

Effectiveness of innovative organic amendments in acid soils depends on their ability to supply P and alleviate Al and Mn toxicity in plants

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Abstract

Purpose: Soil acidity with high Al³⁺ and Mn²⁺ is one of the major constraints to global food production. Lime is effective to increase soil pH, but it is not always readily available and can be expensive. This study aimed to evaluate the effectiveness of organic amendments that may be viable for treating soil acidity.

Materials and methods: Thirteen organic amendments (including manures, composts, biochars and plant residues) were added (1% soil weight) to two acid soils differing in pH buffer capacity, and Al³⁺ and Mn²⁺ concentrations. They included a Dermosol with a pH_{CaCl2} of 4.1, and a Sodosol with pH_{CaCl2} of 4.0. Four inorganic amendments (lime, dolomite, gypsum, and KH₂PO₄) were included for comparison. The Al-sensitive wheat ES8 was grown for 49 days.

Results and discussion: Organic amendments (manures, composts, biosolids, biochars) outperformed or matched the shoot biomass response to lime in both soils. The most effective treatments were poultry litter, poultry-litter-biochar and biosolids which increased shoot biomass by 128%, 158% and 95% for the Dermosol, and by 58%, 43% and 33% for the Sodosol, respectively, compared to the limed controls. Organic amendments increased soil pH_{CaCl2} by up to 0.32 and 0.62 units, and Olsen-P concentration by 16.1 and 30.7 µg g⁻¹ for the Dermosol and Sodosol, respectively. Shoot biomass correlated positively with Olsen-P (R² = 0.85), but negatively with concentrations of extractable Mn (R² = 0.62) and Al (R² = 0.58).

Conclusions: Organic amendments were effective ameliorants for soil acidity. Their effectiveness depends on their ability to supply nutrients, primarily phosphorus, and to overcome Al³⁺ and Mn²⁺ toxicities.

Keywords

Biochar; Biosolids; Compost; Manure; Soil acidification; Soil degradation

1. Introduction

Acidic soils (pH<5.5) are a significant limitation to agricultural productivity around the globe due to increased concentrations of Al and Mn and the low availability of essential plant nutrients, such as P (Kochian et al. 2004). Estimates show that up to 30% of the world's ice-free land is classified as acidic and that nearly half of the agricultural land of ~50 million hectares in Australia has topsoil that is affected by acidity (de Caritat et al. 2011; Von Uexküll and Mutert 1995). These estimated areas are expected to acidify further as current agricultural practices lead to greater soil acidification (Scott et al. 2000). Although liming (i.e. applying CaCO₃) is a beneficial approach to ameliorate acid topsoils, lime is not readily available in some areas and it may not be economically viable for farmers (e.g. developing nations) if purchasing and transport costs are high (Kochian et al. 2004). Furthermore, surface applications of lime are not effective for ameliorating acidic subsoils.

Acid soils present a range of restrictions for plant growth, with Al toxicity often the most significant limiting factor (Ma et al. 2001). The acidification of soils (pH < 5) increases Al³⁺ bioavailability, and as the pH decreases the Al³⁺ concentration exponentially increases to become the dominant Al species in the soil solution (Kinraide 1991). The ability of Al³⁺ to restrict root growth is due to its inhibition of root cell growth and elongation, leading to decreases in root cell division at the root apex (Ryan et al. 1993). Restricted root growth and function result in limited water and nutrient uptake, and this compounds the issue of lower nutrient availability in acid soils. In addition to toxic levels of Al³⁺, acid soils often contain toxic levels of Mn²⁺ ions. Although Mn is an essential plant nutrient, Mn is often considered the second most important metal toxicity in acid soils (Brady and Weil 2008; Kochian et al. 2004). Unlike Al³⁺ toxicity, Mn²⁺ toxicity primarily affects shoot growth (Brady and Weil 2008; Kochian et al. 2004). In addition, P is commonly limiting for plant growth in highly weathered acid soils due to a range of factors such as the greater availability of Al³⁺ and Fe oxides which bind phosphates.

There is increasing interest in the use of organic amendments to improve the chemical, physical and biological properties of soils. The ability of organic amendments to improve soil fertility is well documented (Diacono and Montemurro 2010; Dong et al. 2019; Haynes 2005; Haynes and Naidu 1998; Hornick and Parr 1987; Larney and Angers 2012; Li et al. 2015; Park et al. 2011; Yuan et al. 2011). However, research into the effects of organic amendments applied to acid soils is still incomplete. While there are a variety of studies (Hue 1992; Hue and Mai 2002; Pypers et al. 2005; Shen and Shen 2001; Slavich et al. 2013; Steiner et al. 2007) highlighting increased root growth and corresponding shoot growth for crop species grown in organically-amended acid soils, the key driving mechanisms are still unclear. In addition, the varying nature of soil types and composition of organic amendments often make it difficult to compare results between studies.

This experiment aimed to evaluate a wide range of organic amendments that may be viable alternatives to lime for treating soil acidity. We hypothesised that organic amendments improved plant growth in acid soils with the improved growth resulting from decreased availability of Al³⁺ (via increases in pH or direct binding of Al) and/or increased nutrient supply. We further hypothesised that plant growth would be greater with organic amendments compared than with liming.

2. Materials and methods

2.1 Soil collection and characteristics

Two acid soils were a Dermosol (Isbell 1996) (5-30 cm depth) from Kinglake West, Victoria (37°28'25.38" S 145°15'25.77" E) and a Sodosol (Isbell 1996) (10-15 cm depth) from Holbrook, NSW (35°39'13.80" S 147°15'08.50" E). Soils were air-dried, passed through a 2-mm sieve and mixed well. The Dermosol had an initial $\text{pH}_{\text{CaCl}_2}$ of 4.1, a total carbon of 50.2 mg g^{-1} , a total N of 2.64 mg g^{-1} , an Olsen P of 4.1 $\mu\text{g g}^{-1}$, with a phosphorus buffer index ($\text{PBI}_{+\text{OlsenP}}$) of 504, a pH buffer capacity (pHBC) of 86 $\text{mmol}^{\pm} \text{kg}^{-1} \text{pH}^{-1}$, an extractable Al of 12 $\mu\text{g g}^{-1}$ and extractable Mn^{2+} of 7 $\mu\text{g g}^{-1}$. The Sodosol had an initial $\text{pH}_{\text{CaCl}_2}$ of 4.0, a total carbon of 6.6 mg g^{-1} , a total N of 0.90 mg g^{-1} , an Olsen P of 6.7 $\mu\text{g g}^{-1}$, a $\text{PBI}_{+\text{OlsenP}}$ of 48, a pHBC of 23 $\text{mmol}^{\pm} \text{kg}^{-1} \text{pH}^{-1}$, an extractable Al of 2 $\mu\text{g g}^{-1}$ and an extractable Mn^{2+} of 70 $\mu\text{g g}^{-1}$. Detailed analytical procedures are described in Rayment and Lyons (2011).

