soil solutions were obtained by centrifugation of approximately 200 g of the moist soil at field water holding capacity (Adams et al., 1980). Immediately after collection, pH of the soil solution was measured in order to minimize errors due to CO_2 loss. The soil solution was then stored at 4°C for analyses of soluble C, Al, Ca and Mg. Aluminum in solution was measured colorimetrically by the pyrocatechol method (Kerven et al., 1989). Soluble C was analyzed by the Mn-

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pyrophosphate method (Bartlett and Ross, 1988). The concentrations of soluble

Ca and Mg were determined by atomic absorption spectrometry.

Soil pH measurements were made in water following a 30 min

equilibration of a 1:1 soil/liquid suspension. Aluminum was extracted with $1M$

KCl using a 1:10 soil-to-solution ratio and 30 min shaking and then measured

colorimetrically by the pyrocatechol violet method. Exchangeable Ca, Mg, K,

and Na were extracted with $1M$ NH_4OAc at pH 7.0 using the same soil-to-

solution ratio and extraction time as Al and concentrations were measured by

atomic absorption spectrometry. The leachate was also analyzed for solution Al,

Ca, Mg, K, Na, and soluble C following the same methods used for soil solution

analysis.

6.3.3 Statistical analysis

Statistical analysis consisted of analysis of variance and LSD test at the

5% level of significance for mean separation among treatments at different soil

column depths using SAS procedures (SAS Institute, 1985).

6.4 Results and discussion

6.4.1 Soil solution pH

Soil solution pH of the control remained basically the same regardless of

soil depth (Table 6.1). Liming effectively raised soil solution pH at 5-25 cm

depth, but below this depth however, the increase over the control was not

significant. By contrast, gypsum application caused a slight but insignificant

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decrease in soil solution pH at the 15-25 cm depth compared to the control.

Decreases in soil pH after gypsum application have also been reported by Black

and Cameron (1984) and Mathews and Joost (1990). Black and Cameron

(1984) explained the decrease in pH after gypsum application resulted from an

increase in soluble salts which displaced Al^{3+}/H^+ into the soil solution. In general,

however, subsoil pH changes from gypsum application have been inconsistent

and are not a reliable indication of a favorable gypsum response (McCray and

Sumner, 1990).

Table 6.1 Effect of surface application of $CaSO_4.2H_2O$, $CaCO_3$, chicken manure and sewage sludge on soil solution pH of an acidic Paaloa subsoil following leaching with 37.85 cm of H_2O for 5 days.

	Soil column depth (cm)			
Amendment	5-15	15-25	25-35	35-45
	<----------------------- pH---------------------->			
Control	4.36	4.40	4.44	4.41
$CaSO_4.2H_2O$	4.37	4.34	4.38	4.38
Lime-2X	5.81	4.82	4.55	4.42
Ch. manure	6.40	5.85	5.12	4.89
Sludge	5.81	5.66	4.62	4.60
LSD(0.05)	0.17	0.15	0.14	0.14

Surface application of chicken manure and sewage sludge dramatically

increased soil solution pH over the control at all soil depths. In fact, pH increase

in the chicken manure treatment was significantly higher than lime and gypsum

at all soil depths. At the 5 to 15 cm layer, the sewage sludge treatment had the

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same soil solution pH as the lime treatment. Below the 15 cm depth, sludge-treated soil had significantly higher pH than the limed soil.

6.4.2 Soil solution Al concentration

Table 6.2 shows the concentration of soil solution Al at various soil depths. Compared to their corresponding controls, lime application effectively reduced the concentration of Al to only 12% of original levels at 5 to15 cm and 60% at the 15 to 25 cm depth. In the case of gypsum, soil solution Al concentrations were slightly lower than the control from the 15 to 25 cm depth.

Table 6.2 Effect of surface application of $CaSO_4.2H_2O$, $CaCO_3$, chicken manure and sewage sludge on soil solution Al of Paaloa subsoil following leaching with 37.85 cm of H_2O for 5 days.

