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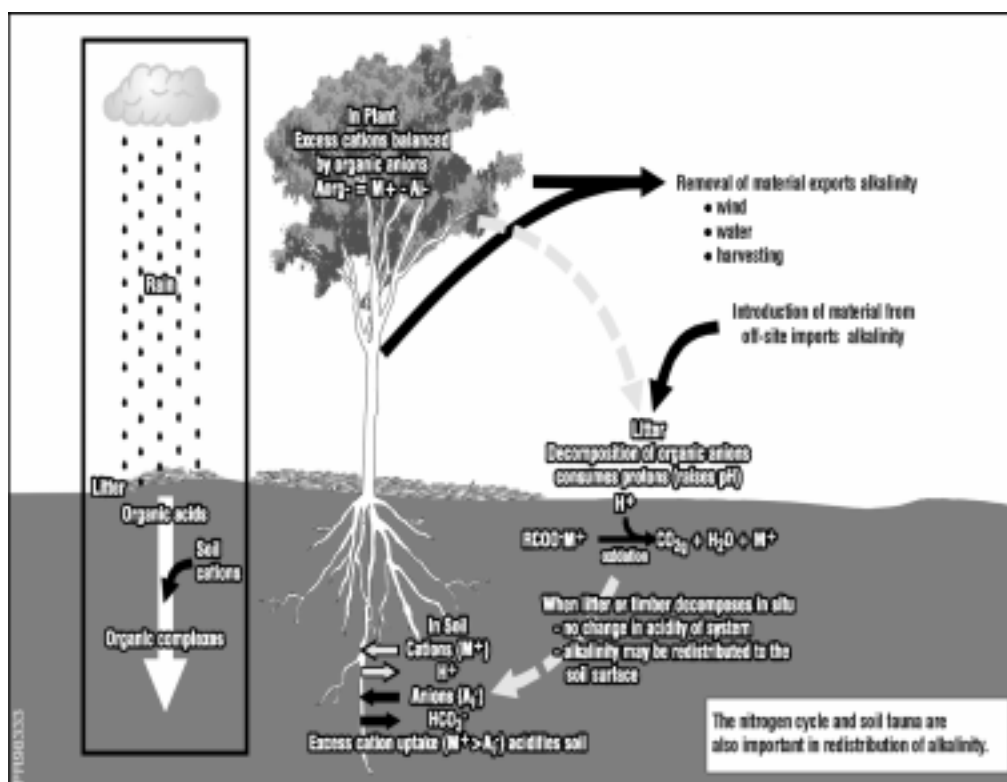


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The Impact of Trees and Fodder Shrubs on Soil Acidification

A report for the
RIRDC/LWRRDC/FWPRDC
JOINT VENTURE AGROFORESTRY PROGRAM
by
A D Noble and P J Randall



The impact of trees and fodder shrubs on soil acidification

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Foreword

Trees have the potential to increase sustainability and productivity of agriculture. Tree planting on farms is becoming more widespread and popular and they are being planted as windbreaks, woodlots, to control rising water tables and for commercial timber production, as well as for aesthetic reasons.

Apart from their effects on water use in the landscape, trees are likely to have impacts on soil fertility and through the uptake and redistribution of nutrients in litter to modify the rates of soil acidification. However, comparatively little is known of such affects and we do not know what properties of tree litter might be important nor how different tree species may differ in such properties.

This report covers work supported by RIRDC grant CSP-4A to CSIRO Plant Industry. It includes laboratory studies describing selected properties of leaf litter from a range of species and the effects on pH and base status of incubating leaf litter with soils. This is complemented with field studies which examine the impact of trees on soil acidification. The ultimate aim of this work is to improve our understanding of the interactions of soil and trees in order to make the best economic and ecological use of trees in farm landscapes.

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Executive Summary

Soil acidification is a major form of land degradation in Australia which affects over 7 million hectares in the more productive parts of the country, areas with above 500 mm rainfall. It is estimated that the cost of lost production due to soil acidity exceeds \$ 300 million compared to \$ 200 million losses due to salinity and \$ 80 million due to erosion.

Soil acidification is a natural process and occurs at a slow rate during the weathering of soils. Its rate can be accelerated by acid inputs from industry (a relatively minor cause in Australia), unwise use of acid sulfate soils which can cause acute local problems, and by acidification from agriculture, horticulture and forestry. The most acidifying systems are those where large amounts of biomass are harvested and removed from the land, where the recycling of nutrients is inefficient and nitrate is allowed to leach from the soil or where ammonium-based fertilisers are used.

The potential role of trees in altering the hydrological balance of a catchment and effects on development of salinity has generated substantial interest; but their possible role in modifying soil acidification processes is not well recognised. The following processes may potentially be important:

- Nutrient recycling. Trees will take up nutrients from deeper soil layers and some will be returned to the soil surface in litter. Thus cations and anions leached from surface soils, particularly as acidity increases, could be recycled, with trees acting as "biological pumps". Cation uptake in excess of anion uptake (or visa versa) would determine how much acidification (or alkalisation) and where in the soil it would occur.
- Complexing of soluble cations. Leaf litter contains soluble organic materials which could potentially complex cations including calcium, iron and aluminium. This could increase their mobility in soil and thus affect soil forming processes. Complexing of aluminium would also render it less toxic to plants.
- Neutralisation of soil acidity. The decomposition of organic substances in leaf litter will consume protons and tend to raise pH. This balances the acidification which occurs as a result of nutrient uptake during growth, and concentrates the alkalinity on the surface. Removal of litter (or trees) will also remove alkalinity and thus leave the soil more acid.
- In addition to the above processes, effects on the nitrogen cycle are likely to be important in affecting rates of acidification. The deeper rooting patterns of trees and shrubs, their perenniality and summer growth contrasts with the shallow rooted winter-growing annual crops and pastures used in southern Australia. Accordingly, they are likely to allow less water to escape the root zone and will capture more of the soil nitrate, thus reducing the risk of nitrate leaching. Nitrate leaching is highly correlated with acidification rate and is of major significance in soil acidification. If the presence of trees were to reduce or prevent nitrate leaching altogether, this would greatly reduce the rates of soil acidification. However, this aspect is being examined in other research and was not part of this project.

The present work included laboratory studies describing selected properties of leaf litter from a range of tree and shrub species including their ash alkalinity (a measure of the

organic anion content of the plant) and cation (Al^{3+}) complexing ability. The effects of incubating leaf litter with soils on pH and base status was examined. These studies were complemented with field studies which examined the impact of trees on soil acidification.

We have identified large differences between tree species in ash alkalinity of the litter. Most eucalypt and acacia species and radiata pine had relatively low ash alkalinity while a number of northern hemisphere deciduous species had higher ash alkalinity. *Melia azederach* or white cedar proved to have litter with the highest ash alkalinity among the species sampled. The conditions under which the trees are grown can interact with the genotype to modify the ash alkalinity. Ash alkalinity values of leaves appear to increase during the season. Over a wide range of species and growth conditions there is a correlation between ash alkalinity and calcium content of the material.

Adding leaf litter to an acid soil and allowing it to decompose increased the pH of the soil. The increase was largely explained by the ash alkalinity of the material, although other factors such as the nitrogen content of the litter and (in the short term) its rate of decomposition may also be important.

We have also shown that species vary greatly in the amount of water soluble material that can be extracted from litter and the cation complexing characteristics of the soluble material is widely different between species. In soil, complexation of soluble aluminium in organic forms would render it less toxic and this would benefit plant root growth. However, such an effect may be relatively short lived, persisting only as long as the organic materials escape attack by soil microbes. The nature of the soluble materials in litter may influence soil forming processes because once cations are complexed in organic forms they are more mobile and would be at risk of accelerated leaching.

The field studies have shown that the soil at several sites under trees is less acid (has a higher pH) than adjacent soil, and has higher exchangeable cations and lower extractable aluminium. However, at one site sampled under oak trees the soil had acidified considerably and had a reduced level of extractable bases and a lower clay content. This site was a sloping one and litter appeared to have been lost down hill by wind and water erosion causing losses of alkalinity from the site.

The work indicates the potential for redistribution of nutrients and alkalinity by trees to ameliorate the surface horizons of acid soils by depositing litter. Increases in pH at the soil surface will be at the expense of acidification elsewhere in the root zone. This may be detrimental in poorly buffered, cation poor soils but less so in those soils where the roots have access to an alkaline base rich horizon, for example, many duplex soils. It is important to realise the observed increases in pH and associated changes in the basic cation concentration on the exchange complex through the addition of litter, does not independently result in the synthesis of alkalinity. It is simply a redistribution of alkalinity.

However, once nutrients and alkalinity are mobilised from the soil and concentrated in the trees there is the potential for loss if timber, litter or ash (after fire) is moved from the site. Such losses would lead to acidification and lower fertility. The potential benefits and risks of loss would vary widely depending on the tree species. This should

be taken into account when selecting species for particular sites.

We have proposed a method for classifying tree species according to their potential for redistributing cations, based on the ash alkalinity of litter, and their potential for assisting podzolisation processes as a consequence of the cation complexing ability of aqueous extracts of their litter. This classification method is discussed in relation to the field studies. It may provide a framework for decisions about the desirability of planting trees in particular soils and for matching tree species to sites. It is further suggested that for the sustainable management of agroforestry systems a knowledge of ash alkalinity of litter, bark and wood of the species is essential in calculating acid budgets for monitoring acidifying effects on soils and upon which to base management decisions concerning harvesting practices and the need for lime applications

Introduction

Soil acidification is a major form of land degradation affecting over 7 million hectares in the more productive parts of Australia, areas with above 450 or 500 mm rainfall. The soils affected are commonly gradational red-brown earths and duplex soils which are poorly buffered against changes in pH and are relatively infertile with production being limited by deficiencies of nitrogen, phosphorus and other nutrients including trace elements. However, in their native state the soil - vegetation ecosystems are likely to have been relatively stable with respect to their hydrology and cycling of nutrients. In humid environments, acidification will occur at faster rates due to processes including base cation uptake (by plants and microbes), leaching of bases with carbonic, organic or nitric acids and humus formation (Ulrich, 1980). With the advent of agriculture, characterised by tree clearing and the establishment of legume-based pastures or cropping systems with the input of fertiliser nutrients, productivity was increased many fold. As a consequence, rates of acidification in these soils have increased (Williams, 1980) and pH has fallen to values where aluminium (Al) and manganese (Mn) are found in the soil solution at levels which are toxic to plants (Bromfield *et al.*, 1983). Poor plant growth due to soil acidification has contributed to the inefficient use of water in landscapes and compounded the effect of vegetation change following clearing. Salinisation in localised areas has followed. Soil acidification thus directly and indirectly contributes to a reduction in productivity. Price (1993) gives estimates of \$300 million annual losses due to acidity compared to \$200 million losses due to salinity and \$80 million due to erosion. The increased rates of acidification under legume based-pastures result from changes in soil organic matter, alkali removal in products and increases in the nitrogen (N) status of the system with increased generation of protons during the nitrification stages of the N cycle (Helyar and Porter, 1989). If the cycle is completed, the protons are consumed when the resulting higher levels of soil nitrate are taken up by plants. Winter crops and annual or summer dormant pastures are unable to immediately capture nitrate accumulated during summer leading to increased risk of nitrate loss by leaching and consequent acidification, first of the surface horizons and later spreading to the subsurface. However, in many cases the base status at depth in these soils remains high.

Applications of ammonium-based fertilisers will have similar effects to those of legume

fixed N. Low pH not only solubilises Al and Mn in the soil to toxic forms but also lowers the availability of phosphate (P) and molybdenum (Mo). Cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+) may also be depleted by leaching. Accordingly, as soils acidify there is a significant loss of fertility.

Nutrient enrichment of surface soil by tree and shrub growth-forms has been recognised by several researchers. In this respect trees may act as nutrient pumps, drawing nutrients from deep horizons and laterally from areas beyond the canopy, depositing them mainly beneath the canopy via litterfall and canopy leaching. The supporting evidence for this mechanism is circumstantial. Trees may play a role in reversing the negative effects of soil acidification through the development of deep root systems that are capable of taking up bases such as Ca and Mg from deep in the profile and returning them to the soil surface as leaf litter containing organic anions. This would have a similar effect to applying lime to the soil surface. However, it should be noted that increases in pH on the surface would be at the expense of acidification elsewhere in the soil profile.

In Spain a study comparing soil chemical properties under oak tree canopies and in the surrounding open grassland found that under the trees, soil organic matter content, total exchange capacity, K, P, total N and exchangeable Ca and Mg were 1.5-2 fold higher than under the grassland away from the canopy. The same trends were observed both for the more biologically active surface horizon (0-5 cm), and for the second horizon (5-20 cm), and the differences were most marked on poor soils (Joffre *et al.*, 1988). These authors suggested that oak trees have the ability to extract nutrients from deep soil layers and concentrating them in the surface horizon, thereby making them available to herbaceous plants and consequently available to grazing animals. The increase in organic matter and nutrient levels under the trees may not be entirely due to litter fall but also to animal excretion since grazing animals are attracted to the scarce trees within these grasslands (Joffre *et al.*, 1988). In Australia, Dann (1992) has stated that soil pH increased under the fodder shrub *Tagasaste* (*Chamaecytisus proliferus*) compared to the adjacent pasture, which was separated by a fence, but he gave few details. Murray and Mitchell (1962) described an accumulation of cations under red gum trees.

This potential biological pumping mechanism may be greater with tree species having litter with a high ash alkalinity and non acidic water-soluble organic extracts. Some trees have shown potential for selectively accumulating certain nutrients. Sanchez *et al.* (1985) report that litter and detritus from *Gmelina arborea* contained twice as much Ca as that of virgin forest or mature pine plantation while the Mg content of litter was three times as much as in *Pinus* litter. Chijoke (1980) reports that 117 and 161 kg Ca ha⁻¹ yr⁻¹ were returned in *G. arborea* litter for two plantations sites in Brazil. Trees that produce base rich litter may have the potential for ameliorating acid soil infertility of surface soils.

The application of organic matter to aluminium toxic soils has increased crop yields by decreasing the activity of phytotoxic Al species in the soil solution (Ahmad and Tan, 1986; Bessho and Bell, 1992; Hargrove and Thomas, 1981; Hue and Amien, 1989). With the addition of organic matter to soils there is an increase in soil pH and ionic strength of the soil solution which results in increases in CEC due to the generation of charge on the variable charge colloids. This results in an increased ability of the soil to retain nutrients.

It is well recognised that decomposing litter on forest floors is a major source of organic acids that buffer soil pH and form soluble complexes with Al^{3+} and other metals, thereby increasing their mobility in the soil profile (Stevenson and Vance, 1989). Field studies in forest ecosystems indicate that higher Al^{3+} concentrations are often found in waters draining from soils under conifers than those under deciduous trees (Driscoll, 1989) suggesting that certain conifers have a more acidic effect. Studies of this nature have encouraged us to examine the issue in more detail.

Many of the processes by which trees may affect soil fertility have been explored (Prinsley and Swift, 1986) and the implications of tree planting for nutrient cycling and site fertility have been extensively studied (see review by Turner (1996)). The potential role of trees in altering the hydrological balance of a catchment and effects in the context of salinity is now well recognised (Bell, 1993); but their possible role as "biological nutrient pumps" in modifying soil acidification processes is not well understood. Their deep and extensive rooting habit, perenniality and summer growth contrasts with the shallow rooted winter-growing annual pastures. Trees in the agricultural landscape are expected to reduce or check soil acidification as a result of the processes listed below:

- Deep-rooted perennials are likely to allow less water to escape the root zone thus reducing the risk of nitrate leaching. They are also likely to capture more of the soil nitrate than would shallow rooted annuals. Prevention of leaching of nitrate would remove a major cause of acidification
- The uptake of excess basic cations from the B horizon, recycling them to the surface and depositing them as litter could transfer alkalinity from the B to the A horizons and thus reduce the rate of acidification of the latter zone.
- Decomposing litter could ameliorate effects of soil acidity on plant growth by precipitation of soluble Al and/or the formation of stable non-phytotoxic Al-complexes.
- Tall aerodynamically rough tree canopies act as effective traps for atmospheric dust. The dust contains nutrients, which wash off the leaves during rainfall events and enrich the subcanopy area with nutrients.
- Though not well quantified, it is often noted that where trees are sparsely spaced in the landscape they act as focal points attracting birds and mammals seeking shade or cover. Herbivores that take refuge in the shade of trees may enhance the local nutrient cycle. In addition, perching birds enrich the soil through their excreta.

Tree species could differ markedly in the way they affected the above processes. Landcare, Greening Australia and other agencies have been active in promoting the reintroduction of trees into catchments. But the selection of species has not been based on knowledge of their effects on processes such as soil acidification. This project attempted to increase our knowledge in this area.

Objectives

The research aimed to improve understanding of the possible role of trees in managing acid soils and how the choice of species for plantation or agroforestry might impact on soil acidification. Specific aims included:-

- description of effects of tree growth on soil pH and soil cations
- testing the hypothesis that trees may act as ‘biological pumps’ to redistribute alkalinity within soil profiles
- documenting differences between species
- relating differences between species to chemical properties of litter and other factors
- measuring the capacity of leaf litter to neutralise soil acidity.
- investigating properties of leaf litter important in the complexing of toxic aluminium in acid soils.

Methods

Our study set out to measure ash alkalinities of litter material and Al complexing behaviour of litter extracts from a range of indigenous and exotic species of trees and shrubs currently grown in Australia with a view to characterising the species for their potential to alter soil pH and ability to complex and detoxify soluble Al. Soil properties under plantings of different species were also measured. It was hoped that this study would provide data on the potential ability of tree / shrub species to affect rates of soil acidification, alter the distribution of acidity in soil profiles and possibly ameliorate acid soils. The identification of sampling sites and choice of suitable tree species was done after consulting officers from State Forestry Services and Departments of Agriculture, CSIRO Forestry, Greening Australia and Landcare groups.

We had preliminary evidence that there were large differences in ash alkalinity between tree species. *Melia azedarach* (white cedar) was of particular interest because it showed an exceptionally high ash alkalinity which is indicative of accumulation of an excess of basic cations balanced by a large organic anion pool. Although indigenous to coastal areas in northern New South Wales and Queensland, the species has a wide range of adaptation and is deciduous. It is commonly planted around homesteads and stock yards where shade is needed in summer and sunshine winter. While it may have limited economic value and may thus not be useful for agroforestry purposes, it was included in this study as a model species to contrast with species of lower ash alkalinity.

The study was subdivided into 5 activities which had the overall objectives of evaluating the possible role that trees may play in managing problems associated with soil acidification. These activities are described as follows:

(1) Characterise litter material of selected tree species with respect to ash alkalinity and basic cation composition.

Objective: An initial study to determine the nutrient content and ash alkalinities of litter from a range of tree species. From this initial assessment a number of species showing a range of characteristics were selected to go forward into the next phase of the study.

Methodology: Litter material from a number of indigenous and exotic tree species was collected from selected sites for a preliminary evaluation of nutrient content and ash alkalinities. The range included eucalypts, acacias, pines, tagasaste and deciduous species including *Melia azedarach* and temperate exotic species. The full list of species is given in the Results section 1.