2.2 Treatments

The experiment was conducted using a total of 19 treatments. The organic treatments covered a wide range of nutrient concentrations and decomposition rates, and are readily available to farmers (either on-farm or via bulk transport). The treatments included 13 organic materials with 5 groups, *a*) manures: poultry litter, cow manure (Fine Farm Organics) and sheep manure (Fine Farm Organics); *b*) plant residues: lucerne (*Medicago sativa* L.) hay, wheat (*Triticum aestivum* L.) straw and kelp (*Durvillaea potatorum*) powder (Agri Solutions); *c*) composts: dairy compost, hot-mix compost; *d*) biosolids; and *e*) biochars: southern blue gum (*Eucalyptus globulus*) biochar, wheat-straw biochar, poultry-litter biochar and Victorian lignite (brown coal) (Morwell, Victoria). Poultry litter was collected from a farm stockpile in Mount Wallace, Victoria, Australia and comprised semi-composted rice hulls and poultry manure from a broiler operation. Mature dairy compost and hot-mix (an immature compost used to stimulate on farm composts) compost were sourced from The Camperdown Compost Company from stockpiles in Camperdown, Victoria, Australia. Biosolids was sourced from Western Water Surbiton Park Recycled Water Plant from a stockpile in Mount Cottrell, Victoria, Australia. Southern blue gum (SGB) biochar was produced at 450-500 °C from SGB fines with phosphoric acid (10%, 1:1 solution to biochar). Wheat-straw biochar and poultry-litter biochar were produced at 350-400 °C using a continuous flow reactor with a residence time of 3-4 mins by Energy Farmers Australia. In addition, there were four inorganic amendments used including lime (CaCO_3 , Sigma Aldrich), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Sigma Aldrich), dolomite ($\text{CaMg}(\text{CO}_3)_2$, Richgro), and potassium phosphate (KH_2PO_4 , Sigma Aldrich). Two controls included non-amended soil with Al-sensitive wheat (*Triticum aestivum* L. cv. ES8, control), and non-amended soil with Al-tolerant wheat (*Triticum aestivum* L. cv. ET8).

Organic amendments were dried at 40 °C. Plant residues were finely-ground using a mixer mill (MM400, Retsch GmbH, Haan, Germany). All amendments prior to soil addition were passed through a 2-mm sieve, except for biosolids which were sieved at 3.4 mm. Stones and foreign materials, such as plastics, were removed. Detailed characteristics of the organic amendments are listed in Table 1.

2.3 Experimental design and conditions

Each pot contained 2.5 kg of soil mixed with the following basal nutrients (mg kg^{-1}): Urea, 160; K_2SO_4 , 148; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 186; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 122; KH_2PO_4 , 114; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 8; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 6; H_3BO_3 , 1.04; and $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$, 0.4. Nutrients were added via aqueous nutrient solution and thoroughly mixed and allowed to dry. Organic amendment treatments were

applied at a rate of 10 g kg⁻¹ of soil (1% w w⁻¹). Lime and gypsum were balanced by calcium content whereas lime and dolomite balanced by neutralising values for their respective soils. Specifically, the amounts of lime, gypsum and dolomite were 8 g kg⁻¹, 13.6 g kg⁻¹ and 7.36 g kg⁻¹ soil for the Dermosol, and 2.8 g kg⁻¹, 4.82 g kg⁻¹, 2.58 g kg⁻¹ soil for the Sodosol, respectively. Lime with a neutralising value of 99% was added to achieve a theoretical pH of 6 (8 g kg⁻¹ soil) in the Dermosol and (2.8 g kg⁻¹ soil) in the Sodosol. Gypsum was added at a rate of 13.6 g kg⁻¹ soil for the Dermosol and 4.82 g kg⁻¹ for the Sodosol with the same amounts of Ca as lime addition. Dolomite with a neutralising value of 70% was added to achieve a theoretical pH of 6 (7.36 g kg⁻¹ soil) the Dermosol and (2.58 g kg⁻¹ soil) the Sodosol with the same amount of carbonate as the lime treatment. For the high-P treatment, the total KH₂PO₄ was added at 338 mg kg⁻¹ soil (including basal). After treatments and basal nutrients were added, soils were thoroughly mixed and watered to 100% field capacity (θ_g = 220 g kg⁻¹ Dermosol and 150 g kg⁻¹ Sodosol) using reverse osmosis (RO) water.

The pots were arranged in a randomised complete block design with three replicates. All treatments were regularly rotated randomly within each block, and blocks were also rotated between glasshouse benches to avoid positional effects.

After an incubation period of three days, ten uniform germinated seeds of ES8 wheat (except for the ET8 control) were hand-sown at a depth of 2 cm in each pot. The glasshouse was set to 22 °C with 14-h light/10-h dark. Soil moisture after sowing was regularly adjusted every three days to 80% of field capacity (θ_g = 176 g kg⁻¹ Dermosol and 120 g kg⁻¹ Sodosol) by weight using RO water. Two weeks after sowing, seedlings were thinned to four plants pot⁻¹. Additional urea (80 mg kg⁻¹ soil per application) was applied twice after three and five weeks via aqueous nutrient solution. Watering was reduced prior to harvest in order to facilitate the collection of roots.

2.4 Soil and plant sampling

After seven weeks of growth, pots were destructively sampled. Plant shoots were cut off at the soil surface, washed with RO water, then 0.1 M HCl followed by a Milli-Q water (MQ) rinse and dried at 70 °C for three days. Roots were carefully removed from each pot and the remaining bulk soil was thoroughly mixed, passed through a 2-mm sieve and sub-sampled twice (approximately 200 g each) with one sample air-dried at 25 °C and the other stored at 4 °C until fresh soil measurements were completed and then frozen at -20 °C. All roots were stored at 4 °C until cleaned using RO water, then 0.01 M BaCl₂ followed by a MQ water rinse for root morphology measurements within 14 days of harvest. Root samples were then dried at 70 °C for three days.