Amendment	Soil column depth (cm)			
	5-15	15-25	25-35	35-45
	<———————— Soluble Al (μM)————————————>			
Control	60.1	60.4	50.4	63.6
$CaSO_4.2H_2O$	59.5	56.2	60.9	53.6
Lime-2X	7.3	36.2	60.7	56.8
Ch. manure	0.01	7.3	10.3	48.7
Sludge	4.3	20.2	28.1	19.3
LSD(0.05)	7.2	7.4	8.5	7.3

Ismail et al. (1993), working with a Malaysian Ultisol, reported both an increase and a decrease of soluble Al concentration over the control with gypsum application. They stated, however, that an increase in soluble Al concentration does not necessarily indicate an increased Al phytotoxicity

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because of the formation of $AlSO_4^+$ complex which is considered non-toxic

(Pavan et al., 1982; Kinraide and Parker, 1987; Sumner et al., 1986). Alva and

Sumner (1988) using solutions containing 40 μM Al amended with

phosphogypsum and gypsum have shown that in the pH range of 4.1to 4.8, up to

62% of the total Al was complexed with SO_4^{2-}. They hypothesized that at pH

< 4.8, ion-pairing is mainly responsible for the alleviation of Al toxicity by gypsum.

Solution Al^{3+} concentration may actually be increased with gypsum application,

but due to increased ionic strength and formation of $AlSO_4^+$ ion pairs (Pavan et

al., 1982; Singh, 1982), Al^{3+} activity is often reduced.

The increase in soil solution pH from the application of chicken manure

and sewage sludge resulted in substantial reductions of soil solution Al

concentration . In fact, the concentrations of soluble Al in the organically

amended soils are significantly lower than the limed soil across all soil depths.

This observation clearly indicates the efficiency of the organic manures over their

inorganic counterparts in correcting subsoil Al toxicity.

6.4.3 Calcium concentration in solution

The response of soluble Ca concentration to the application of the various

organic and inorganic amendments is presented in Table 6.3. Soluble Ca

concentration in the top 5 to 15 cm layer of the limed soil increased dramatically

over the control. Below this depth, however, soluble Ca concentration is not

significantly different from the control.

Table 6.3 Effect of surface application of $CaSO_4.2H_2O$, $CaCO_3$, chicken manure and sewage sludge on soil solution Ca of an acidic Paaloa subsoil following leaching with 37.85 cm of H_2O for 5 days.

Amendment	Soil column depth (cm)			
	5-15	15-25	25-35	35-45
	<------------------ Soluble Ca (mM)------------------>			
Control	0.09	0.09	0.04	0.02
$CaSO_4.2H_2O$	7.58	5.31	1.86	0.37
Lime-2X	2.60	0.53	0.17	0.08
Ch. manure	3.97	1.98	0.95	0.19
Sludge	3.08	1.73	0.54	0.08
LSD(0.05)	0.55	0.60	0.22	0.09

Surface application of gypsum increased Ca in solution more than twice that observed in the lime treatment at the same 5 to15 cm soil depth. With the same amount of initial Ca applied at the start of the leaching process, this observation clearly indicates that Ca in gypsum is relatively more soluble than that present in lime. In fact, solution Ca concentration remained significantly higher over that of lime across all soil depths. Also noteworthy were the increases in solution Ca concentration resulting from the application of chicken manure and sludge. Except at the lowest depth of 35 to 45 cm in the sludge treatment, solution Ca concentration in the organically amended soils was significantly higher than the limed soil across all soil depths.

6.4.4 Magnesium concentration in solution

Across all soil depths soil solution concentrations of Mg in the control and lime treatments were not significantly different (Table 6.4). In the case of

gypsum, Mg in solution increased significantly over that of the control down to the 35 cm depth. Soil solution Mg is also significantly higher in the organically amended soils except for the sludge treatment at the lowest soil depth (35-45 cm). The increase in soil solution Mg concentration in the organically amended soils could have come from Mg in the organic materials which became soluble as a result of leaching with water. Chicken manure and sewage sludge contained 0.98 % and 1.18 % Mg, respectively. This effect would be an added benefit for organic manures as acid soil amendments because of the essential nutrients they release as they decompose in the soil.