Ash alkalinity was measured by ashing and titration as outlined by (Jarvis and Robson, 1983). Ash alkalinity was also estimated as the excess cation content. Samples were analysed for Ca, Mg, K, Na, S, P and Cl by x-ray fluorescence (XRF) spectrometry (Norrish and Hutton, 1977) and the ash alkalinity calculated from the difference between the sums of cations and anions:

$$\text{Ash alkalinity (cation excess)} = \{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^{+} + \text{Na}^{+}\} - \{\text{H}_2\text{PO}_4^{-} + \text{SO}_4^{-} + \text{Cl}^{-}\}$$

(units are $\text{cmol}_c \text{ kg}^{-1}$).

Total organic carbon was measured according to Yoemans and Bremner (1988) and nitrogen was determined with an auto analyser after digestion with $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (Heffernan, 1985)

(2) Evaluate the ability of leaf litter material from several tree species to neutralise soil acidity.

Objective: To evaluate the capacity of leaf litter, incorporated at a range of rates, to neutralise soil acidity and influence the cation distribution on the exchange complex.

Methodology: The surface 0-10 cm depth interval of an acid red brown earth was collected from Book Book, near Wagga Wagga, New South Wales, air dried and passed through a 2 mm sieve. The soils from this site had already been well characterised (Noble *et al.*, 1995).

Litter samples from several trees species (listed in Results sections 2) were dried at 70° C, ground to pass a 2 mm sieve and the following determinations undertaken:

1. Nitrogen content
2. Cations and anions
3. Ash alkalinity

Each of the plant materials were mixed with 300 g soil at application rates of 5, 10, 20 and 40 t DM/ha per 10 cm depth of soil (1.2, 2.4, 4.8, 9.6 g/pot) at a bulk density of 1.25 g cm^{-3} . In addition, a series of treatments containing lime rates of 0, 0.5, 1.0, 2 and 4 t ha^{-1} (0, 0.12, 0.24, 0.48, 0.96 g/pot) were included for comparison. The treated soils were incubated in polyethylene bags at 90% field capacity at 25° C for 8 weeks. The open end of the of the bags was not sealed but folded over to allow aeration. Any lost water was replaced every 2 weeks. The soils were then analysed for pH in 0.01M CaCl_2 (pH_{Ca}) and exchangeable cations in 0.1 M $\text{BaCl}_2/0.1 \text{ M NH}_4\text{Cl}$, 2M KCl-extractable N (NH_4 and NO_3) by standard methods of Rayment and Higginson (1992). Soil organic carbon and rapidly reactive Al was determined using the methodology of Yoemans and Bremner (1988) and Kerven *et al.* (1989).

(3) Assessment of leaf litter extracts from selected tree species for their capacity to complex phytotoxic Al^{3+} .

Objective: To evaluate the Al^{3+} complexing ability of extracts of leaf litter from selected tree species and their effects on the movement of elements in soil profiles.

Methodology: Aqueous extracts of leaf litter material were prepared using the protocol of Shotyk and Sposito (1988). The extracts were diluted to a common concentration of dissolved organic carbon (DOC), 34.8 mg L^{-1} , and equilibrated at pH 4.0 with various concentrations of Al for 1 hr. Labile Al (Al_L) was measured using the methodology of James *et al.* (1983) as modified by Shotyk and Sposito (1988). More details of the methodology are provided in Results section 3.

In a separate but related study, the effects of aqueous extracts of leaf litter percolating through a reconstituted soil column were examined. The leachate from the column was analysed and upon completion of leaching the soil was dried and pH and extractable and exchangeable cations at different depths in the column were measured.

(4) Field study to assess the pH and cation status of soil under stands of selected tree and shrub species.

Objective: To compare the properties of soil under plantings of selected tree / shrub species with adjacent soils under pasture or other land use.

Methodology: The following six comparisons have been made between different land use systems:

1. cork oak plantation / pasture
2. radiata pine plantation / pasture
3. white cedar planting / grass
4. poplar plantation / pasture
5. river red gum planting / ley cropping
6. tagasaste plantation / pasture and crop

The sites were chosen (a) to contain stands of these tree / shrub species in close proximity to the reference site under either pasture or ley cropping; (b) the two systems occurred on the same soil type but separated by a fence to avoid the nutrient transfer effects of stock camping under the trees; (c) the trees had been established for at least 15 years and mostly longer. At each site replicate soil cores from each area were taken and sectioned into the six portions of 0-5, 5-10, 10-15, 15-20, 20-30 and 30-40 cm from the surface. Soil samples were dried and ground and analysed for soil pH_{Ca} and extractable Al in 0.01M CaCl_2 , exchangeable Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Mn^{2+} and Al^{3+} using a 0.1M $\text{BaCl}_2 / \text{NH}_4\text{Cl}$ soil extract (Rayment and Higginson, 1992). In the comparisons of cork oak and pine with pasture, other measurements including clay content were made (see Results section 4).

(5) Greenhouse study to evaluate the ability of selected tree species to accumulate basic cations over a range of soil base saturations.

Objective: To compare the ranking of species for ash alkalinity on a range of soils differing in soil base saturation and the effect of different cation/anion availability ratios. To compare the contribution of roots in different parts of the soil profile to cation and anion uptake and to estimate pH changes in the rhizosphere of some tree species.

Methodology: In order to investigate the constancy of the ash alkalinity characteristics of a species, the cation to anion balance available to the plants in the soil was manipulated experimentally, and altered by using different soils. Seedlings of *Melia azedarach*, *Eucalyptus globulus* and *Pinus radiata*, representing a wide range of ash alkalinity, were grown in each of 4 soils (including the soil from Book Book used in other experiments). The soils differed in soil pH and exchangeable cations. A further range of conditions was induced in the Book Book soil by treatments with lime to modify pH and Ca status and by selectively altering the supply of nitrate compared to ammonium nitrogen by preventing nitrification using a calcium carbide preparation to release acetylene, a potent inhibitor of this process. The tree seedlings were transplanted into pots of the different soils and treatments and grown for 4 months under controlled conditions. The nutrient content of the plants was measured by XRFS and ash alkalinity calculated by difference between cation and anion content.

Seasonal changes in ash alkalinity were monitored in 3 deciduous species (white cedar, *Brachychiton populneus* and *Populus nigra*) by sampling approximately monthly from soon after bud burst to leaf fall in the following autumn.

For further evidence of the effect of soil environment on ash alkalinity we took the opportunity to examine material from another project in which 4 different pasture species were grown on 3 different sites with different soils and with a range of application rates of lime, phosphorus and potassium fertilisers. The results of this provide useful additional information but will be reported only briefly.

We used the indicator method of Haussling *et al.* (1985) to monitor pH in the rhizosphere of *Melia azedarach* and *Eucalyptus globulus* grown in root boxes built with a face that could be removed to expose roots. The indicator bromocresol green was made up in 0.75% agarose and when it had cooled to 30 °C, poured onto the exposed roots. pH was estimated from the colour change from purple to yellow by comparison with a set of standards.

We attempted to assess the contribution of cations from different depths in the soil profile to excess cation uptake by trees using seedlings of *Melia*, eucalypt and pine in reconstituted soil profiles and monitoring uptake using "cold" tracer techniques with strontium and rubidium as markers for calcium and potassium and bromate as a marker for nitrate. These marker ions are present in low concentrations in most soils, are readily taken up by plants, are easily measured using XRF spectrometry and are non hazardous. "Cold" tracer techniques have been used previously, for example to assess rooting depth in the field (Pinkerton and Simpson, 1979). Unfortunately, difficulties with plant roots preferentially passing down the sides of the columns rather than in the soil and proliferating between the soil and the bottom of the column, as well as variability

between plants meant that we obtained no useful data. Attempts to alter the distribution of roots in the soil profile by modifying the conditions with additions of nutrients and lime also failed to encourage root proliferation in specific depth zones, and caused us to abandon the approach.

List of Species examined in the project.

Exotic species

<i>Betula pendula</i>	Silver birch
<i>Castanea sativa</i>	Spanish chestnut
<i>Chamaecytisus proliferus</i>	Tagasaste, Tree lucerne
<i>Fraxinus oxycarpa</i>	Claret ash
<i>Gladitsia sp</i>	
<i>Liquidambar styraciflua</i>	Liquidambar
<i>Paulownia tomentosa</i>	Paulownia
<i>Pinus radiata</i>	Radiata pine
<i>Platanus acerfolia</i>	London plane
<i>Populus nigra var italica</i>	Lombardy Poplar
<i>Populus euramericana</i> ‘First Introduction’	Poplar hybrid
<i>Quercus palustris</i>	Pin oak
<i>Quercus robur</i>	English oak
<i>Quercus suber</i>	Cork oak
<i>Ulmus procera</i>	English elm

Native species

<i>Acacia elata</i>	Cedar wattle
<i>Acacia mearnsii</i>	Black wattle
<i>Acacia. melanoxylon</i>	Blackwood
<i>Brachychiton populneus</i>	Kurajong
<i>Casuarina stricta</i>	Hill oak
<i>Eucalyptus camaldulensis</i>	River red gum
<i>Eucalyptus cloeziana</i>	Gympie messmate
<i>Eucalyptus dunnii</i>	Dunn’s white gum
<i>Eucalyptus elata</i>	River peppermint
<i>Eucalyptus globulus</i>	Southern blue gum
<i>Eucalyptus grandis</i>	Flooded gum
<i>Eucalyptus henryi</i>	Large leaved spotted gum
<i>Eucalyptus. maculata</i>	Spotted gum
<i>Eucalyptus nitens</i>	Shining gum
<i>Eucalyptus pilularis</i>	Blackbutt
<i>Eucalyptus propinqua</i>	Grey gum
<i>Eucalyptus regnans</i>	Mountain ash
<i>Eucalyptus saligna</i>	Sydney blue gum
<i>Eucalyptus triflora</i>	Pigeon House ash
<i>Eucalyptus viminalis</i>	Manna gum
<i>Grevillea robusta</i>	Silky oak
<i>Melia azedarach</i>	White cedar, Melia

Results

(1) Ash alkalinity and mineral composition of litter from selected tree and shrub species.

As the first step in this project, a preliminary study on the range of ash alkalinities of selected tree species was undertaken prior to more comprehensive evaluation of this parameter. The results of this preliminary study were published by Noble et al. (1996). While some of the results from that work are included in this report, the interested reader is referred to the paper (listed also as Paper 5 under Publications arising) for a more detailed discussion. The results discussed in section 1. pertain to a more comprehensive data set from samples collected by the authors as well as by colleagues.

We obtained a range of litter samples from below pure stands of trees or in situations where it was certain that material was from the designated species. In the case of samples from the Flushing Meadows experiment site Wagga Wagga (labelled FM in Table 1.1) litter traps were set-up in a species trial. The traps were cleared each fortnight for 3 months and the litter bulked. These leaf litter samples included several Eucalypt species currently being assessed for their potential as commercial species. As well as leaf litter samples, freshly fallen acorns were collected from oak (*Quercus suber*) and pods from Gladitsia (*Gladitsia sp*) as they are a major component of annual litter fall in these species. These plant parts proved to be relatively low in nutrients and had ash alkalinity values of 28 and 50 cmol_c kg⁻¹ respectively and are at the low end of the range (Table 1.1).

In the majority of the litter samples Ca was the most abundant cation, often several fold higher in concentration than K. However in a few samples K was significantly higher than Ca (*Fraxinus oxycarpa* #15, *Quercus suber* acorns #19, *Eucalyptus triflora* #FM19). In other samples, mainly from the FM group which had been irrigated with sewerage effluent the values for Ca and K were of a similar order (#FM2, FM5, FM8, FM9, FM13, FM16, and FM21). It is of interest that while all 4 samples of poplar litter (#5, 10, FM15 and FM21) had high Ca concentrations, high K was found only in the two from the effluent irrigation site. It is of note that the species *Eucalyptus triflora* accumulated higher concentrations of Na and Cl when compared to all of the other species collected from the Flushing Meadows site (Table 1.1). In a study undertaken to evaluate salt tolerance of Eucalyptus species, Marcar (1989) observed that this species accumulated significant amounts of these two ions compared to other species. The results observed in this study would support Marcar's findings.

Ash alkalinity measured by titration was highly correlated with the value calculated by difference between cations and anions but the absolute value of the former was on average higher.

$$\text{Cation excess} = 0.95 \text{ titration} - 8.8; r^2 = 0.8, n=69$$

The reasons for this difference are likely to include: (1) a proportion of the Cl in the plant material may be lost during ashing leading to over estimation of ash alkalinity in the titration and (2) the calculation by difference treats all the S as being in charged

Table 1.1. Leaf litter samples collected, their elemental composition and their ash alkalinity by two methods.

Lot #	Species	Location	Ca	Mg	Na	K	S	Cl	N	P	Ash Alkalinity (cmol _c kg ⁻¹)		
			(mg g ⁻¹)									Cation excess	Titration
1	<i>Ulmus procera</i>	Stromlo, ACT	30.9	4.4	0.4	11.1	0.9	3.7	8.4	2.4	198	192	
2	<i>Gladitsia</i> sp	Yarralumla, ACT	33.9	2.5	0.2	7.4	1.6	1.7	7.3	0.9	193	147	
3	<i>Gladitsia</i> sp, pods	Yarralumla, ACT	4.2	0.6	0.3	13.7	1.0	0.6	12.7	1.4	50	50	
4	<i>Quercus robur</i>	Yarralumla, ACT	15.1	2.6	0.2	6.5	0.9	0.2	7.4	0.8	107	77	
5	<i>Populus nigra</i>	Acton, ACT	35.5	5.5	0.5	7.3	1.6	2.7	5.4	0.6	225	228	
6	<i>Quercus palustris</i>	Black Mt, ACT	7.2	2.1	0.2	7.1	0.7	0.6	5.0	0.2	65	195	
7	<i>Melia azedarach</i>	Black Mt, ACT	41.7	3.2	0.3	16.1	1.9	1.7	9.8	1.0	257	238	
8	<i>Quercus robur</i>	Yarralumla, ACT	12.3	2.7	0.5	8.5	0.7	1.0	5.2	0.3	100	108	
9	<i>Quercus robur</i> , acorns	Yarralumla, ACT	11.4	0.6	0.1	8.6	0.5	0.0	4.7	0.6	28	28	
10	<i>Populus nigra</i>	Stromlo, ACT	29.0	4.6	0.2	5.7	1.0	9.1	3.9	0.6	164	125	
11	<i>Melia azedarach</i>	Yarralumla, ACT.	34.2	3.3	0.3	15.4	1.6	2.9	9.6	0.6	219	217	
12	<i>Platanus acerfolia</i>	Civic ACT	28.7	2.0	0.3	7.1	2.4	2.6	4.8	0.4	155	150	
13	<i>Castanea sativa</i>	Yarralumla, ACT.	13.9	4.6	0.2	7.4	0.7	0.3	4.5	0.9	120	192	
14	<i>Liquidambar styraciflua</i>	Yarralumla, ACT.	13.0	4.1	0.2	2.3	0.7	0.4	3.5	0.3	99	135	
15	<i>Fraxinus oxycarpa</i>	Curtin ACT.	15.3	3.3	0.4	32.3	2.0	1.4	8.6	0.7	171	164	
16	<i>Melia azedarach</i>	Black Mt ACT	40.5	5.2	0.3	6.4	1.6	1.0	10.5	0.7	248	253	
18	<i>Quercus suber</i>	Glenloch, ACT	12.4	1.7	0.4	2.2	0.8	0.1	6.8	0.6	76	81	
19	<i>Quercus suber</i> , acorns	Glenloch, ACT	0.8	0.7	0.1	8.7	0.7	0.0	8.3	1.0	25	21	
20 ¹	<i>Eucalyptus globulus</i>	Cann River, NSW	12.8	2.6	2.2	5.2	1.0	4.6	9.5	0.6	87	103	
21 ¹	<i>Acacia mearnsii</i>	Cann River, NSW	8.7	1.4	0.9	6.2	1.4	3.6	21.4	0.7	53	58	
22 ¹	<i>Pinus radiata</i> needles		7.7	1.1	0.1	3.3	0.7	0.4	5.1	1.0	48	48	
23 ¹	<i>P. radiata</i> needles		4.8	1.3	0.1	3.6	1.0	0.4	12.9	1.2	34	42	
24	<i>Grevillea robusta</i>	Aranda ACT	18.0	1.1	0.2	5.5	1.1	1.6	8.9	0.3	101	101	
25 ²	<i>Eucalyptus nitens</i>	irrigated treat, Tas.	24.6	2.8	1.6	2.3	0.9	1.1	7.5	0.9	147	122	
26 ²	<i>E. nitens</i>	rainfed treat Tas	18.6	3.0	1.5	1.6	1.0	0.9	8.1	0.8	119	111	
27 ²	<i>E. globulus</i>	irrigated treat, Tas.	14.9	3.2	1.3	1.5	1.1	1.4	9.8	0.7	97	165	
28 ²	<i>E. globulus</i>	rainfed treat Tas	17.6	2.7	1.3	2.0	1.1	0.9	11.1	0.8	108	115	
29 ³	<i>E. maculata</i>	Kiola, NSW	5.7	1.6	1.8	3.5	1.0	1.7	6.7	0.2	47	106	
30 ³	<i>E. maculata</i>	Kiola, NSW	8.0	1.7	1.6	3.0	1.0	1.3	6.8	0.2	58	68	

.....continued.