2.5 Soil and plant measurements

Fresh soil, equivalent to 20 g dry weight (DW) was extracted with 80 ml 0.5 M K₂SO₄ by shaking end-over-end for 1 h before centrifugation at 2000 × g for 6 min. Extracts were passed through Whatman #42 filter papers and stored at -20 °C and dissolved organic carbon (DOC) was analysed via total organic C analysis (GE Sievers Innovox Laboratory TOC analyser, Boulder, USA).

Another fresh soil sample equivalent to 20 g DW, was extracted with 80 ml 0.01 M CaCl₂ by shaking end-over-end for 1 h before centrifugation at 2000 × g for 5 min. Extracts were passed through Whatman #42 filter papers and immediately measured for pH, then stored at -20 °C until analysis for total extractable Al and Mn via ICP-OES (Perkin Elmer Optima 8000, Waltham, USA). Determination of Al and Mn concentrations in the same 0.01 M CaCl₂ extract

used for pH has been shown to be suitable to assess the bioavailability of these toxic elements (Conyers et al. 1991) and we used ICP-OES instead of colourimetric (pyrocatechol violet) analyses as the two approaches showed consistent (1:1) concentrations in extracts. The pH buffer capacity was determined according to the method of Wang et al. (2015).

Olsen P was measured as outlined by Rayment and Lyons (2011) by extracting 5 g of air-dried soil (1:20) with 100 ml of 0.5 M NaHCO₃ (pH 8.5) for 30 min with extracts being filtered through 0.45- μ m Whatman PVDF membrane filters and P concentration in the extracts were determined colourimetrically (882 nm). The PBI_{+OlsenP} was determined as outlined in Rayment and Lyons (2011) by extracting 5 g of air dried soil (1:10) with 50 ml of phosphate equilibrating solution (0.01 M CaCl₂ and 100 mg P L⁻¹) for 17 hours with extracts filtered using 0.45- μ m Whatman PVDF membrane filters and P concentration in the extracts were determined via ICP-OES and PBI_{+OlsenP} calculated.

Root volume, length and diameter were determined using a WinRhizo Pro version 2003b programme (Régent Instruments Inc., Québec, CA). Root samples were subsampled, and measurements calculated on a per weight ratio of the total root and subsampled roots.

Elemental analyses were undertaken on plant shoots and organic amendments by first passing them through a centrifugal mill (ZM200, Retsch GmbH, Haan, Germany) to reduce sample volume and then a sub-sample was taken and finely ground (<0.2 mm) using a mixer mill (MM400, Retsch GmbH, Haan, Germany). Homogenised subsamples were then digested in nitric acid (70% *m v*⁻¹) using a microwave digester (Anton Paar Microwave 3000, Graz, Austria) for plant shoots, while organic amendments were subjected to a block digestion (maximum 185 °C) using nitric acid (70% *m v*⁻¹) and perchloric acid (70% *m v*⁻¹) for organic amendments. The total P, Al, Mn, Ca, Mg, K and Zn concentrations of all samples were determined using ICP-OES. Total N and C in plant shoot and organic amendments was measured by dry combustion using a PerkinElmer Series II CHNS\O Analyser 2400 (PerkinElmer, Massachusetts, USA).

2.6 Statistical analyses

A two-way analysis of variance (ANOVA) was used to test the effects of treatment and soil type, and their interactions, on soil and plant properties. Differences between means were tested using the least significance difference (LSD) at *P*=0.05. Statistical analyses were performed using Genstat 19th edition (VSN International, Hemel Hempstead, England).

3. Results

3.1 Plant biomass

Most inorganic and organic amendments significantly (*P*<0.001) increased shoot and root dry weights of Al-sensitive wheat in both soils when compared to the non-amended ES8 control, except for gypsum, SBG biochar, brown coal, lucerne hay and wheat straw in the Dermosol (Table 2). In the Sodosol, the greatest increases in shoot biomass were observed with poultry litter (a 3.5-fold increase), followed by poultry-litter biochar (3.1 fold), biosolids (2.8 fold), sheep manure (2.6 fold) and dairy compost (2.5 fold) compared to the ES8 control (Table 2). Similarly, in the Dermosol the greatest increases in shoot biomass occurred for poultry-litter biochar (by 19 fold), followed by poultry litter (16.7 fold), biosolids (14.2 fold), sheep manure (6.9 fold) and dairy compost (6.7 fold) (Table 2). Notably in the Dermosol, the Al-sensitive wheat ES8 with lime, dolomite, poultry litter, sheep manure, biosolids, dairy compost and poultry-litter biochar achieved greater shoot biomass than the Al-tolerant wheat ET8 control. In

comparison, in the Sodosol, shoot biomass increased under the potassium phosphate (high phosphate), cow manure, hot-mix compost, wheat-straw biochar, SBG biochar, kelp powder and lucerne hay treatments compared to the ET8 control. Shoot biomass in the Sodosol were significantly ($P<0.05$) greater than that in the Dermosol for all treatments (Table 2). However, the magnitude of difference between the soils was not consistent. For example, wheat shoot growth in poultry-litter biochar-amended soils only increased by 5% with the Sodosol, while in poultry litter-amended soils wheat shoot biomass increased by 32%, leading to a significant amendment \times soil interaction (Table 2).

In general, root biomass showed a similar response to the treatments as shoot biomass in the Dermosol. The largest increases in root biomass were with poultry litter (6.8 fold), biosolids (6.45 fold) and poultry-litter biochar (6.1 fold) compared to the ES8 control. However, this was not the case in the Sodosol where high phosphate (99%), wheat-straw biochar (87%) and lucerne hay (79%) had the greatest increase in root biomass. There were no significant differences in root biomass between the majority of the amendments despite the root biomass from those amendment treatments being significantly greater than the control (Table 2). Nevertheless, increases in root biomass were lower than increases in shoot biomass and subsequently root-to-shoot ratio was decreased by most treatments. In the Sodosol, root diameter of amended soils was not significantly different from the control for all treatments except kelp powder, whereas in the Dermosol root diameter was decreased by 6.3% to 16.3% for manures, biosolids/composts, poultry-litter biochar and kelp powder (Table 2). In the Dermosol, specific root length (root length per unit of root weight) was significantly increased by 49-283% for lime, dolomite, manures, biosolids/composts, poultry-litter biochar and kelp powder. However, in the Sodosol it was decreased by 25-36% in manures, dairy compost and kelp powder treatments (Table 2).

3.2 Soil pH_{CaCl_2} , exchangeable Al and Mn, Olsen P, DOC

The addition of lime and dolomite, on average, increased pH by 0.75 and 1.43 units, and decreased extractable Al by 6.25 and 1.15 $\mu\text{g g}^{-1}$, and Mn by 6.0 and 52.4 $\mu\text{g g}^{-1}$ for the Dermosol and Sodosol, respectively (Table 3).