Table 6.4 Effect of surface application of $CaSO_4.2H_2O$, $CaCO_3$, chicken manure and sewage sludge on soil solution Mg of an acidic Paaloa subsoil following leaching with 37.85 cm of H_2O for 5 days.

Amendment	Soil column depth (cm)			
	5-15	15-25	25-35	35-45
	<------------- Soluble Mg (mM)------------->			
Control	0.05	0.06	0.04	0.04
$CaSO_4.2H_2O$	0.17	0.49	0.42	0.07
Lime-2X	0.10	0.07	0.07	0.05
Ch. manure	0.75	0.39	0.44	0.72
Sludge	0.59	0.73	0.60	0.11
LSD(0.05)	0.06	0.19	0.18	0.09

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6.4.5 Soluble carbon concentration

In order to test the hypothesis that organic anions in solution could facilitate the downward movement of Ca in the soil profile, the concentration of soluble C was measured (Table 6.5). Dissolved organic carbon represents a variety of organic compounds in the soil solution which range from low molecular weight organic acids to complex molecules such as fulvic and humic acids (Thurman, 1985).

The concentrations of soluble C remained essentially the same across all soil depths in the lime treatment and were not significantly different from those of the control, except at the top 5 to 15 cm. On the other hand, $CaSO_4.2H_2O$ application led to a gradual increase in soluble C concentration as soil depth increased.

Table 6.5 Effect of surface application of $CaSO_4.2H_2O$, $CaCO_3$, chicken manure and sewage sludge on soluble C concentration of an acidic Paaloa subsoil following leaching with 37.85 cm of H_2O for 5 days.

Amendment	Soil column depth (cm)			
	5-15	15-25	25-35	35-45
	<————————— Soluble C (mM)————————>			
Control	1.93	2.62	2.20	2.23
$CaSO_4.2H_2O$	2.62	2.67	2.73	3.11
Lime-2X	2.52	2.63	2.68	2.59
Ch. manure	8.58	7.93	7.68	6.27
Sludge	7.04	6.82	5.12	5.37
LSD(0.05)	0.33	0.50	0.53	0.42

Surface application of organic amendments resulted in dramatic increases

of soluble C concentration at all soil depths. Even at 35 to 45 cm depth, the

concentrations of 5.37 mM for sludge and 6.27 mM for chicken manure were

approximately 2 to 3 times higher than the control and inorganic amendments.

Tan et al. (1985) using infrared analysis showed that Ca mobilization from a

sludge-lime combination applied to a Georgia Ultisol was facilitated by the

formation of Ca-chelates formed from the interaction of lime and fulvic acid

produced by the sludge. Organic acids produced by the decomposition of

organic waste also have a strong chelation effect on Ca and other cations

(Sposito et al., 1978) and may cause Ca and Mg to remain soluble and move

freely down the soil profile (DeConinck, 1980; Tan, 1978).

6.4.6   Exchangeable Ca concentration

Figure 6.1 shows exchangeable Ca at different depths as a result of

surface application of the various amendments. In the water treatment,

exchangeable Ca was 0.14 cmol$_c$ kg^{-1} at the 5 to 15 cm depth and remained

basically unchanged from 0.20 to 0.25 cmol$_c$ kg^{-1} at lower depths. Gypsum

application increased exchangeable Ca to 10.74 cmol$_c$ kg^{-1} at 5 to 15 cm and

5.63 cmol$_c$ kg^{-1} at 15 to 25 cm. Exchangeable Ca in the gypsum treated soil is

the highest among all treatments at all soil depths. Downward movement of Ca

from surface application of lime occurred only to a limited soil depth. A quick

calculation shows that approximately 67% of the original Ca in lime stayed at the