Table 1.1 (continued)

Table 1.1 (continued)

Lot	Species	Location	Ca	Mg	Na	K	S	Cl	N	P	Ash Alkalinity ($\text{cmol}_c \text{ kg}^{-1}$)	
											Cation	Titration
											excess	
(mg g ⁻¹)												
31 ³	<i>Eucalyptus maculata</i>	Kiola, NSW	6.7	1.4	0.9	2.4	1.1	0.5	8.8	0.3	46	73
32 ³	<i>E. maculata</i>	Kiola, NSW	6.8	1.4	1.5	3.2	1.0	1.2	6.7	0.2	50	59
33 ³	<i>E. maculata</i>	Kiola, NSW	7.6	1.6	0.8	2.6	1.0	0.6	6.6	0.2	52	86
34	<i>Chamaecytisus pro-</i> <i>liferus</i> (Tagasaste)	Yass, NSW	5.7	2.5	0.2	6.5	0.6	0.6	nd	0.4	60	nd
35	<i>Casuarina stricta</i>	Royalla, NSW	12.3	3.2	0.6	3.8	1.5	2.1	nd	2.0	79	nd
Fm1 ⁴	<i>E. grandis</i>	Wagga NSW.	11.7	1.4	3.1	5.0	1.4	2.7	6.6	1.0	77	81
Fm2 ⁴	<i>E. nitens</i>	as above	6.5	1.6	2.4	7.0	1.3	3.1	14.6	0.9	54	86
Fm3 ⁴	<i>E. propinqua</i>	as above	8.6	1.5	4.1	5.4	1.3	4.1	10.5	0.7	65	144
Fm4 ⁴	<i>E. henryi</i>	as above	8.6	1.5	2.9	5.1	1.3	5.1	11.5	1.2	55	107
Fm5 ⁴	<i>E. pilularis</i>	as above	6.5	2.5	8.0	8.6	1.6	13.5	14.0	0.8	60	91
Fm6 ⁴	<i>E. dunnii</i>	as above	10.4	2.3	3.1	8.3	1.5	8.1	15.1	1.0	70	93
Fm7 ⁴	<i>E. saligna</i>	as above	14.0	2.7	4.6	5.0	1.2	4.8	10.9	0.6	103	114
Fm8 ⁴	<i>E. regnans</i>	as above	5.0	2.2	4.4	6.1	1.3	7.5	14.1	0.9	46	68
Fm9 ⁴	<i>E. globulus</i>	as above	7.0	1.6	3.5	8.1	1.3	4.6	16.2	0.9	61	111
Fm10 ⁴	<i>E. elata</i>	as above	6.4	1.6	5.1	5.7	1.4	5.1	13.0	3.9	47	75
Fm11 ⁴	<i>E. viminalis</i>	as above	7.1	1.4	2.8	6.7	1.4	4.1	13.1	0.9	54	68
Fm12 ⁴	<i>E. cloeziana</i>	as above	4.4	1.9	7.0	3.5	1.5	5.6	9.9	0.9	49	70
Fm13 ⁴	<i>Paulownia tomentosa</i>	as above	15.6	3.4	1.1	16.5	2.4	1.6	22.0	2.1	127	124
Fm14 ⁴	<i>Acacia melanoxylon</i>	as above	6.6	1.7	2.4	6.7	1.3	6.0	16.6	1.0	46	75
Fm15 ⁴	<i>Populus nigra</i>	as above	24.6	5.6	0.5	20.3	4.7	1.5	13.2	1.6	186	181
Fm16 ⁴	<i>Acacia. melanoxylon</i>	as above	6.0	1.4	1.9	6.9	1.3	6.2	15.9	0.7	40	74
Fm17 ⁴	<i>A. melanoxylon</i>	as above	7.1	2.0	3.2	5.4	1.3	5.3	14.4	1.4	52	83
Fm18 ⁴	<i>A. elata</i>	as above	11.2	1.8	2.8	3.7	1.5	7.1	14.8	0.8	65	73
Fm19 ⁴	<i>Eucalyptus triflora</i>	as above	4.9	0.9	10.8	11.0	1.2	15.2	12.4	1.4	53	70
Fm20 ⁴	<i>Populus nigra</i>	as above	29.7	5.9	0.5	18.8	4.6	7.2	13.0	1.1	196	214
Fm21 ⁴	<i>P. nigra</i>	as above	23.5	5.4	0.4	23.7	3.6	3.9	10.0	1.3	187	214

¹ supplied by Partap Khanna, CSIRO Forestry, Canberra. ACT

² supplied by Robin Crommer CSIRO Forestry, Hobart Tasmania.

³ leaf litter fall study - supplied by Eddie Pook, CSIRO Plant Industry.

⁴ species trial Flushing Meadows field study (CSIRO Forestry, Canberra), Wagga Wagga NSW.

forms and all the N in uncharged, organic forms. The calculation used would under or over estimate cation excess in proportion to the organic S or nitrate present, respectively. In the first instance it is of note that in general, species from the Flushing Meadows site had elevated Cl concentrations in their litter, due to the application of sewage effluent, and consequently greater divergence between ash alkalinity determined by difference and titration. Nevertheless, the errors are likely to be relatively small and for purposes of developing broad rankings, either method would be satisfactory.

Substantial differences were found between species in ash alkalinity. Values ranged from approximately $250 \text{ cmol}_c \text{ kg}^{-1}$ for *Melia azedarach* to less than $50 \text{ cmol}_c \text{ kg}^{-1}$ in some eucalypt and pine samples.

The mean concentration of Ca in the eucalypt samples collected at Flushing meadows was 7.76 mg g^{-1} . This value is similar to the mean value of 7.6 mg g^{-1} observed in freshly collected green leaf material from 10 eucalypt species in a trial established in South Africa (Herbert and Robertson, 1991) of which *E. grandis*, *E. nitens*, *E. elata*, *E. saligna* and *E. viminalis* were common to both studies. Mengel and Kirkby (1978) observed that Ca is a relatively immobile element in the phloem of plant species, which is in contrast to Mg and K. This may in part be explained by the role played by Ca in the structural composition of plant material. Since the Ca levels observed in both senesced and fresh leaf material (Herbert and Robertson, 1991) were similar, it is suggested that this parameter may be used in predicting the ash alkalinity of plant material that is Ca dominant. Indeed, a significant relationship between Ca concentration and ash alkalinity was observed between samples collected from Flushing Meadows and Canberra (Figure 1.1). This result supports a previous finding using a smaller set of tree species and would support the notion that ash alkalinity could be estimated from a simple measurement of litter Ca in these tree species (Noble *et al.*, 1996).

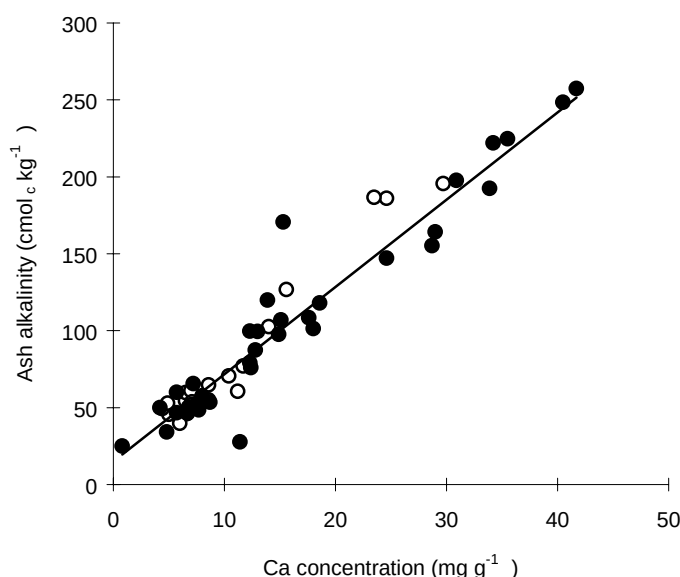


Figure 1.1. Relationship between leaf Ca concentration and ash alkalinity. Samples collected from Wagga Wagga effluent site (○) and those collected elsewhere, mainly in the Canberra area (●). Equation of line: $y = 14.47 (\pm 3.90) + 5.83 (\pm 0.22)x$; $r^2 = 0.927$; $n = 46$.

This study and others (Noble *et al.*, 1996) supports the thesis that there is a wide range of ash

alkalinities in tree and shrub leaf litter materials. In general, the indigenous tree species (ie. eucalypts and acacias) had lower nutrient contents and ash alkalinities than the exotic species, the exception being the indigenous *Melia azedarach* which had the highest ash alkalinity of all species sampled (Table 1.1). These differences may be related to differences in uptake of nutrients or different efficiencies in internal nutrient redistribution prior to leaf senescence. The fact that there appears to be a strong relationship between ash alkalinity and Ca concentration suggest that a simple measure of the latter may be sufficient to assess the liming potential of these materials as will be discussed in section 2 of results.

(2) The ability of leaf litter material to neutralise soil acidity.

Having established that leaf litter varied markedly in ash alkalinity depending on the species we then proceeded to examine the effects of the composition of different litter samples on soil properties. The benefits of incorporating organic matter into acid soils are well recognised (Hue and Amien, 1989). The incorporation of green manures in acid soils has been shown to lower levels of extractable Al and increase yields (Hoyt and Turner, 1975; Hue and Amien, 1989). A major cause of this is likely to be increases in pH. However, until our own work in this project (Noble *et al.*, 1996) and other recent work (Yan *et al.*, 1996), there has been relatively little attention paid to the direct role of organic matter in acidification-alkalisation reactions in the soil. With respect to soil pH, it has been shown that additions of organic matter can increase (Bessho and Bell, 1992; Tyson and Cabrera, 1993) or decrease (Tyson and Cabrera, 1993) soil pH. This may be due to the diversity in composition of organic matter from different sources or the time elapsing between addition and sampling. Soil pH can increase in the presence of reducing conditions due to an increase in microbial biomass during rapid decomposition (van Breemen *et al.*, 1983), the production of NH_3 during decomposition of organic N compounds (Hoyt and Turner, 1975) and the consumption of protons during decomposition of organic anions (Helyar and Porter, 1989; Noble *et al.*, 1996; Yan *et al.*, 1996). On the other hand the generation of protons from the nitrification process is a major contribution to acidification of soil (Helyar and Porter, 1989).

A further factor in the amelioration of acid soils by organic matter could be the formation of organo-Al complexes which lower the level of phytotoxic Al in the soil solution (Bartlett and Riego, 1972.; Bessho and Bell, 1992; Hue *et al.*, 1986). Leaf litter of *Eucalyptus camaldulensis* has been shown to decrease the monomeric Al concentration in solutions through the formation of organo-Al complexes (Harper *et al.*, 1995).

In this section we describe work on the changes in pH due to incubation with leaf litter and in the following section (section 3) the role of litter in complexing Al is examined.

The soil used in this series of incubation studies was an acid red podsolic (Dr 2.21, (Northcote, 1979)) from the Book Book area of NSW taken from the 0-10 cm layer. It had a low pH_{Ca} (3.95) and exchangeable acidity ($\text{Al} + \text{H}$) was the dominant component on the exchange complex. In spite of the low pH and high acid saturation, exchangeable Ca made up >30% of the CEC. Analyses from the batch collected for preliminary study is given in Table 2.1. Batches of soil collected later from the same soil pit gave similar but not identical values for pH and exchangeable cations.

Table 2.1. Chemical properties of the acid soil used in a series of incubation studies.

Horizon	Ca	Mg	K	Na	Al	Al + H	CEC	ECEC ^a	Acid Sat. (%)	pH	Organic Carbon (g kg ⁻¹)
	cmol _c kg ⁻¹										
A ₁											
0-10 cm	0.89	0.14	0.06	0.11	0.77	1.27	2.38	1.97	53.4	3.95	1.52

^a ECEC = Σ of exchangeable Ca, Mg, K, Na and Al
pH measured in 0.01M calcium chloride solution

Plant material was finely ground and mixed with soil at application rates equivalent to 5, 10, 20 or 40 t dry matter/ha/10cm depth of soil. Lime rates of 0, 0.5, 1.0, 2 and 4 t/ha were included for comparison. The soils were brought to field capacity with demineralised water and after 8 weeks incubation the soils were analysed for pH_{Ca}, organic carbon and exchangeable cations and rapidly reactive Al.

As expected, lime increased pH_{Ca}, decreased extractable, exchangeable and labile Al (Table 2.2). Each of the leaf litters at the lowest rate of application raised the pH_{Ca} above the control. Increasing rates of litter application further increased pH_{Ca}. However, in all cases other than in *Melia azedarach* samples, successive increments of litter had progressively less effect on pH_{Ca}. The least effective species in raising the soil pH_{Ca} were *Quercus palustris* (lot # 6), *Quercus robur* (lot # 9), liquidambar (lot # 14). In general the level of total Al in the dilute KCl extract (Al_T) tends to increase with increasing rates of leaf litter. This is assumed to be due to Al added in the litter material being released during decomposition. However, labile Al (Al_L) tends to decrease with addition of litter. The percent Al in forms other than Al_L thus increased considerably with increasing levels of litter addition. This increase is thought to be accounted for by the formation of soluble Al-organic complexes that are disassociated and detected as Al³⁺ by atomic absorption spectroscopy.

It is often assumed that at pH_{Ca} (0.01 M CaCl₂) values below 4.5 phytotoxic levels of Al may exist in the soil solution however, there appears to be a general but imprecise relationship between Al in CaCl₂ and pH_{Ca} since at equivalent pH values the measured Al³⁺ concentrations varied over a considerable range eg a 3 fold range at pH 4 (Figure 2.1). This suggests that the solubility of Al in the litter treatments is not entirely controlled by the same mineral phase as in the lime treatments. This would suggest that organic complexes with Al³⁺ play a greater part in controlling the level of monomeric Al³⁺ in solution in the case of the litter treatments over the period of incubation. However, the formation of organic complexes with Al³⁺ may be transient in that with time these complexes breakdown releasing Al³⁺ back into solution.

Figure 2.1. Relationship between soil pH and extractable aluminium (both measured in 0.01 M CaCl₂) after 8 weeks incubation of the soil with leaf litter or lime.

Table 2.2. Influence of lime and leaf litter material from several tree species on soil pH_{Ca} and selected Al components after an 8 week incubation at field moisture capacity. (Lot numbers refer to samples described in Table 1.1)

Lime or litter source	Lot #	Rate t ha ⁻¹	pH _{Ca}	Al in 0.01 M CaCl ₂ extract mg kg ⁻¹	Exch. Al cmol _c kg ⁻¹	Total Al in 0.005 M KCl (Al _T) μM	Labile Al in 0.005 M KCl (Al _L) μM
Control			3.67	22.2	0.89	40.73	16.13
Lime		0.5	3.69	15.3	0.77	35.56	15.83
		1.0	4.03	4.5	0.38	25.18	7.45
		2.0	4.45	1.4	0.10	48.15	2.48
		4.0	5.26	0.3	0.01	38.51	1.24
<i>U. procera</i>	1	5	3.85	9.8	0.76	30.37	6.21
		10	4.07	3.9	0.37	44.44	3.10
		20	4.44	1.2	0.13	70.37	3.72
		40	4.76	0.5	0.01	62.22	2.79
<i>Gladitsia sp</i>	2	5	4.09	7.5	0.59	35.55	4.34
		10	4.32	3.3	0.33	76.29	3.10
		20	4.52	1.3	0.11	58.51	1.24
		40	4.78	1.1	0.03	75.56	2.79
<i>Gladitsia sp.</i> Pods	3	5	3.84	15.6	0.91	30.37	8.38
		10	3.81	12.6	0.86	30.37	9.93
		20	3.97	8.2	0.63	44.44	9.00
		40	4.11	5.1	0.47	133.33	7.45
<i>Q. robur</i>	4	5	3.83	13.0	0.85	25.93	6.83
		10	3.95	7.9	0.65	29.62	4.34
		20	4.17	3.6	0.41	75.56	4.03
		40	4.34	2.1	0.21	104.44	1.86
<i>P. nigra</i>	5	5	4.10	7.3	0.56	34.07	4.34
		10	4.34	3.0	0.27	54.07	5.27
		20	4.55	1.6	0.10	80.74	5.58
		40	4.88	1.2	0.01	81.48	5.27
<i>Q. palustris</i>	6	5	3.87	14.6	0.98	30.37	7.45
		10	3.93	10.6	0.76	57.78	5.27
		20	3.95	8.2	0.66	85.92	10.55
		40	3.96	7.6	0.63	185.18	9.93
<i>Melia azedarach</i>	7	5	3.95	9.2	0.68	24.44	4.34
		10	4.24	4.2	0.33	62.22	3.41
		20	4.68	1.2	0.03	57.04	1.55
		40	5.64	0.9	0.01	115.55	5.58
<i>Q. robur</i> acorns	9	5	3.88	16.6	0.97	32.59	8.38
		10	3.84	14.1	0.90	35.56	8.06
		20	3.78	16.8	0.93	49.62	16.14
		40	3.87	11.4	0.89	91.11	22.97
<i>P. nigra</i>	10	5	4.01	9.7	0.70	39.26	7.76
		10	4.18	5.3	0.46	47.41	2.79
		20	4.45	2.1	0.18	54.07	2.17
		40	4.66	1.5	0.06	53.33	3.10
<i>M. azedarach</i>	11	5	4.1	9.3	0.69	34.07	4.34
		10	4.29	4.0	0.37	76.29	1.86
		20	4.69	1.4	0.05	51.11	6.83
		40	5.47	0.8	0.03	84.44	9.31

....continued

Table 2.2. (continued)

Litter source	Lot #	Rate t ha ⁻¹	pH _{Ca}	Al in 0.01 M CaCl ₂ extract mg kg ⁻¹	Exch. Al cmol _c kg ⁻¹	Total Al in 0.005 M KCl (Al _T) μM	Labile Al in 0.005 M KCl (Al _L) μM
<i>P. acerfolia</i>	12	5	4.03	11.2	0.77	28.88	9.62
		10	4.12	6.4	0.50	38.51	8.06
		20	4.35	3.2	0.24	60.00	6.83
		40	4.61	1.8	0.09	67.41	6.83
<i>C. sativa</i>	13	5	4.05	11.5	0.70	30.37	13.34
		10	4.13	7.5	0.51	48.89	10.55
		20	4.27	5.4	0.40	104.44	12.41
		40	4.43	3.7	0.20	131.11	15.52
<i>L. styraciflua</i>	14	5	3.86	14.2	0.81	51.85	10.55
		10	3.88	9.4	0.66	88.89	10.86
		20	4.02	6.2	0.54	180.74	13.04
		40	4.08	5.3	0.41	32.59	9.00
<i>F. oxycarpa</i>	15	5	3.92	9.8	0.61	94.81	6.21
		10	4.13	4.5	0.41	94.07	6.83
		20	4.50	1.7	0.12	255.56	8.69
		40	4.96	1.2	0.02	239.25	13.04
<i>M. azedarach</i>	16	5	4.84	7.4	0.53	23.70	7.14
		10	4.34	2.6	0.23	60.0	6.83
		20	4.77	0.9	0.03	71.11	6.83
		40	5.50	0.7	0.01	67.41	7.14
<i>Q. suber</i>	18	5	3.79	13.5	0.69	30.37	13.34
		10	4.26	7.8	0.51	31.11	8.07
		20	4.20	5.6	0.43	43.70	8.38
		40	4.21	4.2	0.34	114.07	6.83
<i>Q. suber</i> acorns	19	5	3.86	12.6	0.67	28.15	9.62
		10	3.87	11.0	0.58	34.81	9.93
		20	3.90	11.0	0.64	50.37	10.86
		40	3.87	8.5	0.57	105.92	12.42
<i>E. globulus</i>	20	5	3.95	13.7	0.81	33.33	20.48
		10	4.22	9.0	0.61	39.62	13.65
		20	4.47	4.6	0.40	81.11	14.27
		40	4.69	2.3	0.29	168.88	36.00
<i>A. mearnsii</i>	21	5	4.05	15.3	0.99	38.51	24.83
		10	4.01	13.1	0.80	38.88	26.69
		20	4.13	8.4	0.63	78.88	14.89
		40	4.45	3.6	0.90	132.22	18.00
<i>P. radiata</i>	22	5	4.04	16.3	0.90	37.77	29.17
		10	4.18	11.2	0.76	35.92	14.89
		20	4.32	7.5	0.60	91.11	15.51
		40	4.40	5.8	0.50	140.37	17.38
<i>P. radiata</i>	23	5	4.05	17.0	0.88	32.96	26.07
		10	4.13	13.6	0.80	28.51	13.03
		20	4.28	8.8	0.65	40.00	11.17
		40	4.38	6.1	0.53	67.40	15.51
<i>G. robusta</i>	24	5	4.11	14.0	0.80	27.40	18.00
		10	4.23	10.0	0.65	25.92	16.13
		20	4.53	4.6	0.39	57.40	8.69
		40	4.85	2.3	0.19	93.33	11.17

Table 2.3 Influence of lime and leaf litter material from several tree species on exchangeable bases in

soil after incubation. (Lot# refer to Table 1.1).