Irrespective of soil type, dairy compost, hot mix compost, poultry-litter biochar, kelp powder and lucerne hay significantly ($P<0.05$) increased soil pH compared to the unamended control (Table 3). However, certain amendments increased pH in one soil and not the other, for example poultry litter significantly ($P<0.001$) increased pH in the Sodosol (0.24 pH units), but not in the Dermosol (Table 3). The greatest increases in soil pH by organic amendments were with dairy compost (0.32 and 0.41) and kelp powder (0.31 and 0.62) for the Dermosol and Sodosol, respectively (Table 3).

Extractable Al was reduced in both soils by the addition of the manures, composts, poultry-litter biochar and kelp powder. The lowest recorded values for extractable Al under organic amendments in the Dermosol was with hot-mix compost (2.42 $\mu\text{g Al g}^{-1}$) and kelp powder (2.44 $\mu\text{g Al g}^{-1}$) (Table 3). While in the Sodosol the lowest values for extractable Al under organic amendments was with sheep manure (0.15 $\mu\text{g Al g}^{-1}$) and kelp powder (0.24 $\mu\text{g Al g}^{-1}$) (Table 3). However, biosolids, wheat straw and brown coal did not decrease soil extractable Al in either soil (Table 3).

Extractable Mn was reduced in the Sodosol by manures, dairy compost, wheat-straw biochar and poultry-litter biochar and lucerne hay (Table 3). The lowest extractable Mn values under organic amendments occurred with wheat-straw biochar (20.8 $\mu\text{g g}^{-1}$) and poultry-litter biochar (23.0 $\mu\text{g g}^{-1}$) in the Sodosol (Table 3). In the Dermosol, the extractable Mn was largely

unaffected by the organic amendments, except for wheat straw where a significant increase in extractable Mn was observed (Table 3).

The amendment of kelp powder and poultry litter resulted in the greatest increases in DOC compared to the unamended control increases of 209 $\mu\text{g g}^{-1}$ and 86 $\mu\text{g g}^{-1}$ in the Dermosol and 493 $\mu\text{g g}^{-1}$ and 97 $\mu\text{g g}^{-1}$ in the Sodosol, respectively (Table 3).

Olsen P was significantly increased by all organic amendments in both soils, except for brown coal, kelp powder and wheat straw treatments (Table 3). The highest Olsen P concentrations were observed for poultry-litter biochar and poultry litter in the Dermosol (20.6 $\mu\text{g P g}^{-1}$, 17.6 $\mu\text{g P g}^{-1}$) and the Sodosol (39.9 $\mu\text{g P g}^{-1}$, 34.0 $\mu\text{g P g}^{-1}$), respectively (Table 3).

3.3 Shoot elemental concentrations

The N concentration in wheat shoots were largely unaffected by amendment type. However, compared to the controls, poultry litter increased shoot N (35.0 mg N g^{-1}), whereas wheat straw decreased it in the Sodosol, and wheat-straw biochar decreased shoot N in both soils (Table 4). In contrast, shoot P concentrations were significantly ($P < 0.001$) increased by manures, biosolids/compost and poultry-litter biochar in both soils (Table 4). The greatest increases in shoot P were observed for poultry-litter biochar and poultry litter in the Dermosol (199%, 165%) and Sodosol (230%, 189%) respectively (Table 4). Shoot Mn concentration in the Sodosol was significantly ($P < 0.001$) decreased by all organic amendments except wheat straw, with the greatest reductions in shoot Mn concentration observed under poultry litter (77%) and poultry-litter biochar (75%) (Table 4).

3.4 Correlations

Shoot biomass was correlated negatively with extractable Al for both soils ($R^2 = 0.58$) (Fig. 1A) and with extractable Mn only for the Sodosol ($R^2 = 0.62$) (Fig. 1B). In contrast, it was positively with Olsen P concentration ($R^2 = 0.85$) (Fig. 1C) with the correlation being much stronger than with any other soil parameters.

There was also a strong negative correlation between shoot biomass and the C/N ratio of the organic amendments (excluding biochars and brown coal due to their different composition) in the sodosol ($R^2 = 0.92$) (Fig. S1).

4. Discussion

4.1 Effects of soil amendments on plant growth

This study showed that organic amendments significantly improved the growth of wheat plants grown in two acid soils. However, such improved growth varied between the organic amendments, from no positive effect to 20-fold greater than the control. This large variance is commonly observed throughout the literature (Hue 1992; Hue and Mai 2002; Hue et al. 2001; Mokolobate and Haynes 2002; Shen and Shen 2001; Slavich et al. 2013; Steiner et al. 2007). Despite this large variance, there was a clear trend towards amendments derived from animal manures, such as poultry litter and poultry-litter biochar, delivering the largest increases in wheat biomass. This trend is well noted in a wide range of reviews on organic amendments (Diacono and Montemurro 2010; Edmeades 2003; Haynes and Naidu 1998).

While lime application is a common practice to ameliorate soil acidity, organic amendments, such as animal manures and blended composts, either outperformed or had similar effects to lime addition in the present study. The principal mechanism by which animal manures and composts outperformed lime is via increased supply of nutrients, primarily P supply. This is in contrast with lime of which the primary mechanism is increased pH and Al detoxification. While animal manures and composts achieved small increases in pH (0.1-0.4 units) and decreased extractable Al, these changes only partly explain the improved plant growth (Table 3). This is highlighted by amendments, such as biosolids, that did not achieve significant increases in pH or decreases in extractable Al, yet achieved significant increases in not only total biomass, but also root biomass of 7.5-fold in the Dermosol and by 33% in the Sodosol (Tables 2 & 3).

It was apparent that the key characteristic of the best manure-based amendments, is their high P concentrations (e.g. poultry litter 19.0 mg P g⁻¹). It is evident that the P concentration in organic amendments correlated positively with the concentration of Olsen P in soil, which in turn correlated closely with shoot biomass production irrespective of amendment type (Fig. 1). Although shoot biomass correlated negatively with the concentration of extractable Al in soil, such a relation was not as strong as the relationship with the concentration of Olsen P. Other studies of acid soils with phytotoxic Al have shown the superiority of manures, compared with lime could be attributed to improved plant nutrition, especially P nutrition (Hue 1992; Shen and Shen 2001). Our study suggested that the ability of the organic amendments to supply P was the key driver for the effectiveness of amendment in acid soils.