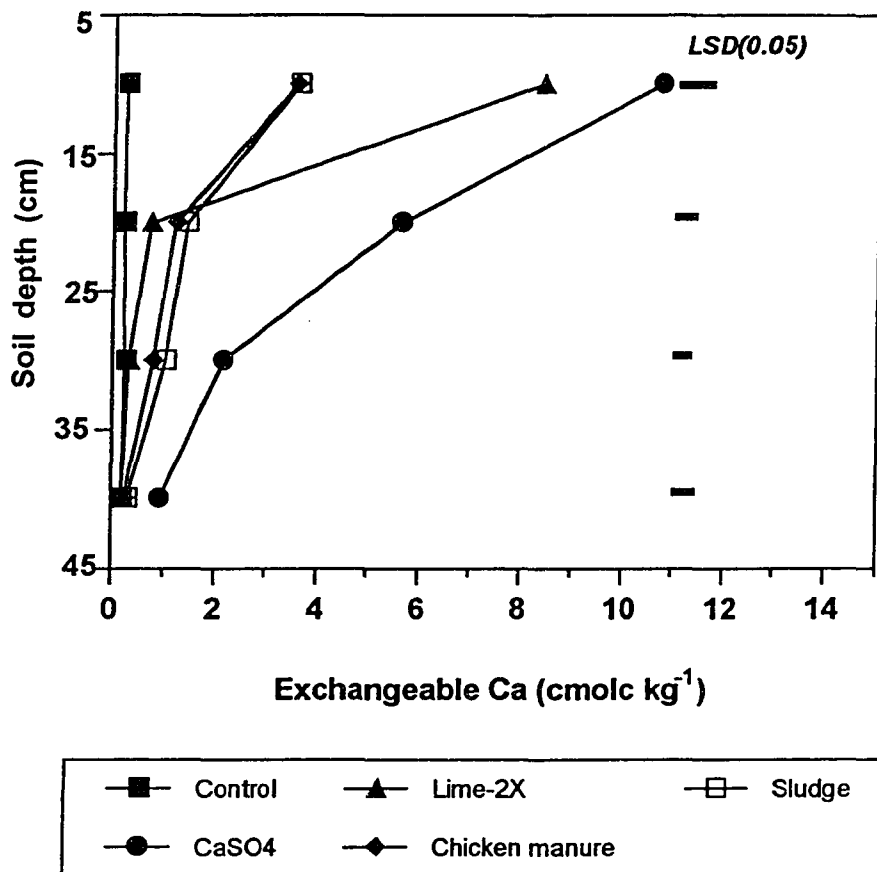0 to 5 cm of incorporation and only 33% moved down below that depth

Fig. 6.1 Exchangeable Ca concentration at different soil depth as affected by the different amendments.

(Figure 6.2). Furthermore, almost all (94%) of the Ca that leached beyond the depth of incorporation (31% of the original) remained at the 5 to 15 cm layer. This relatively slow movement of lime indicates that Ca cannot move down freely unless accompanied by an equivalent anion (Pearson and Abruna, 1961).

On the other hand, Ca from gypsum moved down the soil column much faster than lime. Approximately 70 % of the original Ca applied moved below the depth of incorporation with 40% and 20% found at 5 to15 cm and 15 to 25 cm depths, respectively.

Also worth noting was the movement of Ca from the applied chicken manure and sewage sludge. Almost 63% of the Ca in chicken manure and 55 % in sludge were mobilized below the depth of incorporation.

Tan et al. (1985), showed that a combination of sludge and lime effectively moved Ca down to the subsoil. They believed that fulvic and humic acids formed from the decomposition of sludge chelated Ca to form organic chelates which facilitated the downward movement of Ca in the soil.