Soil after incubation. (Lot# refer to Table 1.1).							
Lime or litter source	Lot #	Rate t ha ⁻¹	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Σ Exch. Bases
cmol _c kg ⁻¹							
Control		0	1.48	0.23	0.15	0.20	1.54
Lime		0.5	1.85	0.24	0.15	0.21	2.24
		1.0	2.23	0.21	0.14	0.16	2.59
		2.0	3.63	0.21	0.13	0.15	3.97
		4.0	5.96	0.20	0.14	0.21	6.30
U. procera	1	5	1.88	0.43	0.29	0.26	2.60
		10	2.37	0.57	0.36	0.21	3.31
		20	3.40	0.89	0.56	0.21	4.85
		40	5.49	1.55	0.97	0.22	8.02
Gladitsia sp	2	5	1.85	0.32	0.24	0.23	2.42
		10	2.52	0.41	0.30	0.20	3.23
		20	3.33	0.57	0.44	0.20	4.35
		40	4.48	0.90	0.72	0.21	6.11
Gladitsia sp. Pods	3	5	1.40	0.28	0.28	0.20	1.97
		10	1.50	0.31	0.41	0.23	2.23
		20	1.62	0.34	0.65	0.20	2.62
		40	1.78	0.42	1.13	0.25	3.35
Q. robur	4	5	1.61	0.33	0.23	0.21	2.18
		10	1.98	0.43	0.28	0.20	2.69
		20	2.74	0.65	0.41	0.24	3.80
		40	3.15	0.89	0.58	0.21	4.63
P. nigra	5	5	1.91	0.42	0.23	0.19	2.57
		10	2.73	0.65	0.30	0.22	3.69
		20	3.56	1.01	0.41	0.21	4.98
		40	5.40	1.73	0.67	0.26	7.81
Q. palustris	6	5	1.53	0.35	0.25	0.22	2.14
		10	1.54	0.38	0.28	0.21	2.21
		20	1.73	0.51	0.39	0.18	2.64
		40	2.27	0.83	0.65	0.21	3.76
M. azedarach	7	5	1.93	0.33	0.34	0.23	2.60
		10	2.64	0.43	0.45	0.20	3.53
		20	4.14	0.64	0.78	0.25	5.57
		40	6.25	0.99	1.47	0.23	8.71
Q. robur acorns	9	5	1.30	0.27	0.26	0.18	1.84
		10	1.31	0.28	0.31	0.18	1.91
		20	1.57	0.35	0.54	0.21	2.47
		40	1.70	0.45	0.89	0.19	3.04
P. nigra	10	5	1.86	0.42	0.22	0.20	2.51
		10	2.40	0.59	0.28	0.17	3.27
		20	3.46	0.95	0.35	0.21	4.77
		40	4.58	1.51	0.52	0.23	6.61

continued

Table 2.3 (continued)

Litter source	Lot #	Rate t ha ⁻¹	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Σ Exch. bases
			cmol _c kg ⁻¹				
<i>M. azedarach</i>	11	5	1.95	0.37	0.31	0.19	2.64
		10	2.51	0.47	0.43	0.18	3.42
		20	3.48	0.64	0.69	0.24	4.81
		40	5.72	1.09	1.29	0.19	8.10
<i>P. acerfolia</i>	12	5	1.74	0.32	0.23	0.23	2.30
		10	2.02	0.35	0.26	0.24	2.64
		20	2.60	0.45	0.33	0.18	3.39
		40	3.68	0.66	0.51	0.20	4.86
<i>C. sativa</i>	13	5	1.20	0.31	0.19	0.17	1.71
		10	1.54	0.47	0.24	0.22	2.26
		20	2.17	0.79	0.35	0.17	3.31
		40	2.78	1.27	0.54	0.18	4.60
<i>L. styraciflua</i>	14	5	1.33	0.34	0.16	0.19	1.84
		10	1.54	0.48	0.18	0.22	2.20
		20	2.09	0.82	0.24	0.20	3.16
		40	2.83	1.32	0.29	0.20	4.44
<i>F. oxycarpa</i>	15	5	1.43	0.33	0.46	0.17	2.23
		10	1.59	0.42	0.71	0.18	2.72
		20	1.99	0.59	1.30	0.21	3.89
		40	2.65	0.90	2.35	0.22	5.90
<i>M. azedarach</i>	16	5	1.69	0.37	0.20	0.19	2.26
		10	2.37	0.54	0.23	0.16	3.14
		20	3.45	0.82	0.36	0.19	4.64
		40	5.72	1.51	0.58	0.22	7.81
<i>Q. suber</i>	18	5	1.36	0.27	0.16	0.16	1.80
		10	1.56	0.31	0.17	0.17	2.04
		20	1.82	0.39	0.19	0.22	2.40
		40	2.53	0.58	0.25	0.19	3.36
<i>Q. suber</i> acorns	19	5	1.16	0.25	0.22	0.19	1.64
		10	1.11	0.25	0.25	0.17	1.61
		20	1.13	0.29	0.39	0.17	1.81
		40	1.16	0.35	0.64	0.14	2.16
<i>E. globulus</i>	20	5	1.63	0.34	0.19	0.25	2.17
		10	1.95	0.42	0.23	0.32	2.60
		20	2.44	0.60	0.29	0.41	3.33
		40	3.09	0.91	0.42	0.54	4.43
<i>A. mearnsii</i>	21	5	1.56	0.32	0.28	0.22	2.17
		10	1.63	0.34	0.24	0.27	2.22
		20	1.91	0.45	0.32	0.25	2.69
		40	6.24	1.68	1.10	0.71	9.03
<i>P. radiata</i>	22	5	1.55	0.30	0.19	0.19	2.05
		10	1.65	0.34	0.22	0.22	2.22
		20	1.82	0.39	0.24	0.19	2.45
		40	2.21	0.53	0.33	0.20	3.07
<i>P. radiata</i>	23	5	1.46	0.30	0.19	0.26	1.95
		10	1.55	0.35	0.20	0.21	2.10
		20	1.65	0.44	0.24	0.25	2.34
		40	2.09	0.66	0.35	0.27	3.10
<i>G. robusta</i>	24	5	1.61	0.29	0.20	0.21	2.10
		10	1.80	0.33	0.24	0.22	2.38
		20	2.21	0.40	0.31	0.21	2.94
		40	3.35	0.60	0.51	0.22	4.46

Table 2.4. Influence of lime and leaf litter from several tree species collected at Flushing

Meadows, Wagga Wagga on exchangeable bases in soil after incubation. (FM# refer to lot numbers in Table 1.1)

Lime or litter source	FM #	Rate t ha ⁻¹	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Σ Exch. bases
cmol _c kg ⁻¹							
Control		0	1.48	0.23	0.15	0.20	1.54
Lime		0.5	1.85	0.24	0.15	0.21	2.24
		1.0	2.23	0.21	0.14	0.16	2.59
		2.0	3.63	0.21	0.13	0.15	3.97
		4.0	5.96	0.20	0.14	0.21	6.30
<i>E. grandis</i>	1	5	1.90	0.43	0.34	0.18	3.60
		10	2.07	0.46	0.38	0.23	3.65
		20	2.61	0.58	0.46	0.35	4.29
		40	3.17	0.70	0.59	0.57	5.22
<i>E. nitens</i>	2	5	1.73	0.45	0.37	0.19	3.29
		10	1.83	0.47	0.41	0.21	3.39
		20	1.94	0.53	0.49	0.26	3.62
		40	2.36	0.69	0.72	0.69	4.52
<i>E. proinqua</i>	3	5	1.78	0.45	0.35	0.21	2.50
		10	1.82	0.47	0.44	0.39	3.66
		20	2.07	0.56	0.44	0.40	3.78
		40	2.56	0.72	0.58	0.64	4.70
<i>E. henryi</i>	4	5	1.69	0.45	0.34	0.16	3.26
		10	1.87	0.49	0.38	0.24	3.53
		20	2.19	0.57	0.46	0.30	3.90
		40	2.59	0.68	0.57	0.50	4.56
<i>E. pilularis</i>	5	5	1.59	0.46	0.36	0.23	3.26
		10	1.75	0.52	0.42	0.36	3.59
		20	1.80	0.59	0.51	0.56	3.84
		40	2.27	0.88	0.79	1.07	5.28
<i>E. dunnii</i>	6	5	1.72	0.45	0.36	0.17	3.31
		10	1.78	0.49	0.39	0.21	3.36
		20	2.18	0.60	0.52	0.33	3.89
		40	2.72	0.78	0.81	0.72	5.14
<i>E. saligna</i>	7	5	1.67	0.43	0.34	0.19	3.19
		10	1.89	0.49	0.36	0.23	3.33
		20	2.28	0.61	0.41	0.35	3.87
		40	1.86	0.83	0.55	0.60	4.94
<i>E. regnans</i>		5	1.55	0.43	0.34	0.18	3.03
		10	1.62	0.47	0.38	0.22	3.20
		20	1.72	0.56	0.48	0.35	3.48
		40	1.57	0.61	0.52	0.41	3.28
<i>E. globulus</i>	9	5	1.51	0.40	0.33	0.17	3.05
		10	1.65	0.44	0.40	0.21	3.16
		20	1.82	0.51	0.51	0.30	3.45
		40	2.17	0.66	0.78	0.54	4.36

(continued)

Table 2.4 (continued)

Lime or litter source	FM #	Rate t ha ⁻¹	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Σ Exch. bases
cmol _c kg ⁻¹							
<i>E. elata</i>	10	5	1.51	0.40	0.32	0.17	3.01
		10	1.66	0.45	0.36	0.25	3.32
		20	1.83	0.53	0.44	0.36	3.57
		40	2.13	0.66	0.59	0.59	4.22
<i>E. viminalis</i>	11	5	1.45	0.38	0.34	0.14	2.88
		10	1.62	0.42	0.40	0.19	3.19
		20	1.77	0.47	0.44	0.25	3.29
		40	2.12	0.58	0.61	0.38	3.91
<i>E. cloeziana</i>	12	5	1.46	0.40	0.31	0.21	2.98
		10	1.52	0.44	0.33	0.29	3.11
		20	1.61	0.51	0.38	0.48	3.38
		40	1.84	0.66	0.43	0.85	4.08
<i>P. tomentosa</i>	13	5	1.59	0.44	0.40	0.11	2.97
		10	1.79	0.53	0.55	0.09	3.31
		20	2.24	0.71	0.84	0.10	4.00
<i>A. melanoxylon</i>	14	5	1.45	0.39	0.31	0.11	2.86
		10	1.59	0.44	0.36	0.17	3.05
		20	1.72	0.51	0.43	0.23	3.18
		40	1.99	0.66	0.57	0.36	3.74
<i>A. melanoxylon</i>	16	5	1.54	0.41	0.32	0.13	2.94
		10	1.55	0.44	0.34	0.18	2.99
		20	1.64	0.50	0.43	0.26	3.22
		40	1.89	0.66	0.57	0.34	3.69
<i>A. melanoxylon</i>	17	5	1.51	0.42	0.30	0.15	2.87
		10	1.49	0.43	0.32	0.18	2.89
		20	1.71	0.54	0.38	0.26	3.22
		40	1.91	0.72	0.49	0.46	3.75
<i>A. elata</i>	18	5	1.49	0.39	0.29	0.13	2.89
		10	1.62	0.46	0.34	0.19	3.08
		20	1.87	0.54	0.34	0.25	3.34
		40	2.38	0.71	0.43	0.38	4.14
<i>E. triflora</i>	19	5	1.37	0.34	0.33	0.24	2.76
		10	1.44	0.37	0.41	0.41	3.07
		20	1.53	0.41	0.55	0.76	3.46
		40	1.81	0.48	0.90	1.42	4.76
<i>P. nigra</i>	20	5	1.81	0.49	0.39	0.10	3.23
		10	2.12	0.61	0.51	0.14	3.58
		20	2.75	0.85	0.77	0.15	4.57
		40	3.98	1.39	1.26	0.10	6.75
<i>P. nigra</i>	21	5	1.74	0.49	0.43	0.10	3.22
		10	2.05	0.61	0.58	0.09	3.56
		20	2.66	0.87	0.97	0.10	4.65
		40	3.60	1.34	1.66	0.11	6.74

In the leaf litter treatments, exchangeable Ca²⁺ and Mg²⁺ increased at the expense of Al (Table 2.3) such that at a rate of 40 t ha⁻¹ in the case of *M. azedarach* (lot# 16) the average saturation percentages of the ECEC (sum of exchangeable Ca²⁺, Mg²⁺, K⁺, Na⁺ and Al³⁺) for Ca²⁺ + Mg²⁺ and Al³⁺ were 90 and 0 % respectively compared to 65 and 34 % respectively in the

control after incubation. In general, the increase in Ca^{2+} and Mg^{2+} on the exchange complex reflected the elemental content of the materials applied. The relationship between Ca applied in litter and Ca^{2+} on the exchange complex after incubation is given in Figure 2.2.

Figure 2.2. Relationship between the amount of Ca applied in the litter to soil and the increase in exchangeable Ca in the soil after 8 weeks incubation. Equation of the regression: $y = 0.285(\pm 0.005) + 0.675(\pm 0.014)x$; $r^2 = 0.941$; $n = 140$.

In order to evaluate the liming potential of each of the leaf litter samples, rates of application were converted to kg CaCO_3 assuming that 1 kmol H^+ requires 50 kg CaCO_3 to be neutralised. A highly significant linear relationship between pH_{Ca} and equivalent CaCO_3 rate was obtained (Figure 2.3).

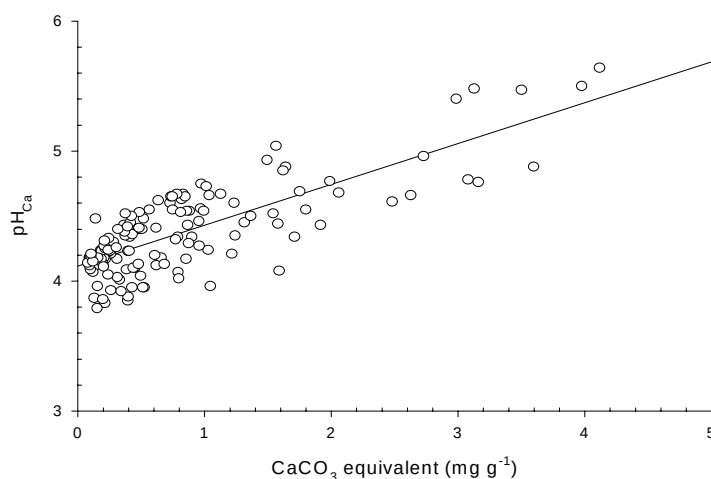


Figure 2.3. Relationship between ash alkalinity, expressed as CaCO_3 equivalents of leaf litter added to soil and final pH_{Ca} after 8 weeks incubation. Equation to regression: $y = 4.115(\pm 0.024) + 0.314(\pm 0.020)x$; $r^2 = 0.789$; $n = 140$.

More detail of the relationship between lime equivalents added as litter and the soil pH after 8 weeks of incubation is shown in Figure 2.4 for a few tree species. The data is taken from the preliminary study. The litter source which was most effective at raising pH_{Ca} was *Melia* which had a neutralisation capacity close to that of lime. Some of the other species diverged from the lime line and this may be directly related to the extent of decomposition in 8 weeks.

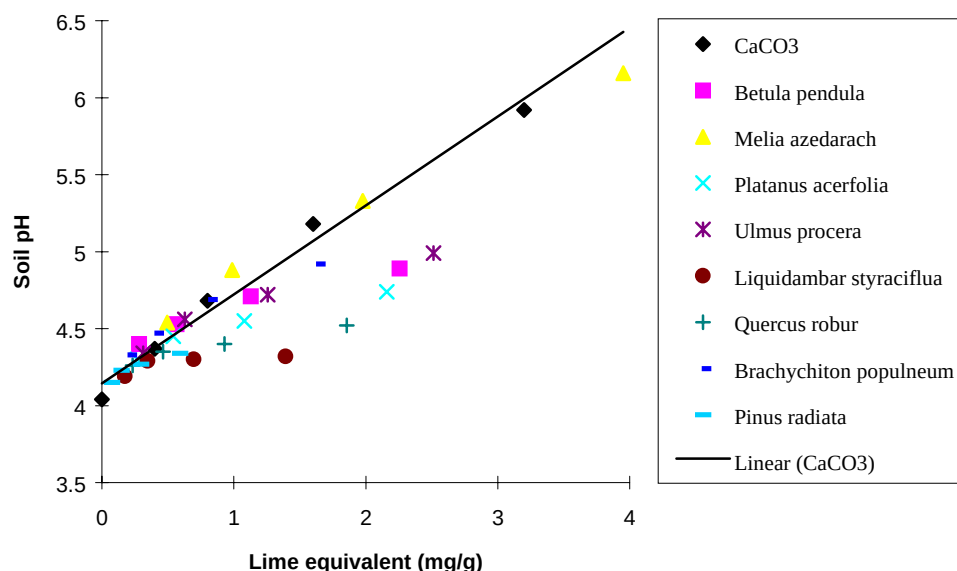


Figure 2.4 Relationship between ash alkalinity, expressed as lime equivalents of leaf litter of 8 species and calcium carbonate added to soil and pH_{Ca} after 8 weeks incubation. Equation for line fitted to lime points: $y = 4.145 + 0.5775x$; $r^2 = 0.984$; $n = 5$.

The suggestion that in 8 weeks the litter from the different species may have decomposed to different degrees is supported by a further examination of the relationship between Ca added in litter and exchangeable Ca^{2+} measured after incubation. Considering all treatments together there was a significant linear regression between the two (Figure 2.2). However, as observed in our preliminary study (Noble *et al.*, 1996) if one considers the selected species individually, there were appreciable differences in this relationship. This is apparent from the slopes of the linear regression equations relating exchangeable Ca^{2+} to Ca added (Table 2.4).

Table 2.4. Slopes of the linear regressions fitted to the relationship between Ca added (x) exchangeable Ca (y) for selected species. Values in brackets represent the S.E.

Species	Slope	r^2
<i>Melia azedarach</i>	0.678 (± 0.020)	0.99
<i>Platanus acerfolia</i>	0.650 (± 0.027)	0.99
<i>Betula pendula</i>	0.442 (± 0.024)	0.99
<i>Ulmus procera</i>	0.683 (± 0.013)	0.99
<i>Brachychiton populneus</i>	0.575 (± 0.066)	0.97
<i>Liquidambar styraciflua</i>	0.573 (± 0.024)	0.99
<i>Quercus robur</i>	0.464 (± 0.069)	0.95
<i>Pinus radiata</i>	0.724 (± 0.041)	0.99

The marked differences in the slopes of the regressions may reflect differences in the release

of Ca from the various organic materials due to differences in the degree of their decomposition over the 8 week incubation period. Given that this proposition is still to be tested, the data suggests that litter from *Melia*, *Platanus*, *Ulmus*, and *Pinus* was more completely decomposed than litter from *Betula* or *Quercus*.