The addition of plant residues achieved significant increases in wheat biomass in the Sodosol despite these residues having lower nutrient concentration and their effects were inconsistent and lower compared to lime and animal manures. The effectiveness of plant residues on wheat biomass production in acid soils was affected by their C/N ratio. For example, plant residues with lower C/N ratios (kelp powder 19.1 and lucerne hay 19.4) performed better than those with a high C/N ratio (wheat straw 54.5). These plant residues with low-C/N (<20) are likely to have minimal N immobilisation and hence adequate N supply to the wheat plant growth during their decomposition (Enwezor 1976). They also achieved significant pH increases, partly due to greater ammonification, an alkalinisation process (hence decreases in Al and Mn toxicities), often greater or comparable to the other organic amendments (Table 3). It appears that the effectiveness of plant residues depended on their ability to increase soil pH and thereby reduce Al and Mn toxicities. In other studies, Shen and Shen (2001) reported wheat straw amendments achieved mung bean shoot biomass significantly greater or similar to lime, whereas Hue et al. (2001) found that cowpea green manure actually caused a decrease in soybean shoot biomass due to the creation of a strong reducing environment leading to increases in Mn availability.

4.2 Effect of soil amendments on soil properties

Increases in Olsen P, resulting from organic amendments, had the greatest correlation with shoot biomass ($R^2 = 0.85$) of all the soil properties (Fig. 1). Hence, the organic amendments with the greatest increase in shoot biomass (poultry-litter biochar, poultry litter, biosolids, sheep manure and dairy compost) in both soils, also resulted in the highest Olsen P concentrations (Tables 2 & 3). The ability of decomposing organic residues to increase P supply to plants in acid soils is reviewed by Haynes and Mokolobate (2001) who indicated that the release of soluble humic materials and organic acids leads to a reduction in the specific absorption of added nutrients supplied by the organic residues by soil colloids. Additionally, there is a slow continuous release of organic P and inorganic P, which may be directly acquired by the plant roots or indirectly by increased cycling of microbial P before it can be adsorbed by the soil or complexed with metal

ions. Hence, the ability of organic amendments to increase soil Olsen P is critical to overcoming the constraints of soil acidity including Al toxicity on plant growth.

In addition to their ability to increase Olsen P, the organic amendments increased soil pH in most scenarios by 0.1 and 0.4 units in the Sodosol and the Dermosol by Week 7 (Table 3). While many of these pH increases were significant, they were not of a significant magnitude to either completely detoxify the soil of extractable Al or explain the biomass increases observed (Tables 1 & 3). Generally, short-term (1-2 months) studies with applications of organic residues have shown an initial increase in soil pH of 0.2-0.6 units, followed by declines and sometimes the pH is at or below the initial pH (Ashgar and Kanehiro 1980; Hue 1992; Wong et al. 2000). Most of the initial increases in soil pH are associated with microbial decomposition and decarboxylation of organic acid anions (Mengel 1994; Tang et al. 1999; Yan et al. 1996). Not all amendments achieved significant increases in soil pH (Table 3) and it is hypothesised that there may have been an initial increase in pH immediately following the residue incorporation with soil, which would favour seedling establishment. However, this pH increase might have diminished later in the experiment. This hypothesis is similar to what occurs in long-term field studies with organic amendments that have no sustained positive effect on soil pH (Schjønning et al. 1994; Van Antwerpen and Meyer 1998). It is speculated that amendments high in N such as poultry litter may have caused nitrification to occur which re-acidified the soil.

Significant decreases in soil extractable Al were observed with most organic amendments, however, not all of these can be attributed to pH increases. For example, organic amendments, such as dairy compost, that achieved the greatest increases in pH, generally had low extractable Al. There were some amendments, such as poultry litter, that did not increase pH in the Dermosol, still reduced extractable Al significantly by 35% compared to the control (Table 3). In addition to this decrease in extractable Al independent of pH, it was observed that DOC was significantly increased in the poultry litter treatment compared to the ES8 control (Table 3). It is speculated that the decomposition of the organic residues leads to the release of soluble humic materials and organic compounds that complex with soluble Al and Mn. In addition, the increase in soil organic matter content leads to increased complexation of Al and Mn (Haynes and Mokolobate 2001; Jones and Brassington 1998). Many amendments containing significant amounts of P increased Olsen P, therefore, it is speculated that these amendments created the conditions by which bioavailable Al was complexed with P. However, biosolids recorded no decrease in extractable Al and no significant change in pH of either soil, despite containing various organic compounds and a significant P content. Thus, it appears that organic amendments used in this study showed the ability to complex Al independent of pH changes in the soil

In the Sodosol, Mn toxicity was also a significant factor limiting plant growth with the plant shoot tissue concentration for the unamended control reaching 1102 $\mu\text{g g}^{-1}$ which is significantly greater than the critical toxic concentration of 700 $\mu\text{g g}^{-1}$ (Reuter and Robinson 1997). Seven of the thirteen organic amendments decreased soil extractable Mn, which was poorly correlated with soil pH. For example, the addition of hot-mix compost (pH 4.51) and kelp powder (pH 4.78) significantly increased soil pH but did not decrease extractable Mn (Table 3). In contrast, wheat-straw biochar, despite a non-significant increase in soil pH of 0.08 pH units, resulted in the greatest reduction in soil extractable Mn (by 61%) (Table 3). There are a range of possible mechanisms by which the wheat-straw biochar decreased the Mn^{2+} toxicity with either precipitation due to reactions with products such as alkaline oxides and silicates or via complexation by oxygen functional groups (Dai et al. 2017). Thus, biochars appear to show promise in alleviating Mn toxicity independent of changes in soil pH.

4.3 Impact of soil type

This study showed that the effectiveness of organic amendments differed between the two acid soils used (Dermosol and Sodosol). These two soils had similar initial pH values, but differed in pH buffer capacity (pHBC), background nutrient availability (e.g. Olsen P), extractable Al and Mn, and P-fixing capacity (PBI). Clearly, the Dermosol had a lower P availability and 11-fold higher P-fixing capacity than the Sodosol although it had a higher soil organic C content and lower extractable Mn concentration. There are a variety of results which contradict the expected responses. Some amendments had increased soil pH to a lesser extent in the Sodosol than in the Dermosol although the Sodosol had a lower pH buffer capacity ($23 \text{ mmol kg}^{-1} \text{ pH}^{-1}$) than the Dermosol ($86 \text{ mmol kg}^{-1} \text{ pH}^{-1}$). An example was lucerne hay-amended soils where pH increased by 0.24 units in the Dermosol and 0.16 units in the Sodosol (Table 3). It is speculated that the process of reacidification occurs at different rates between the two soils. After initial incorporation and decomposition of the amendment, the Sodosol would have achieved a larger increase in soil pH initially, which favoured the N transformation, particularly nitrification, with the lucerne hay (low C/N ratio). The greater nitrification in the Sodosol led to a faster reacidification process and hence a smaller net increase in pH at the end of the experiment than in the Dermosol. Unfortunately, we did not measure the dynamics of inorganic N in soil. Due to the dynamic nature of amendments in different soils, care needs to be taken in interpreting results and determining overall amendment effectiveness from short-term studies such as this one.