6.4.7 KCl-extractable Al and Al saturation

Exchangeable Al in the control was basically unaffected at all soil depths with concentrations ranging from 2.67 to 2.75 $cmol_c kg^{-1}$. (Figure 6.3). Surface application of lime effectively reduced Al to only 0.42 $cmol_c kg^{-1}$ in the 5 to15 cm layer which is just below the depth of lime incorporation. At the 15 to 25 cm depth, the effectiveness of lime was greatly diminished as concentration of Al increased to 2.12 $cmol_c kg^{-1}$ albeit significantly lower than the 2.83 $cmol_c kg^{-1}$ of
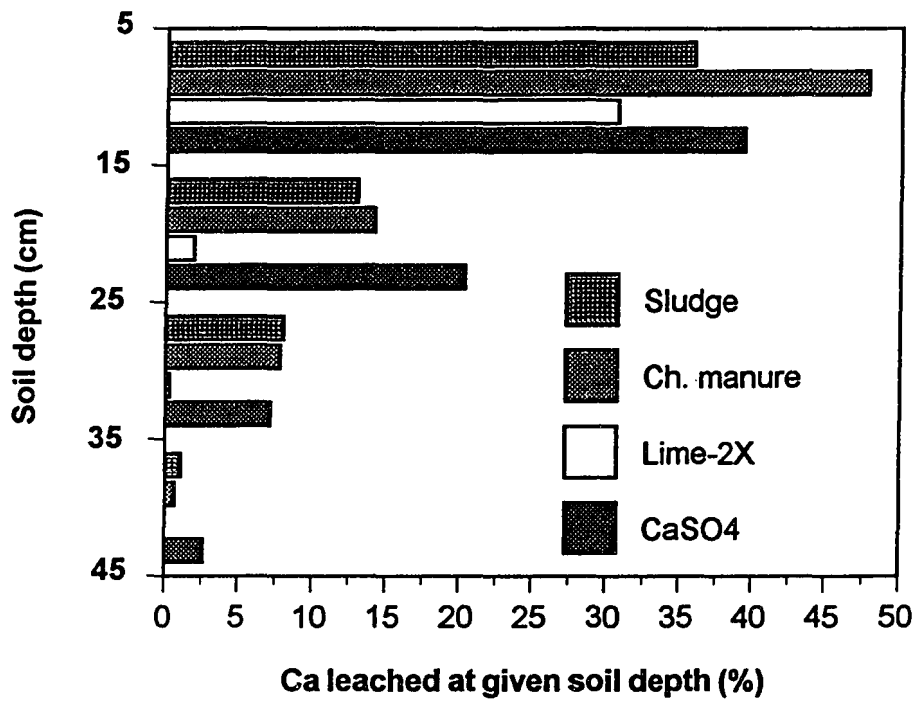
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Fig. 6.2 Percent Ca leached from the various amendments to different soil depths.
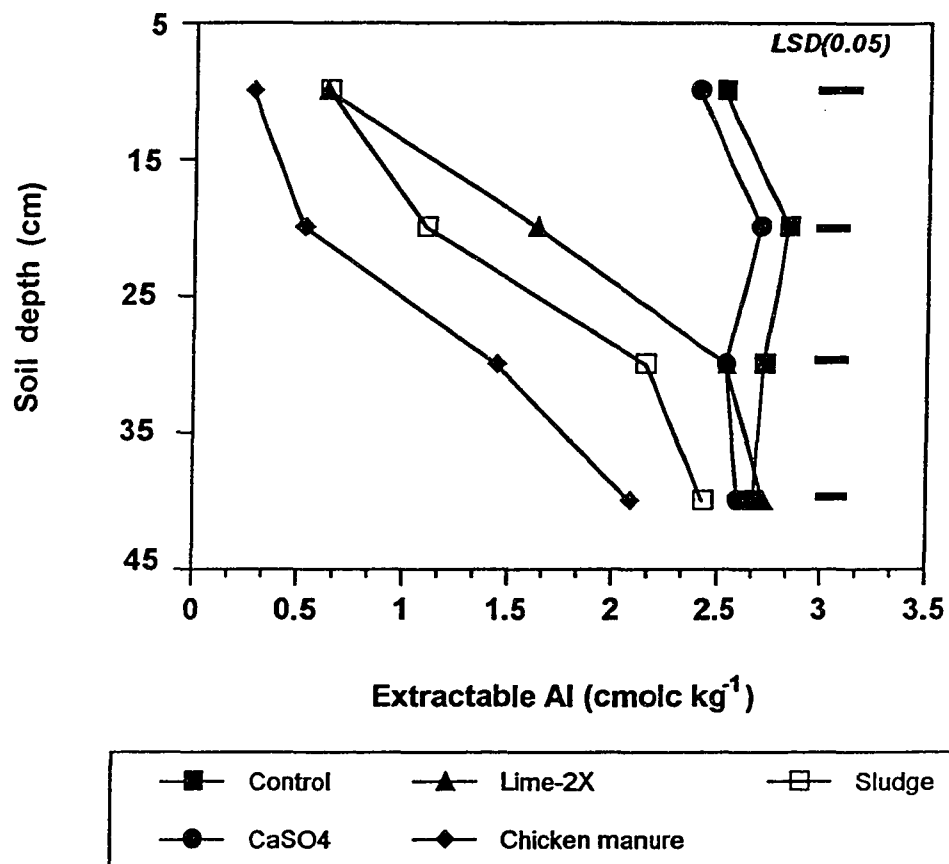
Fig. 6.3 KCl-extractable Al of the soil profile as affected by the different amendments.