The results clearly indicate that the changes in pH_{Ca} can to a large extent be attributed to the neutralisation capacity of the litter material as measured by the ash alkalinity. As is evident from Figure 2.3 there is divergence about a general liming potential line. This may in part be attributed to the degree of decomposition that was achieved over the 8 week incubation period. There is evidence from recent studies by Marschner and Noble (1998) that after a 3 week period of incubation the decomposition of selected litters was less than 50%. It could be argued that differences between species and treatments may be in part attributable to differences in net mineralisation or immobilisation. In the initial study undertaken with a limited range of species, Noble *et al.* (1996) observed that lime tended to increase the soil nitrate level when compared to the control (Table 2.5), indicating net mineralisation of N resulting in a greater pool of protons to be neutralised. In contrast, leaf litter treatments markedly lowered soil nitrate indicating net immobilisation of N during decomposition of leaf litter. This would have resulted in a net consumption of protons.

Table 2.5. Influence of lime and leaf litter on soil mineral N after incubation.

Treatment	Rate (mg g^{-1})	Mineral N ($\mu\text{g g}^{-1}$)	
		NH_4	NO_3^-
Control		4.0	25.3
Lime	0.4	3.6	26.8
	0.8	4.0	29.4
	1.6	4.4	37.2
	3.2	4.0	56.9
<i>Melia azedarach</i>	4	3.4	5.1
	8	3.3	3.2
	16	1.9	2.3
	32	3.7	0.2
<i>Liquidambar styraciflua</i>	4	4.5	7.3
	8	4.7	1.9
	16	5.0	1.6
	32	4.7	1.3
<i>Pinus radiata</i>	4	4.9	4.7
	8	10.3	1.5
	16	10.1	0.8
	32	10.2	1.1
LSD (0.05)		1.8	8.3

However, the contribution of the N-cycle processes to the change in pH would have been relatively smaller compared to that of organic anion decomposition. For example, calculations using the treatment with *M. azedarach* added at 32 mg g^{-1} showed that the net effect of changes in soil nitrate and ammonium (relative to the control) would have been equivalent to

adding 0.88 mg CaCO₃ per gram of soil. Consequently it can be concluded that in the 8 week period of incubation, the N-cycle contributed relatively little to the overall proton pool.

The results discussed above show that decomposing leaf litter increases soil pH and that ash alkalinity of the litter can be used to predict the extent of the effect. Further discussion of these effects is to found in Paper 8 (listed under Publications arising) where samples collected from the mainly indigenous species grown at the Flushing Meadows site are compared with selected samples collected in Canberra from mainly exotic deciduous species.

(3) The capacity of leaf litter extracts to complex phytotoxic Al.

Within natural plant communities the percolation of water through the litter layer dissolves organic compounds which then influence the pedogenic development of soil horizons. Research into the addition of plant materials and manures to acid soils has shown that there is a reduction in the levels of phytotoxic Al and an increase in crop yield. The reduction of phytotoxic Al in soil by decomposing litter has been thought to be due, in part, to the formation of organo-Al complexes particularly with low-molecular weight organic acids (Hue and Amien, 1989). Soluble metal chelates can reduce the concentrations of toxic metal ions in solution. Bloom *et al.* (1979) has shown that the chelation of Al³⁺ by humic acids in acid soils controls the soil solution concentration of toxic Al³⁺. Similar results have been reported by Hue *et al.* (1986) who showed that Al³⁺ chelation with short chain carboxylic acids, such as citric, oxalic and tartaric acids, is an important Al detoxifying process in acid subsoils where deep roots would otherwise suffer Al³⁺ toxicity. McColl and Pohlman (1986) found that organic acids from *Pinus ponderosa* litter leached more Al and other metals than mineral acids at comparable pH and concentration. They identified oxalic, malic, citric, protocatechuic and salicylic acids as chelating organic acids. In terms of binding and transporting capacity of metals, it is generally agreed that fulvic acids are the most important organic fractions.

In this section the Al complexing ability of the water soluble fraction of leaf litter extracts is described. The water soluble fraction of each of the leaf litters was extracted using the methods of Shotyk and Sposito (1988). In brief 10 g of oven dried leaf litter was extracted in 400 mL of deionised water over 16 hr on a reciprocating shaker. The extract was filtered under vacuum through a Whatman 42 filter paper, 0.45 µm and 0.22 µm Millipore membrane filter. The filtered extract was stored under N₂ gas at 4°C until use. The dissolved organic carbon concentration was determined on the filtered extract using the modified Mebius method of Yoemans and Bremner (1988).

The complexing ability of the leaf litter extracts was measured at a standard pH of 4.0 and at a dissolved organic carbon concentration of 34.8 mg L⁻¹. This was to make a qualitative comparison of the different extracts. Aliquots of leaf litter extract were transferred to a glass beaker and the volume made up to 48 mL. The pH of the extract was adjusted to 4.5 with either HCl or NaOH (0.05, 0.005 or 0.0005 M) while continuously stirring in order to prevent the possible formation of polymeric Al species. Various amounts of the AlCl₃ stock solution were added to the extracts to give a range of total Al (Al_T) concentrations of 0 to 60 µM in 10 µM increments. The pH of the Al-extract mixtures were then adjusted to pH 4.0 and allowed to equilibrate for 1 hr. Duplicate samples were analysed.

Labile Al (Al_L) was measured in the Al-extract mixtures using the method of James *et al.* (1983) with the modifications as proposed by Shotyk and Sposito (1988). Replicate

absorbency measurements were made on the organic phase in each case. The 8-hydroxyquinoline 15 second reaction for the measurement of Al_L has been interpreted to measure the approximate concentrations of Al^{3+} and $AlOH^{2+}$ in solution (Hodges, 1987; James *et al.*, 1983).

Standard solutions over the same range of Al concentrations as in the Al-leaf litter extracts were prepared at pH 4.0 and 4.5 using the same stock solutions. The Al_L concentration was measured using the methodology previously described and Al speciation undertaken for each of the solutions using the computer program GEOCHEM and the Al hydrolysis equilibrium constants of May *et al.* (1979). GEOCHEM predicted that Al_L (Al^{3+} and $AlOH^{2+}$) in the standard solutions was 99.4 and 94.2 % of the total Al at pH 4.0 and 4.5 respectively. The predicted concentration of Al_L was then plotted against the absorbency for each of the standard solutions. Highly significant linear correlations were observed with the same slope regardless of the pH of the solution. From this standard curve the concentration of Al_L was determined in the test solutions containing the Al-leaf litter extracts.

The lot numbers of the samples used refer to the list in Table 1.1. In addition to the first set of species tested (Table 3.1a) litter from the shrub tagasaste grown near Yass NSW and from a group of largely indigenous species collected from a species trial established at Flushing Meadows, NSW, was tested for their Al complexing ability. In this case a single sample was used to evaluate the complexing ability which is presented in Table 3.1b. Since the trees in the latter case, were grown on the same soil under the same management it is assumed that variability due to environmental differences would be minimal.

The effects of varying levels of total Al (Al_T) on the concentration of kinetically reactive Al_L in the presence of leaf litter extracts are presented in Tables 3.1a and 3.1b. Highly significant differences in Al complexing ability were observed between species over this range of Al_T . At an Al_T concentration of 60 μM the concentration of labile Al ranged from approximately 3 μM in extract of leaf litter from *Eucalyptus nitens* to 46.0 μM in extract from *Acacia melanoxylon*. Leaf litter extracts from several Eucalypts, *Castanea sativa* and *Quercus suber* all showed high complexing ability with Al_L concentrations of <10 μM at an Al_T concentration of 60 μM (Table 3.1a). In contrast, leaf litter extracts from *Melia azedarach*, *Paulownia tormentosa*, *Grevillea robusta*, *Acacia sp* and one of the collections of *Pinus radiata* had low complexing ability. (Table 3.1a) Within the eucalypts the concentration of labile Al at a nominal concentration of 60 μM Al ranged between 1 (*E. grandis*) to 21 (*E. elata*) μM , however the majority of the species had levels considerably below this upper limit (Table 3.1b)

Table 3.1a. Labile Al measured in mixtures of leaf litter extract and added Al.

Lot #	Species	Total Al Concentration (μM)					
		10	20	30	40	50	60
		Labile Al Concentration (μM)					
1	<i>Ulmus procera</i>	4.7	9.5	16.0	17.0	20.3	26.6
2	<i>Gladitsia sp</i>	4.3	9.5	11.3	18.2	26.1	29.7
4	<i>Quercus robur</i>	3.1	4.7	7.8	11.3	15.4	21.0
5	<i>Populus nigra</i>	3.2	7.2	12.0	18.1	23.4	29.4
6	<i>Quercus palustris</i>	1.0	3.7	5.9	9.7	11.0	15.2
7	<i>Melia azedarach</i>	3.6	7.5	13.0	17.8	23.2	28.0
8	<i>Quercus robur</i>	0.6	2.4	4.9	7.9	11.2	13.8
10	<i>Populus nigra</i>	2.8	5.4	9.9	14.9	20.1	24.9
11	<i>Melia azedarach</i>	3.4	8.0	12.9	16.5	24.5	30.2
12	<i>Platanus acerfolia</i>	3.8	9.4	14.5	19.6	25.1	29.6
13	<i>Castanea sativa</i>	0.4	1.8	2.2	2.9	4.9	7.7
14	<i>Liquidambar styraciflua</i>	2.4	4.5	6.4	8.0	9.0	11.7
15	<i>Fraxinus oxycarpa</i>	4.2	9.2	13.4	17.9	21.1	28.5
16	<i>Melia azedarach</i>	3.1	7.8	11.1	15.2	18.5	25.1
18	<i>Quercus suber</i>	0.8	1.4	2.8	3.9	5.2	7.7
20	<i>Eucalyptus globulus</i>	0.3	1.3	3.0	5.2	6.9	8.9
21	<i>Acacia mearnsi</i>	5.9	10.2	13.6	20.6	25.7	29.7
22	<i>Pinus radiata</i>	4.6	8.9	14.4	18.3	25.0	31.4
23	<i>P. radiata</i>	3.6	5.9	7.4	8.2	10.2	14.4
24	<i>Grevillea robusta</i>	5.2	9.9	16.5	20.5	27.0	32.1
25	<i>Eucalyptus nitens</i>	0.1	0.3	1.2	2.3	5.5	6.5
26	<i>E. nitens</i>	1.5	4.1	5.9	7.6	13.6	19.4
27	<i>E. globulus</i>	2.4	3.9	7.0	10.1	13.5	17.9
28	<i>E. globulus</i>	0.4	1.3	2.9	4.9	7.6	9.5
LSD				2.7			
5%							

Table 3.1b. Labile Al measured in mixtures of leaf litter extract and added Al

Lot #	Species	Total Al Concentration (μM)					
		10	20	30	40	50	60
		Labile Al Concentration (μM)					
FM1	<i>Eucalyptus grandis</i>	0.31	0.95	1.27	1.43	1.27	1.11
FM2	<i>E. nitens</i>	0.0	4.78	5.09	6.68	14.65	14.65
FM3	<i>E. propinqua</i>	1.27	1.27	2.86	3.50	5.41	6.37
FM4	<i>E. henryi</i>	0.31	1.27	3.18	3.82	6.37	7.64
FM5	<i>E. pilularis</i>	0.0	0.0	0.95	1.27	4.14	3.18
FM6	<i>E. dun nii</i>	0.95	6.68	4.45	9.55	14.97	14.97
FM7	<i>E. saligna</i>	0.95	2.86	5.41	7.96	9.87	14.65
FM8	<i>E. regnans</i>	2.86	5.41	9.24	12.74	18.47	19.43
FM9	<i>E. globulus</i>	1.75	2.70	3.82	6.52	9.39	11.94
FM10	<i>E. elata</i>	1.91	5.73	11.14	14.01	16.56	21.34
FM11	<i>E. viminalis</i>	7.00	8.44	12.90	14.97	14.81	17.83
FM12	<i>E. cloeziana</i>	1.27	2.86	3.50	4.93	10.98	10.83
FM13	<i>Paulownia tomentosa</i>	4.77	10.19	15.28	20.06	26.75	34.56
FM14	<i>Acacia melanoxylon</i>	7.32	13.69	21.66	27.55	37.90	46.82
FM15	<i>Populus nigra</i>	1.91	5.09	10.83	13.85	18.15	21.34
FM16	<i>A. melanoxylon</i>	5.57	12.10	17.99	18.63	23.09	32.49
FM17	<i>A. melanoxylon</i>	5.73	11.78	18.47	20.06	22.45	27.07
FM18	<i>A. elata</i>	8.28	10.98	17.04	21.66	25.16	26.43
FM19	<i>E. triflora</i>	1.11	2.38	3.18	5.41	7.00	11.62
FM20	<i>Populus nigra</i>	3.18	6.68	9.55	6.68	19.74	27.55
FM21	<i>Populus nigra</i>	4.30	7.96	14.33	17.99	20.06	28.50
34	<i>Chamaecytisus proliferus</i>	1.5	4.1	5.9	7.6	13.6	19.4

The metal complexing ability of these water soluble organic extracts would be dependent on the organic molecules present, their concentration and acidic properties of organic functional groups (Bloomfield, 1964). To further examine the ability of the leaf litter extracts to complex Al so that comparative assessments of these materials could be made, simple linear regressions of Al_T versus labile Al were undertaken for each of the species analysed in detail (data included in Table 3.1a) and regressions are given in Table 3.2. The intercept was forced through zero and the slopes of the lines used to compare species. Highly significant linear correlations were observed in all cases, although in the case of *E. nitens* the best fit of the data was described by an exponential function. The greater the slope of the line the lower the ability of the extract to complex Al. The range of slopes varied from 0.088 in *E. nitens* to 0.533 in *Grevillea robusta*.

Table 3.2. Organic carbon and pH of 1:40 extract of ground leaf litter in water, the labile Al after reaction with 60 μM Al and the slope of the regression of labile Al following reaction of extract with Al. The reaction was at pH 4.0 and all extracts were diluted to a common dissolved organic carbon concentration of 0.117 mg L^{-1} (lot numbers refer to Table 1.1)

Lot #	Species	Properties of initial extract		Labile Al after reaction of extract with 60 μM Al μM labile Al	Regression of labile Al after reaction on initial Al added		
		Organic carbon (%)	pH		Slope	St. error	r^2
1	<i>Ulmus procera</i>	0.279	5.96	26.6	0.439	0.015	0.98
2	<i>Gladitsia sp</i>	0.240	5.61	29.7	0.483	0.018	0.98
4	<i>Quercus robur</i>	0.121	4.98	21.0	0.309	0.020	0.96
5	<i>Populus nigra</i>	0.292	5.59	29.4	0.462	0.016	0.98
6	<i>Quercus palustris</i>	0.237	4.40	15.2	0.232	0.010	0.98
7	<i>Melia azedarach</i>	0.238	5.63	28.0	0.454	0.010	0.99
8	<i>Quercus robur</i>	0.233	5.67	13.8	0.211	0.014	0.96
10	<i>Populus nigra</i>	0.331	6.12	24.9	0.388	0.016	0.98
11	<i>Melia azedarach</i>	0.269	5.57	30.2	0.471	0.018	0.98
12	<i>Platanus acerfolia</i>	0.154	5.72	29.6	0.493	0.006	0.99
13	<i>Castanea sativa</i>	0.241	4.18	7.7	0.103	0.010	0.92
14	<i>Liquidambar styraciflua</i>	0.284	3.80	11.7	0.196	0.005	0.98
15	<i>Fraxinus oxycarpa</i>	0.256	4.83	28.5	0.452	0.009	0.99
16	<i>Melia azedarach</i>	0.169	6.23	25.1	0.391	0.009	0.99
18	<i>Quercus suber</i>	0.065	4.30	7.7	0.110	0.007	0.96
20	<i>Eucalyptus globulus</i>	0.339	4.45	8.9	0.132	0.009	0.95
21	<i>Acacia mearnsi</i>	0.206	5.28	29.7	0.502	0.009	0.99
22	<i>Pinus radiata</i>	0.129	4.30	31.4	0.497	0.011	0.99
23	<i>P. radiata</i>	0.224	3.66	14.4	0.229	0.012	0.95
24	<i>Grevillea. robusta</i>	0.172	5.41	32.1	0.533	0.006	0.99
25	<i>Eucalyptus nitens</i>	0.175	4.06	6.5	0.088	0.014	0.87
26	<i>E. nitens</i>	0.169	3.90	19.4	0.268	0.024	0.93
27	<i>E. globulus</i>	0.155	3.98	17.9	0.271	0.012	0.98
28	<i>E. globulus</i>	0.146	4.82	9.5	0.139	0.012	0.94

Whilst there is clearly considerable variation in the ability of these soluble leaf litter extracts to complex Al the aforementioned study does not allow one to extrapolate to field conditions without some form of validation. Therefore a more detailed experiment was undertaken to evaluate the ability of two of these species to effect changes on soil chemical properties. The two species selected for further evaluation were:

- *Melia azedarach* (high ash alkalinity, Table 1.1 and low complexing ability, Table 3.2)
- and *Castanea sativa* (moderate ash alkalinity and high complexing ability).

We made extra measurements on the water soluble extracts and, in addition, we leached the extracts through soil packed in columns and measured the composition of the leachate and changes in chemistry of the soil. The columns consisted of 15 cm long perspex tubes with an internal diameter of 5 cm, split longitudinally and taped together with masking tape. Columns were packed to a depth of 10 cm with 300g of soil at a uniform bulk density of 1.52 Mg m^{-3} and a total pore

volume of 82.66 cm³. The water soluble leaf litter extracts of the two species were filtered through a 45 µm HAWP Millipore filter and antibiotics Cefotaxime (30 mg dm⁻³ and Trimethoprim (20 mg dm⁻³) were added to reduce microbial growth (Kerven *et al.* 1991). The leaf litter extracts were applied at a rate of 5 cm³ h⁻¹ through a peristaltic pump. A 3 mm thick piece of inert sponge was placed on top of the soil surface to distribute the extract evenly and prevent surface impact. The columns were leached over 4 days with approximately 2.5 pore volumes of extract. After leaching the columns were allowed to drain, then split open and sectioned into 1 cm sections for the top 2 cm of the column and into 2 cm sections for rest of the column. Soils were dried at 40 °C in a forced draft oven for 48 h, and passed through a 2 mm mesh sieve before being stored in polyethylene bags. Soil pH was measured in 1:5 soil : 0.01 M CaCl₂. Soluble salts were washed from samples by shaking in 60 % ethanol (w/w), centrifuged and the supernatant discarded. Exchangeable cations were extracted using 0.1 M BaCl₂/0.1 M NH₄Cl (Gillman and Sumpter 1986). The soil cation exchange capacity was determined using the compulsive exchange method of Gillman and Sumpter (1986). Labile Al was extracted with 0.005 M KCl, close to the ionic strength of the soil solution and measured by the 8-hydroxyquinoline 15 second reaction as previously described after filtration through a 0.45 µm Millipore membrane filter. Total Al was determined by atomic absorption spectrophotometry using a nitrous oxide/acetylene flame.

Composition of litter and extracts

The concentrations of most of the elements measured were higher in *M. azedarach* litter than in *C. sativa* litter (Table 1.1). The exceptions were K and P which were slightly higher in *C. sativa*. The cation excess, the difference between total cations and major inorganic anions, was higher in *M. azedarach* litter than in *C. sativa* litter, due largely to the three-fold higher Ca concentration in the former.