Irrespective of amendments, the plants grown in the Sodosol consistently produced higher biomass than those in the Dermosol despite of higher soil Mn availability and higher Mn concentrations in shoots of the plants in the Sodosol. This difference was primarily due to the greater availability of P, together with lower PBI in the Sodosol. It is evident that shoot biomass production correlated positively with the concentration of Olsen P irrespective of soil type (Figure 1). Nine out of 19 treatments appeared to be P-adequate for the Sodosol compared to only 4 for the Dermosol (Table 4). Furthermore, while the shoot concentrations of N, K, Ca, Mg and Zn were at marginal to adequate levels in both soils, the concentrations of P in the shoot were, on average, 52% higher in the Sodosol than in the Dermosol (Table 4). Therefore, to maximise the effectiveness of an organic amendment in ameliorating soil acidity, it is recommended to determine the soil characteristics such as pHBC and PBI which are linked to soil clay content and to maintain key plant nutrients at adequate levels.

5. Conclusion

The ability of organic amendments to increase the availability of key plant nutrients such as P in the soil solution, not just alleviating soil acidity and reducing Al and Mn availability, seems to be the key factor in selecting an effective amendment. Poultry litter and poultry-litter biochar stood out from this study as the most successful amendments with this being attributed to their high P contents. The soils after basal nutrient addition would still be P deficient as indicated by the concentrations of Olsen-P in soil and P in wheat shoots below the critical levels. Hence, organic amendments, that contain high P concentrations and can increase and maintain the plant-available P pool, are likely to be effective soil amendments for acid soils with low available soil P and high P-fixing capacity, such as the Dermosol in this study. Furthermore, the high P supply would help to alleviate Al toxicity due to the complexation with Al^{3+} . However, a wide range of materials including those able to be generated on farm such as crop residues can be suitable provided the soil's ability to resist changes in pH and bind P is low. Due to the short-term nature of this study, it is difficult to assess the relative effectiveness of the amendments

over longer periods. Future studies should compare the long-term effectiveness of organic amendments in amelioration of soil acidity and examine whether the benefits are long-lived and cost-effective in farming systems.

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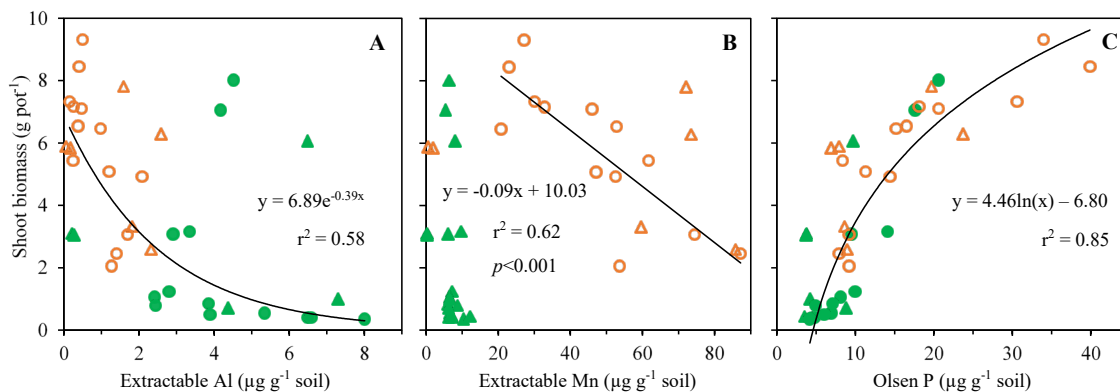
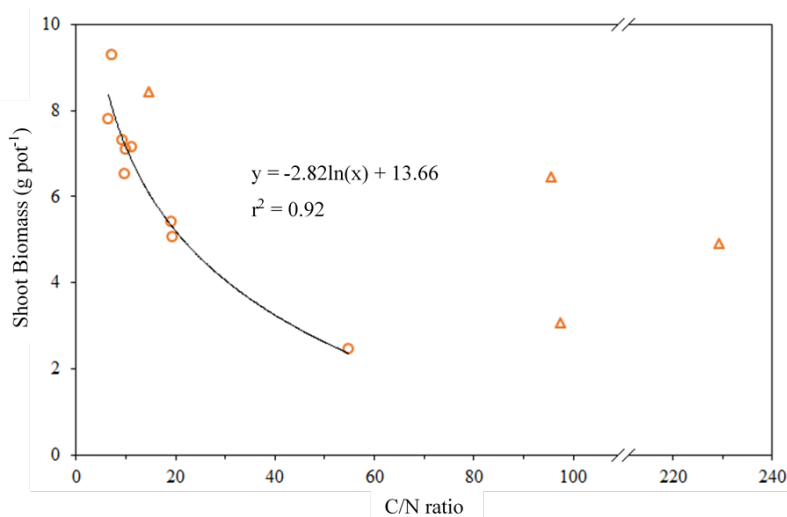


Figure 1. Relationships between soil CaCl_2 -extractable Al (A), CaCl_2 -extractable Mn (B) and Olsen-P (C) and shoot biomass of Al-sensitive wheat (ES8) after 7 weeks of growth in a Dermosol (green closed symbols) and Sodosol (orange open symbols) with 17 amendments and non-amended (control). Data of Al-tolerant wheat (ET8), KH_2PO_4 with high phosphate, lime, dolomite, gypsum and biosolids (triangle symbols) are not included in the trendline for A and C. Data of Dermosol (triangle symbols) not included in trendline for B (n=3).



Supplementary Fig. S1. Relationship between shoot biomass of Al-sensitive wheat (ES8) after 7 weeks growth and the C/N ratio of the organic amendments (excluding biochars and brown coal) in a Sodosol (orange open symbols). Data of poultry-litter biochar, wheat-straw biochar, southern blue gum biochar and brown coal (triangle symbols) are not included in the trendline.