the control at this same depth. Below the 25 cm depth, the difference in Al concentration with the control was no longer significant.

Surface application of gypsum reduced extractable Al at all soil depths although less dramatically compared to the reduction by lime at the 5 to 25 cm layer. Reeve and Sumner (1970) proposed that the reduction in exchangeable Al after gypsum application could be the result of "self-liming " effect resulting from SO_4^{2-} induced Al polymerization by ligand exchange for OH groups (Chang and Thomas, 1963). Some exchange of SO_4^{2-} for OH⁻ may take place when gypsum is added without a significant increase in soil pH (Sumner et al., 1986).

Chicken manure and sewage sludge application dramatically reduced KCl-extractable Al at all soil depths. In fact, the concentration of KCl-extractable Al in the chicken manure treatment was the lowest among all treatments at all soil depths. Sewage sludge was also more effective when compared to lime and gypsum in reducing extractable Al concentration.

As a result of increased Ca and decreased Al in the different treatments, Al saturation was dramatically lowered (Figure 6.4). Chicken manure was comparable to lime in reducing Al saturation at the topmost layer. Below that depth, chicken manure was definitely more effective. Gypsum was better than sludge in reducing Al saturation at the 5-15 cm layer but the reverse was true below that depth. Among the amendments, chicken manure seems to be the most effective in reducing Al saturation.
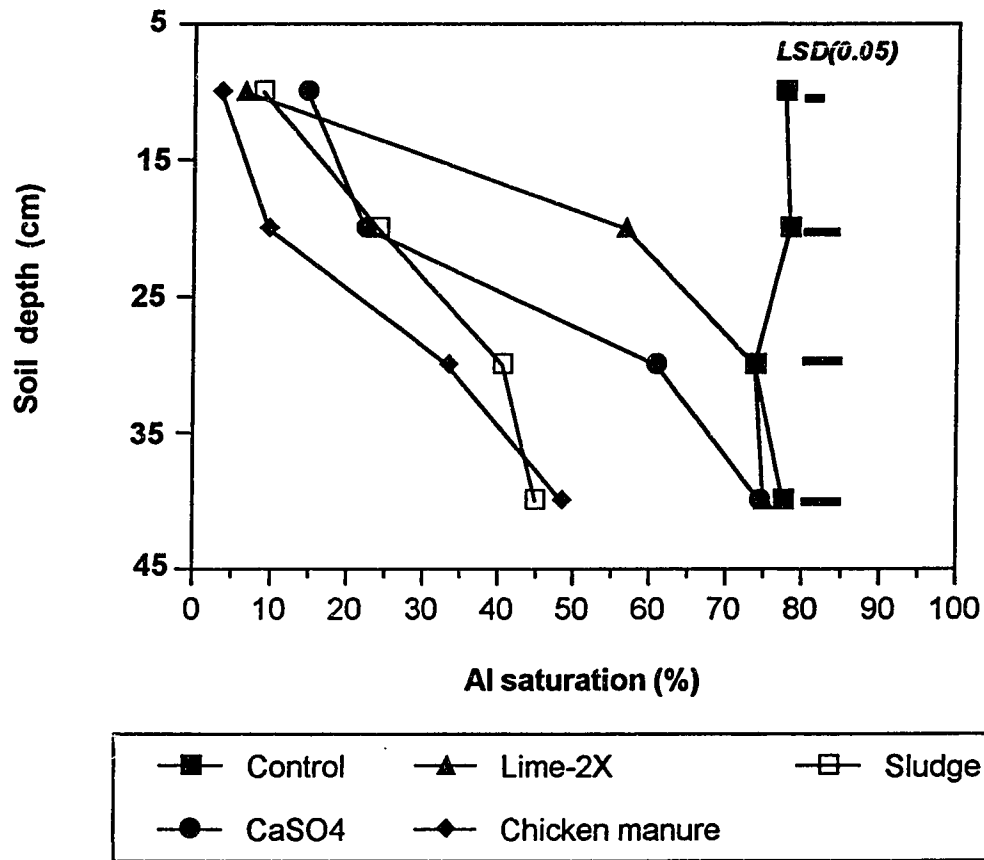
Fig. 6.4 Percent Al saturation at different soil depth as affected by the different amendments.