The pH, EC, organic carbon and elemental concentration of the water extracts of leaf litter are presented in Table 3.3. The pH of the extract from *M. azedarach* was 2.2 pH units higher than that from *C. sativa*. *M. azedarach* extract was lower in Al, Fe, Mn and carbon, but higher in Ca, Mg, Na, and K. The mineral composition of the extracts reflected differences in the mineral content of the litter of the two species and differences in extraction percentages. *M. azedarach* contained 40.5 mg Ca g⁻¹ and about 50 % of this was in the extract, whereas *C. sativa* litter had lower Ca (13.9 mg g⁻¹) and only about 4 % of this was in the extract.

Table 3.3. Chemical composition of water soluble extracts from *M. azedarach* and *C. sativa* leaf litter. (Units are: electrical conductivity (EC), dS m⁻¹; organic carbon, mg mL⁻¹; inorganic elements, µg mL⁻¹)

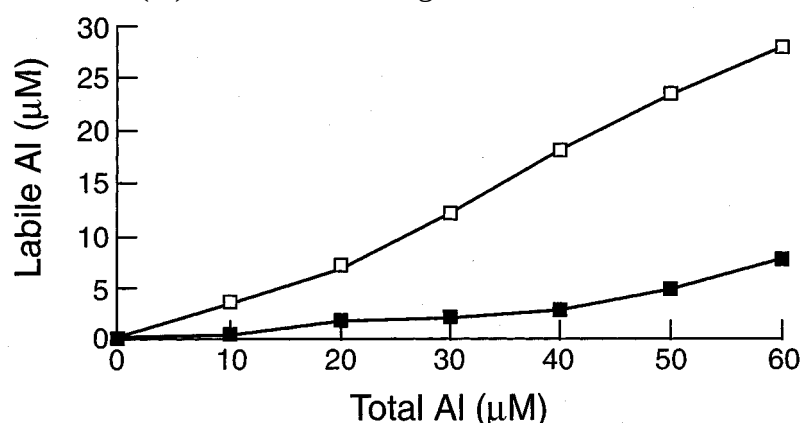
Component	<i>Melia azedarach</i>	<i>Castanea sativa</i>
pH	6.45	4.25
EC	0.017	0.001
Organic C	1.7	2.4
Al	0.06	1.31
Fe	1.1	44
Mn	0.8	19
Ca	509	15
Mg	121	68
K	164	150
Na	7.5	3.4

Aluminium complexing ability

In order to assay qualitative differences Al complexing ability, the leaf litter extracts were compared at equivalent dissolved organic carbon concentrations as previously described.

In agreement with Table 3.1a, at all Al concentrations tested, *C. sativa* litter extract was more effective in complexing Al than *M. azedarach* extract (Figure 3.1)

Figure 3.1 Influence of water soluble leaf litter extracts from *Castanea sativa* (■) and *Melia azedarach* (□) on labile Al with graded concentrations of total Al.



For *M. azedarach* at 60 μM total Al concentration, 50.4 % of the total Al added remained in a form that was kinetically reactive with 8-hydroxyquinoline in the 15 s reaction. For *C. sativa* this value was 12.9 %. Labile Al measured in this way approximates the sum of the concentrations of the ionic species Al^{3+} and AlOH^{2+} (Hodges, 1987; James *et al.*, 1983), and furthermore, that those ionic species are the most phytotoxic to Al-sensitive plants, the leaf litter extract from *C. sativa* would be more effective in reducing Al toxicity than extracts from *M. azedarach*.

Linear regressions with intercepts forced through zero for total Al (x) against labile Al (y) (both units μM) were as follows:

M. azedarach (linear): $y = 0.452 (\pm 0.012)x$; $r^2 = 0.99$

C. sativa (linear): $y = 0.102 (\pm 0.009)x$; $r^2 = 0.78$

Although the correlation coefficients were highly significant, an exponential relationship gave a better fit to the data for *C. sativa*:

C. sativa (exponential): $y = 0.518 \exp 0.045x$; $r^2 = 0.98$.

This suggests that a degree of site saturation had occurred as the concentration of total Al increased.

Treated soils after leaching

The soil used was the same acid red podsollic as described in section 2. The two water extracts of leaf litter differed in their effects on pH_{Ca} , Al^{3+} , Mn^{2+} , Ca^{2+} , Mg^{2+} and K^{+} in the reconstituted soil profiles and the effects varied with depth (Table 3.4). The addition of *C.*

sativa extract had no effect on the soil pH in the surface 1 cm and only a small effect below that when compared with the initial pH of the soil. In contrast, *M. azedarach* extract substantially increased soil pH down to about 5 cm with the effect being greatest in the surface 1 cm and progressively less with depth. In the surface 2 cm the pH was raised to above 5. The differences between the two plant species can in part be ascribed to the higher pH of the *M. azedarach* extract (pH 6.45) and therefore potential acid neutralising capacity compared to *C. sativa* (pH 4.25). In addition, the downward displacement of acidity (Al^{3+} and / or H^+) could be due to the higher Ca^{2+} concentration in the *M. azedarach* extract.

Table 3.4. Effect of water soluble leaf litter extracts of *Castanea sativa* and *Melia azedarach* on soil pH and exchangeable cations. pH was measured in 0.01 M CaCl_2 . Effective cation exchange capacity (ECEC) is the sum of exchangeable cations including Al.

Depth (cm)	pH _{Ca}	Exchangeable Cations						ECEC	CEC
		Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Mn ²⁺	Al ³⁺		
		cmol _c kg ⁻¹							
	4.07	1.47	0.22	0.10	0.11	0.03	0.79	2.70	2.80
				<i>C. sativa</i>					
0 - 1	4.06	1.29	1.79	0.45	0.13	0.47	0.26	3.9	2.5
1 - 2	4.11	1.08	1.03	0.39	0.08	0.12	0.56	3.1	2.3
2 - 4	4.17	1.40	0.34	0.38	0.11	0.04	0.75	2.9	2.5
4 - 6	4.13	1.47	0.22	0.24	0.12	0.04	0.78	2.8	2.5
6 - 8	4.14	1.34	0.21	0.13	0.12	0.04	0.79	2.6	2.3
8 - 10	4.18	1.40	0.22	0.11	0.15	0.04	0.74	2.6	2.4
				<i>M. azedarach</i>					
0 - 1	5.61	5.58	1.08	0.44	0.08	0.01	0.02	7.2	2.7
1 - 2	5.36	4.37	1.09	0.43	0.08	0.01	0.09	6.1	2.9
2 - 4	4.88	3.20	1.05	0.40	0.09	0.02	0.32	5.1	2.3
4 - 6	4.31	1.58	0.69	0.25	0.08	0.03	0.82	3.4	2.1
6 - 8	4.10	1.62	0.44	0.14	0.08	0.05	0.91	3.2	1.2
8 - 10	4.03	1.60	0.32	0.12	0.09	0.05	0.85	3.0	1.2

The two litter extracts had marked effects on exchangeable Al^{3+} and as with pH, extracts of *M. azedarach* had the greatest effect. *M. azedarach* extract decreased exchangeable Al in the 1 cm sample from approximately 0.79 cmol_c kg⁻¹ in the control to 0.02 cmol_c kg⁻¹. Below 5 cm exchangeable Al increased to greater than the background concentration suggesting that it had been transported from the upper zones in the column. As discussed previously, the pH of the soil in the top 2 cm was greater than 5 and consequently little or no exchangeable Al would be expected (Aitken, 1992.). In contrast, treatment with *C. sativa* extract did not change the pH_{Ca} in the surface 1 cm of the column, but the exchangeable Al^{3+} concentration decreased from the background concentration to 0.26 cmol_c kg⁻¹. Decreases in Al^{3+} were measured in the surface 2 cm with *C. sativa* extract and down to 4 cm depth with *M. azedarach*.

Exchangeable Mn^{2+} was also affected by the addition of the two extracts (Table 3.4). The initial concentration of 0.03 cmol_c kg⁻¹ was decreased to 0.01 cmol_c kg⁻¹ in the surface soil sample by *M. azedarach* extract but gradually increased at depth within the profile, probably as a result of transportation of displaced Mn^{2+} . In contrast, *C. sativa* extract increased the

Mn²⁺ concentration to 0.47 cmol_c kg⁻¹ in the surface sample, falling to 0.04 cmol_c kg⁻¹ in the 2-4 cm sample. The concentration of Mn²⁺ at depth in the *C. sativa* treatment was higher than the initial concentration of Mn²⁺ in the soil, suggesting that this may represent strongly bound Mn²⁺ carried in the extract. The increase in exchangeable Mn²⁺ near the surface is ascribed to the higher concentration of soluble Mn²⁺ in the *C. sativa* extract (Table 3.3). The amount of Mn²⁺ added in the *C. sativa* extract (c. 0.19 cmol_c kg⁻¹) was almost equivalent to the increase on the exchange complex (c. 0.18 cmol_c kg⁻¹).

M. azedarach extract considerably increased exchangeable Ca²⁺ down to 4 cm (Table 3.4). There was a very large increase in exchangeable Ca²⁺ (from 1.47 to 5.58 cmol_c kg⁻¹) in the top 1 cm of the column; 5.58 cmol_c kg⁻¹ was twice the CEC of the untreated soil (2.8 cmol_c kg⁻¹). With increasing depth there was a gradual decline in exchangeable Ca²⁺ to values similar to the initial background concentration. The total exchangeable Ca²⁺ found in the soil column increased from an initial amount of 0.44 cmol_c to 0.78 cmol_c after treatment with extract from *M. azedarach*. This increase in Ca²⁺ on the exchange complex was 64 % of the amount of Ca²⁺ applied in the extract. In contrast, the addition of *C. sativa* extract had a slight depressive effect on exchangeable Ca²⁺ in the 0-2 cm depth interval, but below that had no influence.

The addition of the litter extracts resulted in an increase in exchangeable Mg²⁺ down the entire depth of the column in the case of *M. azedarach*, whilst *C. sativa* had less of an influence at depths greater than 4 cm (Table 3.4). In the *M. azedarach* and *C. sativa* treatments 68 and 47%, respectively, of the total amount of Mg²⁺ added in the extracts was recovered on the exchange complex. This species difference can be ascribed to the higher concentration of Mg²⁺ in the extract of the former species. Extracts of either species increased exchangeable K⁺ most in the surface with the effect progressively decreasing down the column (Table 3.4).

In the *M. azedarach* treatment the effective cation exchange capacity (ECEC = sum of exchangeable Ca²⁺, Mg²⁺, K⁺, Na⁺ and Al³⁺) increased to a maximum of 7.2 cmol_c kg⁻¹ in the 0-1 cm depth interval and below that decreased to a level approaching the background ECEC of 2.7 cmol_c kg⁻¹. In contrast, the CEC of the soil as determined by the compulsive exchange method of Gillman and Sumpter (1986) indicated that there was effectively little change in the top 6 cm and thereafter a decrease with depth to a low of 1.2 cmol_c kg⁻¹. Possible reasons for this are discussed in the next paragraph. *C. sativa* extract increased ECEC to 3.9 cmol_c kg⁻¹ in the top 1 cm of the column with less effect below that. The CEC was a little lower than the background CEC of 2.8 cmol_c kg⁻¹.

From the clay mineralogy of the soil it is unlikely that any increase in ECEC could be attributed to an increase in pH-dependent negative charge. The apparent charge generation observed may have been due to the presence of organic anions added in the litter extracts which upon treatment with the BaCl₂/NH₄Cl solution released cations (Ca, Mg, K and Mn) which were then measured as "exchangeable". This argument is supported by the fact that there was no increase in CEC as determined by the compulsive exchange method, and in the case of the *M. azedarach* treatment, a decrease in CEC toward the bottom of the column (Table 3.4). The addition of MgSO₄ may have been ineffective in dislodging Ba²⁺ or NH₄⁺ from exchange sites on the organic component thereby resulting in a decrease in the measured CEC. In the case of the *M. azedarach* treated column where there was a decrease in CEC from 2.8 cmol_c kg⁻¹ initially to 1.2 cmol_c kg⁻¹, we can only speculate that this permanent decline in CEC was the result of precipitation of organic moieties on the surfaces of clay minerals.

The level of Al^{3+} in the soil solution is of particular importance in determining the phytotoxicity of soil. In order to examine how leaf litter extracts affect soil Al, total and labile Al fractions were measured in 0.005 M KCl extracts.

Table 3.5. Influence of leaching with leaf litter extracts on the concentration of Al at different depths in the soil column. Total Al and labile Al were extracted using 0.005 M KCl.

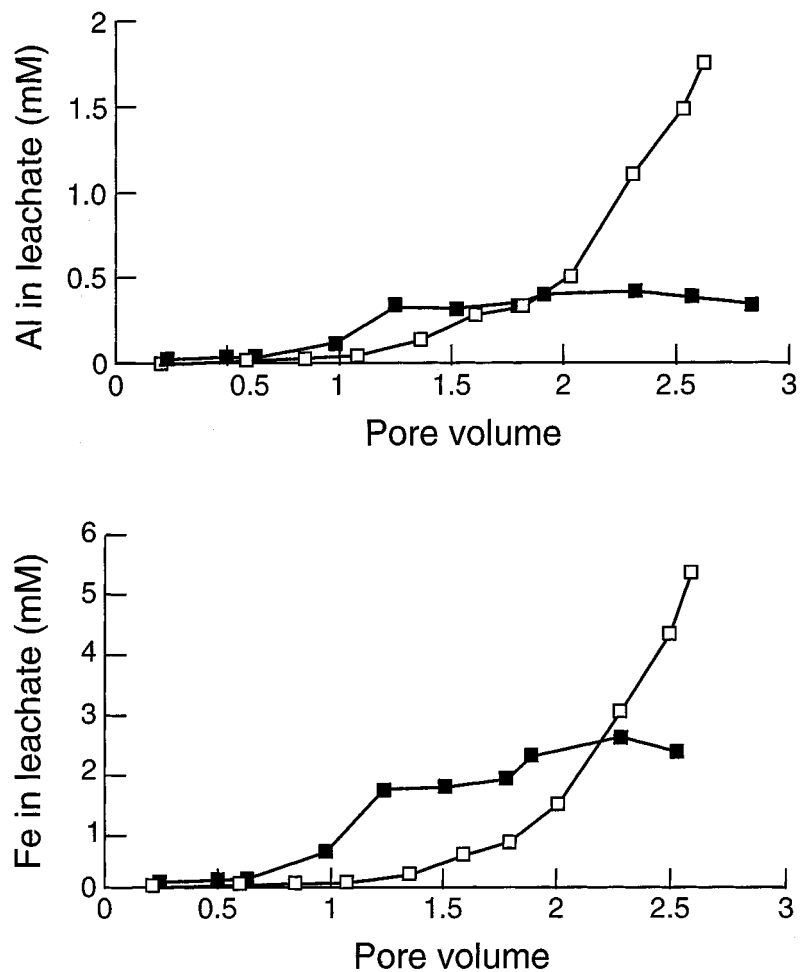
Depth (cm)	<i>C.sativa</i>	<i>M.azedarach</i>	<i>C.sativa</i>	<i>M.azedarach</i>	<i>C.sativa</i>	<i>M.azedarach</i>
	Total Al (μM)		Labile Al (μM)		% Al complexed	
Initial levels	26.4		5.5		79.11	
0-1	241.0	129.6	25.8	3.6	89.3	97.2
1-2	218.0	245.1	26.7	39.2	87.7	84.0
2-4	120.0	278.5	22.3	74.8	81.5	73.1
4-6	75.5	273.3	20.7	112.2	72.6	58.9
6-8	49.6	206.2	20.3	96.2	59.1	53.3
8-10	54.0	161.4	15.1	53.4	71.9	66.9

Leaching with leaf litter extracts of the *M. azedarach* and *C. sativa* increased the concentration of total Al above the initial value in the unleached soil (Table 3.5). This indicated that the leaf litter extracts were able to mobilise Al^{3+} from the exchange/solid phase component of the soil. In general, the concentration of total Al decreased with increasing depth in the case of *C. sativa*, whereas with *M. azedarach* the concentration tended to increase with depth, probably due to a net mobilisation of Al^{3+} . The concentration of labile Al^{3+} in all cases other than the 0-1 cm depth interval for *M. azedarach* exceeded the initial value. Labile Al showed the same trends with depth down the column as described for total Al. With both the leaf litter materials the percentage non-reactive Al decreased down the column. However, comparing at the same sampling depth, the proportion of complexed (non-reactive) Al was higher for *C. sativa* than for *M. azedarach* except in the 0-1 cm sample where labile Al for *M. azedarach* was below the initial level. This is consistent with the superior Al complexing ability of the *C. sativa* leaf litter (Figure 3. 1). It is worth noting that the measurement of labile Al gives only an estimate of the concentrations of Al^{3+} and AlOH^{2+} and that other inorganic and organic ionic species may also be kinetically reactive.

Leachate composition

The breakthrough curves for Al^{3+} and Fe^{2+} are presented in Figures 3.2a and 3.2b, respectively. The general shapes of the curves are indicative of non-equilibrium interaction between the soil exchange complex and the solution phase (Biggar and Nielsen, 1963; Cho, 1985; Phillips *et al.*, 1988). The maximum concentration of Al^{3+} in the leachate from the *C. sativa* extract treatment was obtained at just over 1 pore volume, and the concentration remained relatively constant for the entire duration of the leaching process thereafter. In contrast, the Al concentration was still increasing after 2 pore volumes in the case of *M. azedarach*. The concentration of Fe^{2+} in the leachate followed the same pattern as that for Al^{3+} in the two species; however, the concentration of Fe^{2+} was approximately an order of magnitude higher.

Figure 3.2. Breakthrough curves for (a), above, Al^{3+} and (b), below, Fe^{2+} concentrations in the leachate fraction from columns treated with the leaf litter extract of *Castanea sativa* (■) and *Melia azedarach* (□) respectively.



Since treatment with extract from either tree species caused leaching of Al^{3+} from the soil column, a mass balance of this cation was undertaken including the initial and final concentrations on the exchange complex, the concentration in the leachate and the total amount of Al added to columns in the leaf litter extract (Table 3.6).

Table 3.6. Balance sheet for Al following leaching with extracts from *Melia azedarach* and *Castanea sativa* litter. The Al initially on the soil exchange complex (1) and the Al added in the leaf litter extracts (2) was compared with Al on the exchange complex after leaching (3) and Al in the leachate (4) with the balance (deficit) assumed to be Al precipitated in the column.

Treatment	Initial exchangeable Al	Added soluble Al	Exchangeable Al after treatment	Al in leachate	Deficit
	1	2	3	4	= (1+2)-(3+4)
			$\text{cmol}_c \text{ kg}^{-1}$		
<i>C. sativa</i>	2.21	0.04	1.94	0.25	0.06
<i>M. azedarach</i>	2.27	< 0.01	1.20	0.28	0.79

A balance was almost achieved for the *C. sativa* extract treatment, with 97 % of the Al being accounted for (Table 3.6). For treatment with the *M. azedarach* extract, which added little

extra Al, the total Al accounted for on the exchange component and in the leachate was only 65 % of the total initially on the exchange complex. As the *M. azedarach* extract substantially increased the pH_{Ca} of the soil (Table 3.4) the most likely mechanism to account for this deficit would be the formation of Al precipitates within the column.