1 **Table 1.** Chemical characteristics of organic amendments.

Organic amendment	C	N	C/N ratio	P	K	Ca	Mg	Mn	Zn	Al	pH
	(mg g ⁻¹)	(mg g ⁻¹)		(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	(0.01 M CaCl ₂)
<i>Manures</i>											
Poultry litter	239	34.2	7.0	19.0	27.5	33.4	7.3	0.72	0.50	2.8	6.7
Sheep manure	169	18.4	9.2	7.2	15.1	14.1	4.7	0.51	0.34	15.4	7.5
Cow manure	145	14.6	9.9	6.6	18.0	21.4	8.1	0.26	0.19	31.2	6.9
<i>Biosolids/Compost</i>											
Biosolids	249	38.4	6.5	23.7	3.3	29.0	6.8	0.29	0.83	21.6	7.0
Dairy compost	199	18.0	11.1	8.7	11.7	43.1	7.3	0.31	0.21	17.3	7.7
Hot-mix compost	245	25.2	9.7	10.0	15.1	31.2	5.2	0.24	0.17	13.6	6.7
<i>Biochars/Coal</i>											
Poultry-litter biochar	378	26.0	14.5	28.5	40.7	50.2	9.9	1.01	0.97	1.6	9.0
Wheat-straw biochar	583	6.1	95.6	4.5	28.3	10.7	5.3	0.56	0.02	7.3	10.1
SBG biochar	619	2.7	229.3	7.4	5.2	8.0	2.3	0.15	0.02	6.5	5.8
Brown Coal	604	6.2	97.4	0.1	0.1	4.7	2.1	0.05	0.01	0.1	4.0
<i>Plant residues</i>											
Kelp powder	294	15.4	19.1	1.8	14.5	27.5	9.5	0.02	0.13	0.5	5.8
Lucerne hay	422	21.8	19.4	3.2	27.1	7.7	1.6	0.04	0.01	0.8	5.9
Wheat straw	409	7.5	54.5	0.5	16.1	2.1	1.1	0.05	0.01	0.3	4.5

2 SBG, Southern blue gum.

3

4 **Table 2.** Shoot and root biomass, root-to-shoot ratio, root diameter, root length-to-root weight ratio of wheat (ES8, Al³⁺ sensitive) at 7 weeks after sowing in
 5 Derosol and Sodosol with 17 amendments and non-amended (control). Al tolerant wheat cultivar (ET8), 225 mg kg⁻¹ KH₂PO₄ (High Phosphate). * and ***
 6 indicate $P \leq 0.05$ and $P \leq 0.001$ for two-way analyses of variance (Treatment \times Soil type) (n=3).

Treatment	Shoot biomass		Root biomass		Root/shoot		Root diameter		Root length	
	(g)		(g)		(g g ⁻¹)		(μ m)		(m g ⁻¹)	
	Derosol	Sodosol	Derosol	Sodosol	Derosol	Sodosol	Derosol	Sodosol	Derosol	Sodosol
Controls										
Control	0.40	2.05	0.48	1.69	1.21	0.83	320	278	84	165
ET8	0.99	3.32	0.92	2.12	0.93	0.64	248	254	168	190
Inorganics										
Lime	3.10	5.89	1.81	2.46	0.58	0.42	237	283	236	164
Dolomite	3.04	5.84	1.73	2.68	0.57	0.46	224	256	238	170
High phosphate	0.71	6.28	0.67	3.37	0.94	0.54	309	277	103	146
Gypsum	0.44	2.59	0.42	1.83	0.95	0.71	330	288	91	165
Manures										
Poultry litter	7.06	9.31	3.74	2.20	0.53	0.24	271	296	135	106
Sheep manure	3.16	7.33	2.29	2.19	0.73	0.30	272	279	133	118
Cow manure	1.24	7.10	0.94	2.26	0.76	0.32	268	279	138	120
Biosolids/Composts										
Biosolids	6.06	7.81	3.58	2.25	0.59	0.29	300	300	136	139
Dairy compost	3.07	7.16	2.27	2.16	0.74	0.30	292	294	143	124
Hot-mix compost	1.06	6.54	0.77	2.07	0.73	0.32	269	298	132	150
Biochars/Coal										
Poultry-litter biochar	8.01	8.44	3.43	2.36	0.43	0.28	287	277	154	144
Wheat-straw biochar	0.85	6.46	0.75	3.16	0.88	0.49	303	280	101	166
SBG biochar	0.54	4.92	0.56	2.35	1.05	0.48	304	286	94	148
Brown Coal	0.40	3.06	0.41	2.13	1.01	0.70	301	280	91	152
Plant residues										
Kelp powder	0.79	5.44	0.63	2.05	0.81	0.38	294	312	125	116
Lucerne hay	0.49	5.08	0.43	3.03	0.87	0.60	308	272	99	162
Wheat straw	0.35	2.46	0.42	1.53	1.20	0.62	339	276	74	151
<i>Interaction LSD (P=0.05)</i>	0.26		0.28		0.10		23		30	
Significance level										
<i>Treatment</i>	***		***		***		***		***	
<i>Soil type</i>	***		***		***		*		***	
<i>Treatment \times Soil type</i>	***		***		***		***		***	

7 SBG, Southern blue gum.

8 **Table 3.** Soil pH, extractable Al³⁺ and Mn²⁺, dissolved organic carbon (DOC) and Olsen P at 7 weeks after sowing in a Dermosol and Sodosol with 17
 9 amendments and non-amended (control). Al tolerant wheat cultivar (ET8), 225 mg kg⁻¹ KH₂PO₄ (High Phosphate). *** indicates $P \leq 0.001$ for two-way analyses
 10 of variance (Treatment \times Soil type) (n=3).