6.4.8 Exchangeable Mg, K, and Na

Liming did not affect the level of exchangeable Mg which was basically the same as the control at all soil depths (Table 6.6). Gypsum application decreased the level of exchangeable Mg in the 5 to 15 cm layer and then

Table 6.6 Effect of surface application of $CaSO_4.2H_2O$, $CaCO_3$, chicken manure and sewage sludge on exchangeable Mg, K, and Na of an acidic Paaloa subsoil following leaching with 37.85 cm of H_2O for 5 days.

Amendment	Soil column depth (cm)			
	5-15	15-25	25-35	35-45
	<——————— Exchangeable Mg ($cmol_c kg^{-1}$) ——————>			
Control	0.21	0.21	0.24	0.21
$CaSO_4.2H_2O$	0.15	0.29	0.38	0.30
Lime-2X	0.24	0.20	0.21	0.21
Ch. manure	1.20	1.21	0.66	0.38
Sludge	0.52	0.58	0.60	0.45
LSD(0.05)	0.10	0.12	0.09	0.07
	<——————— Exchangeable K ($cmol_c kg^{-1}$)——————————>			
Control	0.08	0.09	0.09	0.09
$CaSO_4.2H_2O$	0.07	0.08	0.09	0.09
$CaCO_3$	0.09	0.10	0.10	0.09
Ch. manure	0.53	0.56	0.42	0.44
Sludge	0.12	0.13	0.11	0.11
LSD(0.05)	0.08	0.03	0.04	0.02
	<——————— Exchangeable Na ($cmol_c kg^{-1}$)——————————>			
Control	0.30	0.27	0.25	0.26
$CaSO_4.2H_2O$	0.25	0.28	0.22	0.22
$CaCO_3$	0.30	0.23	0.26	0.26
Ch. manure	0.35	0.48	0.56	0.40
Sludge	0.32	0.36	0.36	0.41
LSD(0.05)	0.04	0.08	0.05	0.07

increased slightly over the control at the lower soil depths. This result seems to indicate that gypsum application may displace Mg from the topsoil and move it to lower depths in the soil profile where it could be leached away from the rooting zone. Similar effects of reduced exchangeable Mg in the topsoil brought about by gypsum application have been noted previously (Ritchey et al., 1980; Pavan et al., 1984; Oates and Caldwell, 1985). Farina and Channon (1988) observed similarities between Mg and extractable SO_4-S accumulation curves and suggested that a substantial portion of Mg moves with sulfate. To remedy the problem of potential Mg deficiency in the topsoil, Reeve and Sumner (1972) suggested the use of dolomitic lime in conjunction with gypsum.