(4) Field study to compare soil acidification under stands of trees and pastures or other land use - fenceline comparisons of soil properties.

Field sites examined

Soils were sampled under established tree plantings and for comparison under a different land use adjacent to the plantation. There were six comparisons made, designated A to F.

A. *Quercus suber* (Cork oak) plantation / pasture

B. *Pinus radiata* plantation / pasture

Location: Canberra (near Glenloch interchange)

Situation: These two plantations were separated by a 200 m wide strip of subterranean clover/annual grass pasture which served as a common reference. The site was on an east facing slope.

Management: pasture has been moderately stocked with sheep and/or cattle; plantations were ungrazed Cork had been harvested from the *Q. suber* plantation on 3 occasions.

Age: *Q. suber* 76 years; *P. radiata* 38 years.

Soil: yellow podsol.

Sampling : 5 cores under trees 10 m from southern edge of *Q. suber* plantation, northern edge of *P. radiata* plantation; 5 cores in pasture 10 m from boundary fence with *Q. suber* plantation.

Soil samples were collected from the top 50 cm (0-5, 5-10, 10-15, 15-20, 20-30 and 30-50 cm depths) from adjacent sites carrying monocultures of *P. radiata* and *Q. suber* growing on a deep-surfaced yellow podsol soil and changes in soil pH and other soil chemical properties examined. In the surface 0-5 cm the soil pH_{Ca} were similar at the three sites (Table 4.1). Below that depth soil pH was lower and exchangeable Al significantly greater under the *Q. suber* stand compared to the other two sites. Consistent with a decrease in soil pH there was significantly less exchangeable Ca²⁺ under *Q. suber* (Table 4.2). The clay content was lower under the *Q. suber* stand and this could be evidence of the impact of soil acidification.

Table 4.1. Mean values of pH_{Ca}, extractable Al and Mn, exchangeable Al, soil organic carbon and clay content for soils sampled under *Q. suber*, *P. radiata* and adjacent pasture.

Depth (cm)	<i>Q. suber</i>	Pasture	<i>P. radiata</i>	Sig. level	LSD (0.05)
pH					
0-5	5.09	4.84	5.04	n.s.	-
5-10	4.11	4.86	5.14	**	0.38
10-15	4.17	5.08	5.25	**	0.34
15-20	4.47	5.37	5.50	**	0.31
20-30	4.50	5.68	5.41	**	0.35
30-50	5.10	5.94	5.75	*	0.52
Extractable Al (0.01 M CaCl ₂) (mg kg ⁻¹)					
0-5	1.55	0.90	1.42	-	-
5-10	11.32	0.75	0.90	**	5.33
10-15	9.55	0.17	0.55	**	2.08
15-20	4.18	0.10	0.38	**	0.76
20-30	3.50	0.05	0.15	**	1.68
30-50	0.53	0.02	0.25	*	0.32
Extractable Mn (0.01 M CaCl ₂) (mg kg ⁻¹)					
0-5	74.8	48.7	86.8	n.s.	-
5-10	38.0	45.4	70.6	*	23.4
10-15	85.0	39.0	57.0	n.s.	-
15-20	33.4	37.2	55.4	n.s.	-
20-30	17.9	21.9	32.3	n.s.	-
30-50	26.3	5.9	10.8	*	12.8
Exchangeable Al (BaCl ₂ /NH ₄ Cl)(cmol _c kg ⁻¹)					
0-5	1.27	1.60	1.30	n.s.	-
5-10	4.61	1.69	1.46	*	0.23
10-15	4.30	1.01	0.95	**	0.04
15-20	2.28	0.29	0.41	**	0.01
20-30	1.72	0.43	0.30	**	0.03
30-50	1.16	0.07	0.14	**	0.02
Clay (%)					
0-5	3.59	5.68	6.57	*	2.30
5-10	4.36	5.36	7.05	*	1.67
10-15	4.24	5.22	6.34	*	1.81
15-20	3.76	6.26	6.93	*	2.15
20-30	3.83	7.48	9.54	*	2.61
30-50	8.10	15.7	16.1	*	5.55
OC (mg g ⁻¹)					
0-5	31.79	20.76	18.86	**	7.26
5-10	13.30	12.47	11.10	n.s.	-
10-15	10.02	11.10	8.16	n.s.	-
15-20	5.47	7.93	6.18	n.s.	-
20-30	3.84	6.18	5.17	n.s.	-
30-50	5.11	4.84	2.99	ns	-

Table 4.2. Exchangeable cations removed by a BaCl₂/NH₄Cl extractant from the exchange complex of soils from under *Q. suber*, *P. radiata* and pasture.

Depth (cm)	<i>Q. suber</i>	Pasture	<i>P. radiata</i>	Sig. level	LSD (0.05)
Ca (cmol _c kg ⁻¹)					
0-5	4.98	2.48	3.18	n.s	-
5-10	0.77	1.97	2.57	**	0.86
10-15	0.42	2.27	2.77	**	1.22
15-20	0.39	2.35	2.69	**	1.01
20-30	0.42	2.36	3.22	**	1.07
30-50	1.08	3.19	4.00	**	1.02
Mg (cmol _c kg ⁻¹)					
0-5	1.78	0.80	1.08	*	0.71
5-10	0.72	0.67	0.80	n.s.	-
10-15	0.63	0.77	0.73	n.s.	-
15-20	0.55	0.83	0.67	n.s.	-
20-30	0.65	1.01	0.95	n.s.	-
30-50	1.43	2.23	2.08	n.s.	-
K (cmol _c kg ⁻¹)					
0-5	0.86	0.52	0.47	*	0.31
5-10	0.53	0.47	0.44	n.s.	-
10-15	0.47	0.40	0.39	n.s.	-
15-20	0.36	0.35	0.33	n.s.	-
20-30	0.30	0.34	0.37	n.s.	-
30-50	0.38	0.44	0.56	n.s.	-

We made an estimate of Ca in the top 50 cm of the soil and biomass and calculated that 7.5 t ha⁻¹ was in the *P. radiata* ecosystem and 2.6 t ha⁻¹ in and under the *Q. suber*. This suggests that considerable losses of Ca have taken place under *Q. suber* probably by leaching. We found evidence for more active Fe and Al movement under *Q. suber* than under pasture and *P. radiata*. The Fe and Al composition of the oxalate extract from concretionary material at 10-30 cm under *Q. suber* was consistent with a process similar to podzolisation. Pseudogleying of Fe and Al probably accompanied the leaching of bases from the system and a reduction of pH.

Although the total uptake of Ca by radiata *P. radiata* was considerable, the podsolising effect of this species on the soil has not been as great as the *Q. suber* even considering the different ages of the plantations.

Further studies of the water extracts of leaf litter have shown significant differences in the properties of the water soluble components from *Q. suber* litter and *P. radiata* litter. The aqueous extract of *Q. suber* complexes more Al than that from *P. radiata*, compared at the same soluble carbon concentration (Figure 4.1). *Q. suber* extracts percolating through soil mobilise more Fe than *P. radiata* extracts (Figure 4.2).

Figure 4.1. Al remaining in labile form after reaction of water soluble leaf litter extract from

Q. suber (●) and *P. radiata* (○) at a constant organic carbon concentration with Al at pH 4.0

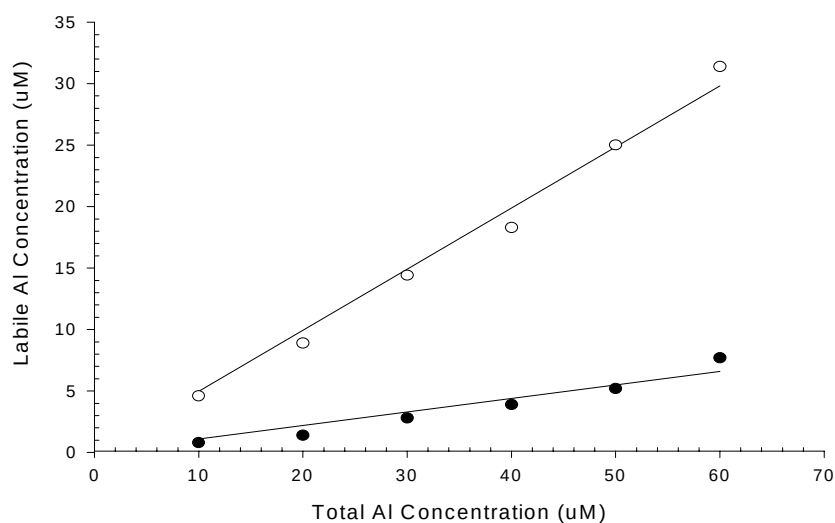
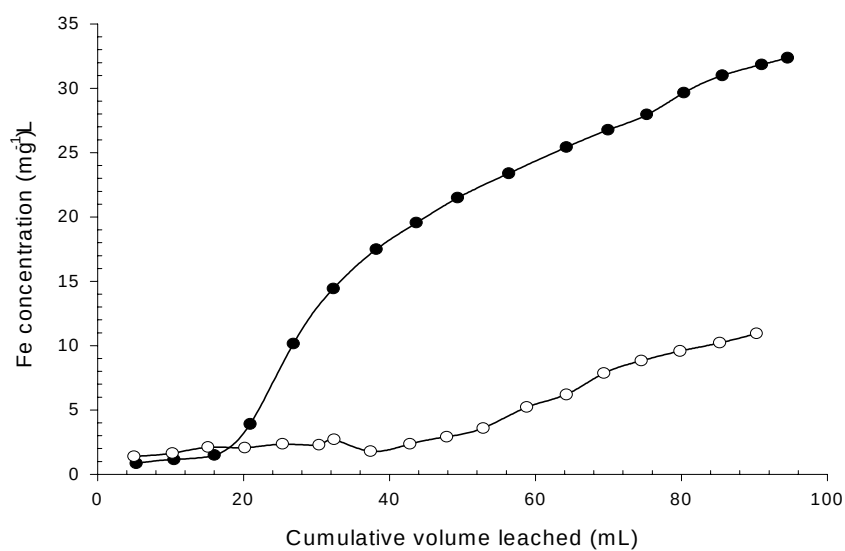


Figure 4.2. Concentrations of Fe in the leachate from soil columns treated with the leaf litter extract of *Q. suber* (●) and *P. radiata* (○). Values have been corrected for the initial Fe concentration in the extracts.



Additional soil sampling at the *Q. suber* site has shown that on the upslope (western) boundary, soil pH in the plantation tended to be lower than outside, while on the downslope boundary the reverse was the case (Table 4.3).

Table 4.3 Fenceline comparisons of soil pH at the upslope and down slope boundaries of the *Q. suber* plantation.

Depth cm	Western (upslope) boundary		Eastern (downslope) boundary	
	<i>Q. suber</i>	Pasture	<i>Q. suber</i>	Pasture
	mean pH			
0-5	4.26	4.39	5.49	4.80
5-10	3.41	4.30	5.09	4.52
10-15	3.47	4.11	5.23	4.63
15-20	3.51	4.10	5.11	4.84
20-30	3.47	4.52	4.81	4.99
30-40	4.00	4.47	4.80	5.19
	mean exch. Ca (cmol _c kg ⁻¹)			
0-5	4.4	2.1	10.0	2.0
5-10	0.7	1.4	3.8	1.5
10-15	0.2	1.2	3.3	1.8
15-20	0.2	1.2	2.9	2.0
20-30	0.5	1.9	2.5	2.1
30-40	2.6	1.7	2.4	2.7
	mean exch. Ca as % of CEC			
0-5	54.2	57.2	78.6	59.5
5-10	18.7	46.3	67.5	53.6
10-15	7.8	42.8	64.0	61.6
15-20	8.0	43.0	56.7	64.8
20-30	16.1	53.2	46.4	62.3
30-40	53.9	53.4	39.4	58.5

Comparing pH and exchangeable Ca in the middle of the slope (Table 4.2) with higher up and lower down the slope (Table 4.3) it appears that within the *Q. suber* plantation there is a gradient with lower values up the slope. This was particularly noticeable in the 10-20 cm horizon. This is consistent with a depletion of nutrients up slope and a transfer of cations and alkalinity down slope. In several places there was evidence of leaf litter accumulating lower on the slope, apparently having been washed there or blown by the westerly prevailing wind. It may be that such transfer of litter could account for the pH differences noted (Table 4.3). Such movement of litter may also contribute to loss of nutrients from the soil in the intensively sampled mid slope area within the *Q. suber* plantation as indicated above (Table 4.3). Nutrients could also be lost by the movement of organic complexes in runoff and in subsurface lateral drainage at this sloping site. The data for exchangeable Ca expressed as % saturation of the exchange complex (Table 4.3) supports the contention that severe depletion of Ca in the 5-30 cm depths of soil under the *Q. suber* trees at the top of the slope with less effect or an accumulation occurring at the bottom of the slope.

C. *Melia azedarach* (White cedar)

Location: Tumblong NSW

Situation: roadside planting

Management: not managed

Age: uncertain, at least 30 years.

Soil: Red Kandosol; texture change down profile is not sharp and soil structure not well developed in red B horizon.

Sampling : 6 cores under trees 1.5 m from trunk; 4 cores 10 m away from trees (of the 4 'away controls' - 2 cores were in the roadside area away from the trees but the same distance from the road; 2 cores were in the adjacent grazed paddock. The pH and cation values for the 4 'controls' were similar and were averaged and described as 'under grass').

There was a clear difference between the samples under grass and under trees (Table 4.4). The higher pH under the trees may be the result of deposition of litter under the trees and reflect the high ash alkalinity of leaves of this species (section 1) and the increase in pH found when water extract from the litter was applied to soil (section 2).

Table 4. 4. Soil pH, extractable Al and extractable Mn under *Melia azedarach* trees compared with an adjacent area under grass

Sampling depth (cm)	Soil pH (1:5 0.01 M CaCl ₂)		Ext. Al (1:5 0.01 M CaCl ₂) (mg kg ⁻¹)		Ext. Mn (1:5 0.01 M CaCl ₂)	
	under trees	under grass	under trees	under grass	under trees	under grass
0 - 5	5.73	4.33	<1	9	10	52
5 -10	5.72	4.16	<1	10	12	55
10 -15	5.62	4.20	<1	4	17	60
15 - 20	5.46	4.25	<1	4	24	58
20 - 30	5.38	4.35	<1	6	19	65
30 - 50	5.36	4.56	<1	3	11	47
LSD 5%	0.34		7		39	

Soil under the trees had higher levels of exchangeable cations (Table 4.5), particularly Ca²⁺ (in keeping with the high Ca concentration noted in leaves of this species) and a higher CEC.

Table 4.5 Exchangeable cations in soil with depth under grass and *Melia azedarach* trees.

Soil depth (cm)	Exchangeable cations													
	Al		Ca		K		Mg		Mn		Na		ECEC	
	cmol _c kg ⁻¹													
	Tree	Grass	Tree	Grass	Tree	Grass	Tree	Grass.	Tree	Grass	Tree	Grass	Tree	Grass
0-5	<0.1	0.4	11.8	2.8	0.9	0.4	2.7	0.8	0.1	0.3	0	0	15.5	4.4
5-10	<0.1	0.6	7.1	1.7	0.8	0.2	1.5	0.4	0.1	0.2	0	0	9.3	3.0
10-15	0.	0.6	3.6	1.4	0.6	0.1	0.9	0.3	0.1	0.2	0	0	5.3	2.5
15-20	0.1	0.5	2.5	1.6	0.6	0.1	0.8	0.3	0.2	0.2	0	0	4.0	2.6
20-30	0.1	0.3	1.6	2.1	0.4	0.1	0.5	0.4	0.2	0.2	0	0	2.6	2.9
30-50	<0.1	0.2	1.7	2.4	0.3	0.2	0.5	0.7	0.1	0.2	0	0	2.7	3.5
LSD 5%	0.2		1.3		0.2		0.5		0.1		NS		1.8	

D. *Populus euramericana* cv 'First Introduction' (Poplar)

Location: Gocup NSW

Situation: commercial plantation /pasture

Management: cattle graze both inside and outside the plantation

Age: 30 years.

Soil: Brown Dermasol; no sharp texture change down the profile and soil structure present in B horizon

Sampling : 5 cores under trees 1.5 m from trunk; 5 cores 20 m away from trees

pH_{Ca} values were higher under the trees than the pasture at all depths sampled and the differences decreased with depth below 10 cm (Table 4.6). In both locations the values were highest in the surface 5 cm. Under the trees there was a marked decline in pH_{Ca} with depth, while under the pasture the decline was smaller. Extractable Al was highest in the 5-15 cm layer under the pasture and was generally low under the trees. Differences below 20 cm were not significant. Extractable Mn was highest in the surface of the pasture soil and differences between pasture and trees were not significant below 15 cm.

Table 4.6. Soil pH, extractable Al and extractable Mn under *P. euramericana* trees compared to an adjacent pasture.

Depth (cm)	pH *		Al (mg kg ⁻¹)*		Mn (mg kg ⁻¹)*	
	Trees	Pasture	Trees	Pasture	Trees	Pasture
0-5	5.9	4.8	0.2	1.4	7.3	21.0
5-10	5.6	4.5	0.4	2.8	8.1	17.5
10-15	5.2	4.4	0.5	1.9	10.4	14.9
15-20	5.0	4.4	0.5	1.4	10.6	12.7
20-30	4.8	4.4	0.4	0.8	6.6	6.7
30-50	4.8	4.5	0.3	0.4	3.3	2.7
LSD 5%	0.3		0.5		4.4	

* in 0.01 M CaCl₂ extract.

Table 4.7. Exchangeable cations in soil at various depths under pasture and *P. euramericana* trees.

Soil depth (cm)	Exchangeable cations													
	Al ³⁺		Ca ²⁺		K ⁺		Mg ²⁺		Mn ²⁺		Na ⁺		ECEC	
	cmol _c /kg													
	Tree	Past.	Tree	Past.	Tree	Past.	Tree	Past.	Tree	Past.	Tree	Past.	Tree	Past.
0-5	0	0.1	15.5	9.0	1.0	0.4	6.3	4.2	0.2	0.2	0.2	0.2	23.2	14.1
5-10	0.1	0.6	7.3	5.1	0.7	0.2	3.8	2.4	0.1	0.2	0.2	0.1	12.2	8.6
10-15	0.2	0.6	5.9	5.1	0.5	0.2	3.4	2.4	0.2	0.2	0.2	0.1	10.4	8.6
15-20	0.3	0.6	6.0	5.1	0.4	0.2	3.4	2.5	0.1	0.2	0.3	0.1	10.5	8.7
20-30	0.3	0.5	5.5	4.9	0.3	0.2	3.2	3.2	0.1	0.1	0.4	0.1	9.8	8.9
30-50	0.2	0.3	5.0	5.4	0.2	0.2	4.2	5.7	0.0	0.0	0.4	0.1	10.1	11.7
LSD	0.2		1.8		0.2		1.4		0.1		0.1		2.9	
5%														

Exchangeable cations, particularly Ca²⁺ and Mg²⁺, were higher under the *P. euramericana* trees than the adjacent pasture in the surface 10 cms, and this was reflected in the cation exchange capacity in this horizon. This data is consistent with a substantial transfer of alkalinity to the upper layers of the soil under the trees. It is likely to be an effect of the trees rather than grazing. Cattle were grazed both in the plantation and in the adjacent paddock but the stocking rates were probably lower in the plantation.