Treatment	pH		Al		Mn		DOC		Olsen P	
	(0.01 M CaCl ₂)		($\mu\text{g g}^{-1}$)		($\mu\text{g g}^{-1}$)		($\mu\text{g g}^{-1}$)		($\mu\text{g g}^{-1}$)	
	Dermosol	Sodosol	Dermosol	Sodosol	Dermosol	Sodosol	Dermosol	Sodosol	Dermosol	Sodosol
Controls										
Control	4.07	4.16	6.49	1.27	6.2	53.6	299	104	4.5	9.2
ET8	4.10	4.22	7.29	1.82	6.5	59.6	314	113	4.2	8.6
Inorganics										
Lime	4.87	6.29	0.22	0.05	0.2	0.5	254	153	3.8	7.9
Dolomite	4.77	4.89	0.27	0.18	0.3	1.9	220	105	3.7	6.9
High phosphate	4.09	3.99	4.36	2.59	6.2	73.4	299	129	8.8	23.7
Gypsum	4.17	4.28	19.67	2.32	12.1	85.8	268	95	3.5	8.9
Manures										
Poultry litter	4.09	4.40	4.17	0.50	5.4	27.1	385	201	17.6	34.0
Sheep manure	4.22	4.23	3.34	0.15	9.6	30.0	330	143	14.1	30.6
Cow manure	4.17	4.27	2.80	0.47	7.1	46.0	314	143	10.0	20.6
Biosolids/Composts										
Biosolids	4.14	4.14	6.49	1.59	8.1	72.1	344	151	9.7	19.7
Dairy compost	4.39	4.57	2.91	0.26	6.0	32.8	306	132	9.5	17.7
Hot-mix compost	4.27	4.51	2.42	0.38	6.5	52.9	308	147	8.1	16.5
Biochars/Coal										
Poultry-litter biochar	4.28	4.34	4.52	0.40	6.4	23.0	330	135	20.6	39.9
Wheat-straw biochar	4.16	4.24	3.85	0.98	6.1	20.8	282	106	7.1	15.2
SBG biochar	4.26	4.19	5.35	2.08	6.5	52.5	304	123	6.9	14.4
Brown Coal	4.15	4.25	6.58	1.70	7.1	74.5	320	109	4.8	9.2
Plant residues										
Kelp powder	4.38	4.78	2.44	0.24	8.7	61.7	508	597	4.8	8.4
Lucerne hay	4.31	4.32	3.89	1.21	6.9	47.2	346	158	6.0	11.3
Wheat straw	3.99	4.12	8.01	1.41	10.4	87.2	340	136	4.2	7.9
<i>Interaction LSD (P=0.05)</i>										
	0.13		0.47		4.9		19		0.9	
Significance level										
Treatment	***		***		***		***		***	
Soil type	***		***		***		***		***	
Treatment \times Soil type	***		***		***		***		***	

11 SBG, Southern blue gum.

12 **Table 4.** Nutrient concentrations of wheat shoots harvested at 7 weeks after sowing in a Dermosol (D) and Sodosol (S) with 17 amendments and non-amended
 13 (control). Al tolerant wheat cultivar (ET8), 225 mg kg⁻¹ KH₂PO₄ (High Phosphate). *** indicates $P \leq 0.001$ for two-way analyses of variance (Treatment \times Soil
 14 type). Critical concentrations were estimated based on Reuter and Robinson (1997) (n=3).

Treatment	Shoot N		Shoot P		Shoot K		Shoot Ca		Shoot Mg		Shoot Mn		Shoot Zn		Shoot Al	
	(mg g ⁻¹)		(mg g ⁻¹)		(mg g ⁻¹)		(mg g ⁻¹)		(mg g ⁻¹)		(μ g g ⁻¹)		(μ g g ⁻¹)		(μ g g ⁻¹)	
	D	S	D	S	D	S	D	S	D	S	D	S	D	S	D	S
Controls																
Control	27.2	31.5	0.81	1.32	15.8	25.9	1.70	3.82	1.72	1.42	148	1102	14	43	60	44
ET8	31.7	26.2	2.04	1.25	28.6	26.7	1.77	2.85	1.72	1.30	219	970	33	51	37	21
Inorganics																
Lime	28.2	32.3	1.49	1.44	22.6	30.5	4.08	5.65	1.86	1.78	248	291	26	28	21	20
Dolomite	28.8	26.1	1.59	1.21	25.9	24.1	2.25	2.76	2.42	1.86	179	322	33	29	18	25
High phosphate	27.0	30.0	0.85	2.13	15.2	27.5	1.40	3.21	1.51	1.10	140	976	16	30	58	49
Gypsum	29.5	28.2	0.83	1.27	17.1	24.9	4.05	3.79	1.92	1.49	148	1252	37	46	53	35
Manures																
Poultry litter	30.9	35.0	2.15	3.81	28.8	32.5	1.66	2.01	1.43	1.12	163	253	29	26	15	48
Sheep manure	29.2	32.9	1.53	3.50	24.6	34.4	2.06	2.54	1.77	1.33	227	456	32	37	24	48
Cow manure	27.0	29.8	1.24	2.54	21.2	30.8	2.06	3.01	1.76	1.43	201	536	31	42	30	40
Biosolids/Composts																
Biosolids	29.8	32.3	1.81	2.57	23.5	29.2	2.28	3.71	1.72	1.66	145	827	34	57	21	35
Dairy compost	26.8	30.6	1.57	2.58	23.5	31.5	2.17	3.25	1.46	1.35	177	448	25	40	25	27
Hot-mix compost	28.3	31.0	1.30	2.41	22.1	33.1	2.06	3.18	1.64	1.47	178	614	26	45	34	36
Biochars/Coal																
Poultry-litter biochar	28.7	33.4	2.42	4.35	29.3	30.3	1.58	1.78	1.38	1.21	195	279	30	27	26	49
Wheat-straw biochar	23.3	27.2	1.12	1.82	18.7	26.3	1.57	1.94	1.47	1.08	155	378	19	29	46	35
SBG biochar	25.9	28.0	0.93	1.65	16.3	28.3	2.01	3.47	1.61	1.26	151	893	16	36	58	30
Brown Coal	27.3	25.6	0.83	1.19	13.9	23.5	1.68	3.06	1.72	1.36	138	955	16	41	72	34
Plant residues																
Kelp powder	28.4	30.4	1.23	1.74	20.5	29.4	1.91	2.22	2.03	1.86	234	614	40	55	16	19
Lucerne hay	27.3	31.0	0.93	1.36	18.0	28.5	1.83	2.56	1.64	1.29	189	647	22	39	38	18
Wheat straw	26.4	26.7	0.76	1.27	15.5	25.6	2.24	2.15	1.72	0.99	187	945	11	49	57	14
<i>Critical concentrations</i>	27-31		1.8-2.2		20		1.2-2.0		<1.5-2.0		35-100 (adequate)		<20			
<i>Interaction LSD (P=0.05)</i>	2.2		0.21		2.3		0.26		0.19		95		13		16	
Significance level																
<i>Treatment</i>	***		***		***		***		***		***		***		***	
<i>Soil type</i>	***		***		***		***		***		***		***		*	
<i>Treatment \times Soil Type</i>	***		***		***		***		***		***		***		***	

15 SBG, Southern blue gum.