Exchangeable K was not significantly affected by gypsum and lime application (Table 6.6). The movement of K has been found to be more dependent on the type of soil. In a number of Georgia Ultisols, Sumner (1990) and Syed-Omar and Sumner (1991) found virtually no movement of K except in a very sandy soil even 4 years after treatment with 10 Mg gypsum ha^{-1}. On the other hand, chicken manure significantly increased exchangeable K at all soil depths which could have come from the K in the material itself. There was slight increase in K from sludge application but this was not significantly different from the control. Chicken manure and sewage sludge contain 1.92% K and 0.12% K, respectively. Lime and gypsum did not have any significant effect on exchangeable Na concentration compared to the unamended soil. On the other

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hand, surface application of chicken manure and sludge significantly increased

exchangeable Na concentration from the 15 cm to the lowest soil depth.   This

could be a cause of concern because of possible salt injury to plants.

6.4.9 Chemical composition of leachate

The chemical composition of the leachate is presented in Table 6.7. The

organically amended soils had significantly higher concentrations of soluble C

than the control and inorganically amended soils. As mentioned earlier, the

production of organic anions from the animal manures could have facilitated the

downward transport of Ca to the deeper soil profile which could also explain the

high concentrations of soluble Ca in the leachates of the organically amended

soils. Leachate Ca was highest in the gypsum treatment indicating that Ca from

gypsum could move readily down the subsoil where this nutrient is often

deficient.

Table 6.7 Soluble C and ionic composition of the leachates.

Treatment	C (mM)	Al (μM)	Ca	Mg	K	Na
			<----------mM---------->			
Control	1.52	11.2	0.04	0.01	0.05	0.55
CaSO$_4$.2H$_2$O	1.72	16.4	0.78	0.20	0.06	0.80
CaCO$_3$	1.22	12.0	0.05	0.02	0.04	0.54
Ch. manure	4.39	47.1	0.38	0.38	0.55	5.6
Sludge	2.75	28.9	0.40	0.49	0.15	11.4
LSD(0.05)	0.21	11.2	0.10	0.04	0.10	0.97

Leachate Al in the control and inorganic amendments were not different.

Pavan et al. (1984) did not observe an increase in the concentration of Al in the

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leachate of a Brazilian Oxisol given surface application of $CaSO_4.2H_2O$. They explained that the decrease of exchangeable Al resulting from gypsum application was due to polymerization of Al into an insoluble form and thus not lost into the leachate. Aluminum was highest in the leachate from the chicken manure treatment. It was 3 to 4 times higher than those of the control and the inorganically amended soils and 1.5 times greater than that of the sludge treatment. This seems to indicate that the animal manures can effectively leach soluble Al away from the surface soil (rooting zone) thus allowing roots to move deeper into the subsoil.

Concentrations of K, Mg, and Na in the leachate of the organically amended soils followed a pattern similar to their distribution as exchangeable cations in the lower soil depths. Concentrations of these cations were significantly higher in the organic treatments than in the control and inorganic amendments.

6.5 Summary and conclusions

Amelioration of subsoil acidity by surface application of lime, gypsum, chicken manure and sewage sludge was investigated in a greenhouse column leaching study. The soil columns were leached with deionized water until a total of 1000 mL (37.85 cm) leachate was collected in 5 days.

Lime did not alter soil solution pH, soluble and exchangeable Al and Ca below the 15-cm depth. Gypsum effectively increased soluble and

exchangeable Ca concentration across all soil depths, but did not change soil pH and Al appreciably.

The use of surface-applied chicken manure and sewage sludge as ameliorants for acidic and Ca-deficient subsoils is very promising. Both organic amendments were superior to lime and gypsum in increasing soil pH, supplying Ca, and reducing soil Al concentration, especially at lower soil depths (15-45 cm). Besides effectively correcting subsoil acidity, the organic amendments also increased the supply of Mg, K, and Na in solution. The downward movement of Ca from the organic amendments was probably due to the formation of Ca-organic chelates which facilitated Ca transport to deeper soil layers.

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