E. *Eucalyptus camaldulensis* (River Red Gums)

Location: Arianah Park

Situation: windbreak, erosion control planting adjacent to paddock

Management: occasional sheep grazing under the trees; paddock had been under wheat/ canola/ lucerne/pasture ley farming

Age: 35 years.

Soil: red brown earth.

Sampling : 5 cores under trees 1.5 m from trunk; 5 cores 12 m away from trees in a canola crop.

Table 4.8 shows small differences in pH_{Ca} between the soil in ley farming paddock and the soil under trees, with the pH_{Ca} in the tree soil being significantly higher in the 5-15 cm depth interval. As expected from these pH_{Ca} values, extractable Al and Mn values (not shown) were low and would not present a problem for plant growth.

Table 4.8 The pH of soil under *E. camaldulensis* compared with adjacent crop/pasture land.

Sampling depth (cm)	pH (0.01 M CaCl ₂ extract)	
	trees	cultivated
0 - 5	5.2	4.9
5- 10	5.2	4.6
10 - 15	5.2	4.7
15 - 20	5.1	5.0
LSD 5%	0.37	

The exchangeable cations (except Al) were clearly higher in the surface 10 cm of the soil

under trees. Exchangeable Ca^{2+} was increased fourfold and Mg^{2+} was double. There was a marked decline in these exchangeable cations with depth under the trees and the tree/ley farmed soil difference had disappeared at 20 cm depth (Table 4.9). This data is consistent with an accumulation of cations under the trees as a result of litter fall.

Table 4.9 Exchangeable cations in soil at various depths under ley farmed (cultivated) paddock and *E. camaldulensis* plantation.

Soil depth (cm)	Exchangeable cations													
	Al		Ca		K		Mg		Mn		Na		ECEC	
	cmol _c /kg													
	Tree	Cult.	Tree	Cult.	Trees	Cult.	Trees	Cult.	Tree	Cult.	Tree	Cult.	Trees	Cult.
0-2.5	<0.1	<0.1	19.8	5.1	1.8	1.5	4.4	1.8	0.5	0.3	0.3	0.1	26.7	8.8
2.5-5	<0.1	*	23.2	*	1.4	*	5.6	*	0.5	*	0.2	*	31.0	*
5-7.5	<0.1	0.1	22.0	5.0	1.1	1.3	5.9	2.1	0.5	0.3	0.2	0.1	29.9	9.1
7.5-10	<0.1	*	14.2	*	1.2	*	3.9	*	0.4	*	0.1	*	19.9	*
10-15	<0.1	<0.1	6.7	4.7	1.1	1.3	2.4	2.1	0.3	0.2	0.1	0.1	10.7	8.5
15-20	<0.1	<0.1	3.9	5.2	0.9	1.0	1.9	2.3	0.3	0.2	0.1	0.1	7.3	8.8
LSD			8.5		0.4		1.5		0.1		0.1		10.1	
5%														

*Cores in cultivation divided into 4 (0-5, 5-10, 10-15 and 15-20 cm). Values given in 0-2.5 cm and 5-7.5 cm apply to 0-5 and 5-10 cm layers, respectively.

F. *Chamaecytisus proliferus* (Tree lucerne or Tagasaste).

Location: Yass

Situation: Experimental plantation of *C. proliferus* established for 16 years in a pasture paddock. Trees were 60 cm apart in rows 4 m apart.

Management: plantation had been fenced until previous year when the fence was removed and sheep allowed to graze under the trees; paddock had been under poor subterranean clover pasture and had recently been cultivated prior to cropping.

Soil: Red Chromosol, red duplex soil with sharp texture change at about 30 cm.

Sampling : 4 cores in row between the trees. 4 cores between rows and 4 cores 12 m away from trees in the paddock. The 3 sets of cores were taken at equivalent positions on the slope.

The pH_{Ca} values were not significantly different between tree, inter-row and cultivation sites, although the slightly higher pH in the surface 0-10 cm samples in the plantation compared to the surrounding paddock is consistent with the lower extractable Al^{3+} and Mn^{2+} (Table 4.10).

Table 4.10. Soil pH_{Ca}, and extractable Al and Mn measured in 0.01 M CaCl₂. Sample cores were taken between trees in the row (Row), between rows (Inter-row) and in the cultivated area 12 m from the edge of the plantation in a similar position on the slope (Cult.).

Sample depth (cm)	pH			Al ³⁺ mg kg ⁻¹			Mn ²⁺ mg kg ⁻¹		
	Row	Inter row	Cult.	Row	Inter-row	Cult.	Row	Inter-row	Cult.
0-5	4.18	4.08	*3.81	2.3	5.4	*7.1	13.7	48.1	*31.4
5-10	4.08	3.81	*	2.5	7.2	*	13.1	17.0	*
10-20	4.14	4.22	3.98	1.6	0.8	2.0	2.8	6.4	13.5
20-30	4.42	4.62	4.55	0.5	0.2	0.3	2.6	0.8	2.6
30-40	4.68	4.78	4.79	0.2	0.3	0.3	1.1	0.2	1.6
LSD 5%	NS			2.6			19.3		

* For the 'Cult.' sample the 0-5 and 5-10 cm samples were combined because of the mixing in the recent cultivation.

Table 4.11 Exchangeable cations in soil at various depths in the tree rows under a plantation of *C. proliferus* (Tag) and under the surrounding pasture ley /farmed paddock (Cult) area.

Soil depth (cm)	Exchangeable cations													
	Al ³⁺		Ca ²⁺		K ⁺		Mg ²⁺		Mn ²⁺		Na ⁺		ECEC	
	Tag	Cult.	Tag	Cult.	Tag	Cult.	Tag	Cult.	Tag	Cult.	Tag	Cult.	Tag	Cult.
0-5	0.21	0.63	2.2	1.4	0.54	0.47	1.02	0.57	0.49	0.38	0.02	0.02	4.46	3.45
5-10	0.23	#	2.3	#	0.40	#	0.93	#	0.44	#	0.04	#	4.33	#
10-20	0.23	0.30	2.1	1.7	0.35	0.39	0.90	0.95	0.19	0.20	0.03	0.02	3.77	3.55
20-30	0.10	0.05	1.9	2.3	0.37	0.38	0.82	0.99	0.07	0.04	0.04	0.02	3.37	3.78
30-40	0.05	0.02	2.4	2.0	0.50	0.31	1.41	1.30	0.03	0.03	0.09	0.04	4.44	3.69
LSD 5%	0.15		0.61		NS		NS		NS		NS		NS	

in the farmed area the 0-10 horizon was not divided

Note: values for samples between the rows of trees were intermediate between the Tree (in row) and the cultivation area values.

Exchangeable Ca²⁺ was higher in the surface 0-5 cm under the trees compared to the surrounding paddock, and exchangeable Al³⁺ was lower (Table 4.11).

The site has been used for agriculture for many years and the low surface pH_{Ca} could be a consequence of this. While the soil is very acid in the surface, the pH_{Ca} rises at depth and the texture of the B horizon would allow roots to grow there. Taken together, the increase in exchangeable Ca²⁺ in the surface soil under the trees, the lower exchangeable Al³⁺ and the trends in pH are consistent with a transfer of nutrients to the surface soil under the trees. The relatively small difference in pH between the soil under the trees and in the surrounding paddock may reflect not only the limited time since establishment of the plantation, but the low cation excess in this species (60 cmol_c kg⁻¹) compared to approximately 180 cmol_c kg⁻¹

for poplar and over 200 cmol_c kg⁻¹ for *M. azedarach* and the low fertility of the site.

(5) Factors affecting ash alkalinity of trees

Seasonal variation in ash alkalinity of leaves.

Measurements of ash alkalinity have shown a considerable range in values depending on species. However, our collections of litter of the same species from different sites have shown some variation in ash alkalinity (examples are given in Table 5.1 below).

Table 5.1. Examples of ash alkalinity measured in different samples of litter from four species.

<i>Melia azedarach</i>	<i>Eucalyptus maculata</i>	<i>E. globulus</i>	<i>Populus nigra</i>	<i>Pinus radiata</i>
217	106	103	180	48
252	68	165	213	42
237	73	115	213	
	58	111	227	
	86		124	
		means		
235	78	124	191	45

The reasons for this variation - genetic, nutrient supply or seasonal factors - are not known.

As a step in understanding the variation between samples we have measured the seasonal variation in nutrients in leaves (only Ca data presented) and calculated excess cations (an estimate of ash alkalinity) in leaf samples of *Melia azedarach*, *Brachychiton populneus* and *Populus nigra* (Table 5.2). The trees sampled were growing on the lower slopes of Black Mountain, ACT within 300 m of each other. Leaves including petioles were picked from the same 3 trees of each species and bulked on each occasion.

Table 5.2. Effect of sampling date on calcium content and excess cations in leaf samples of *Melia azedarach*, *Brachychiton populneus* and *Populus nigra*.

Date of sampling	<i>Melia azedarach</i>		<i>Brachychiton populneus</i>		<i>Populus nigra</i>	
	Ca (%)	Excess cations	Ca (%)	Excess cations	Ca (%)	Excess cations
2 Nov 95	2.4	166	1.3	106	1.4	138
15 Dec 95	2.9	195	1.7	131	2.2	187
8 Jan 96	3.7	233	1.8	134	2.8	215
8 Feb 96	3.8	240	1.7	127	2.2	180
20 Mar 96	4.4	264	2.1	153	3.2	234
26 Apr 96	5.1	298	2.1	151	3.9	272

Both Ca and excess cations increased through the season. Mg followed the same pattern as Ca as did Si and Cl while P was high earlier in the season and declined later. For both Ca and excess cations the species ranked in the same order throughout the season.

While samples listed in Table 5.1 were mainly fallen senescent leaves, data from the samples

picked at different times (Table 5.2) suggests that leaves shed prematurely could account for some of the variation in data for the same species collected at different times at different locations. In order to examine other factors we grew selected tree species in a range of soils and with different treatments imposed.

Soil factors affecting ash alkalinity in trees.

Three species were used. They were chosen largely on the basis of the ash alkalinity measured in litter collected in the field. They were:

- *Melia azedarach* - high ash alkalinity (~ 235 cmol_c/kg)
- *Eucalyptus globulus* - medium ash alkalinity (~ 124 cmol_c/kg)
- *Pinus radiata* - low ash alkalinity (~ 45 cmol_c/kg)

The glasshouse experiments compared growth and composition;

(a) on different soils,

(b) on an acid soil with different rates of lime

(c) on a soil treated with either ammonium-based N fertiliser (+ a calcium carbide-based nitrification inhibitor to maintain the level of ammonium in the soil) or nitrate fertiliser (ammonium would compete with other cations and thus possibly reduce ash alkalinity)

Table 5.3 gives the concentration of elements in young plants of *M. azedarach*, *E. globulus* and *P. radiata* grown in 4 soils, and Table 5.4 shows the soil pH and exchangeable soil Ca²⁺ and the excess cations in the plants.

Table 5.3. Yield and elemental composition of plants of *Melia*, *Eucalyptus* and *Pinus* grown in 4 soils (Expt 1)

Species	Soil	Plant wt	Ca	Mg	K	Na	S	Cl	P
		g					concentration %		
<i>Melia</i>	Book-Book	0.85	1.04	0.20	2.18	0.02	0.21	0.16	0.11
	Cavan	6.10	1.65	0.11	1.04	0.01	0.11	0.03	0.11
	Griffith	4.75	1.59	0.21	0.78	0.02	0.09	0.23	0.12
	Cowra	6.62	1.65	0.10	0.83	0.02	0.10	0.02	0.11
<i>Eucalypt</i>	Book-Book	5.77	0.60	0.12	0.97	0.15	0.12	0.11	0.05
	Cavan	9.21	1.12	0.13	1.12	0.04	0.11	0.05	0.07
	Griffith	9.64	1.31	0.09	0.94	0.06	0.06	0.34	0.16
	Cowra	10.02	1.02	0.12	1.02	0.05	0.10	0.02	0.08
<i>Pinus</i>	Book-Book	0.26	0.32	0.08	1.82	0.06	0.17	0.42	0.05
	Cavan	0.38	1.07	0.09	2.08	0.01	0.17	0.27	0.05
	Griffith	1.29	0.78	0.22	1.80	0.04	0.19	0.27	0.09
	Cowra	0.81	1.06	0.09	1.74	0.03	0.16	0.12	0.07
	lsd 5%	1.05	0.45	0.04	0.54	0.41	0.08	0.20	0.05

Table 5.4. Excess cations in *Melia*, *Eucalyptus* and *Pinus* grown in 4 soils (Expt 1)

Soil	Soil pH at trans planting	Exch. Ca ²⁺ in soil	ECEC of soil	Species		
				<i>Melia azedarach</i>	<i>Eucalyptus globulus</i>	<i>Pinus radiata</i>
(cmol _c kg ⁻¹)			Excess cations (cmol _c kg ⁻¹)			
Sedimentary (Cavan)	5.88	17.3	20.5	107	86	93
Grey clay (Griffith)	6.20	8.6	12.1	102	81	81
Red-brown earth (Cowra)	6.1	8.9	11.0	103	79	89
Red podsol (Book Book)	3.70	0.9	2.6	103	58	46
				Soil, species and interactions: sig <i>P</i> <0.001 l.s.d between pairs of means: 12.5, <i>P</i> =0.05		

It should be noted that the absolute values for cation excess (Table 5.4) were lower than those in litter collected in the field eg. Table 5.1. With *M. azedarach*, for example, cation excess values over 200 cmol_c/kg were found in the field samples and Ca was 4% or more (compared to 1 - 1.6% in Table 5.3). The present data is for relatively young plants and therefore may not be inconsistent with the data in Table 5.2 which showed that alkalinity values (and % Ca) increased significantly as leaves aged. In this and the following two experiments the absolute values are probably less of importance than the relative values which can be used to compare treatments and species.

The effect of lime added to an acid soil on plant composition is shown in Table 5.5 and on excess cations in Table 5.6.

Table 5.5. Effects of lime on elemental composition in stems and leaves of *Melia*, *Eucalyptus* and *Pinus* grown in an acid red podsolic soil from Book Book(Expt 2)

Species	Lime (t/ha)	Plant wt g	Ca	Mg	K	Na	S	Cl	P
Concentration %									
Leaves									
<i>Melia</i>	0	0.59	1.00	0.19	1.96	0.04	0.20	0.18	0.10
	1	2.00	1.87	0.14	1.26	0.02	0.18	0.12	0.09
	2	4.43	2.18	0.13	0.97	0.02	0.18	0.08	0.11
<i>Eucalyptus</i>	0	5.71	0.56	0.11	0.91	0.14	0.12	0.11	0.06
	1	6.95	0.74	0.09	0.78	0.12	0.12	0.09	0.06
	2	8.70	1.24	0.09	0.84	0.12	0.15	0.10	0.07
<i>Pinus</i>	0	0.36	0.31	0.06	1.70	0.05	0.16	0.33	0.06
	1	0.30	0.86	0.08	1.67	0.09	0.14	0.44	0.05
	2	0.33	1.09	0.06	1.27	0.06	0.11	0.24	0.04
lsd 5%			0.46	0.04	0.55	0.41	0.08	0.21	0.05
Stems									
<i>Melia</i>	0		0.34	0.11	1.20	0.12	0.10	0.11	0.06
	1		0.41	0.06	1.19	0.04	0.09	0.08	0.07
	2		0.43	0.06	0.98	0.03	0.09	0.07	0.08
<i>Eucalyptus</i>	0		2.24	0.03	0.77	0.07	0.07	0.10	0.12
	1		1.39	0.05	0.88	0.07	0.08	0.13	0.10
	2		1.94	0.03	0.73	0.07	0.07	0.11	0.11
lsd 5%			1.01	0.04	0.47	0.16	0.04	0.09	0.04

Lime raised the excess cation value in leaves of all three species. There were interesting differences between leaf and stem. Stem values were lower than leaf values in *M. azedarach*, but higher in Eucalypt. Lime had no effect on stem values in *M. azedarach* but increased them in Eucalypt (Table 5.6). A similar pattern is seen in the Ca concentrations with Eucalypt having higher concentrations in stem than leaf and *M. azedarach* having lower values in stem tissue (Table 5.5). This suggests that differences in distribution of Ca between leaf and stem may account in part for the differences in ash alkalinity between species.

Table 5.6. Effects of lime on excess cations in *Melia*, *Eucalyptus* and *Pinus* grown in the Book Book soil (Expt 2)

Soil		Treatment	pH at transplanting	Species		
				<i>Melia</i>	<i>Eucalyptus</i>	<i>Pinus</i>
Excess cations (cmol _c kg ⁻¹)						
Leaves + petioles						
Book	Book	Basal	3.70	96	53	44
		Basal + lime (1 t/ha)	5.41	119	57	72
		Basal + lime (2 t/ha)	6.45	127	81	78
				Lime and species effects: sig $\underline{P}$ <0.001 Interaction NS l.s.d between pairs of means: 12.6, $\underline{P}$ =0.05		
Stems						
Book	Book	Basal	3.70	50	81	nd
		Basal + lime (1 t/ha)	5.41	47	107	nd
		Basal + lime (2 t/ha)	6.45	42	134	nd
				Lime, species and interaction effects: sig $\underline{P}$ <0.001 l.s.d between pairs of means: 12.6, $\underline{P}$ =0.05		

The proportion of nitrogen available to plants in the cationic NH⁴⁺ form compared to the anionic NO₃⁻ form can influence the internal cation excess by affecting the uptake of other ions. In experiment 3, the N was applied as either ammonium sulfate or sodium nitrate. Nitrification of the ammonium to nitrate was prevented by adding calcium carbide in a polymer matrix. The carbide in the matrix reacts with soil moisture and releases acetylene which is a powerful inhibitor of nitrification. The effects of the form of N on nutrient composition of leaves is shown in Table 5.7.

Table 5.7. Elemental concentrations in leaves of 15 week old *Melia*, *Eucalyptus* and *Pinus* growing in the soil from the A horizon of an acid red podsolic from Book Book with N supplied as either ammonium sulfate or sodium nitrate. (Expt 3)

Species	N form	Ca %	Mg %	K %	Na %	S %	Cl %	P %
<i>Melia</i>	Ammonium	0.59	0.18	1.77	0.04	0.43	0.24	0.10
	Nitrate	1.05	0.15	2.58	0.09	0.22	0.15	0.12
<i>Eucalyptus</i>	Ammonium	0.51	0.11	0.99	0.16	0.20	0.11	0.05
	Nitrate	0.36	0.08	0.66	0.42	0.11	0.07	0.05
<i>Pinus</i>	Ammonium	0.22	0.06	1.53	0.04	0.30	0.44	0.04
	Nitrate	0.26	0.06	1.73	0.62	0.16	0.40	0.06
lsd 5%		0.24	0.04	0.34	0.20	0.07	0.13	0.02

Ammonium sulfate increased S content of leaves and sodium nitrate increased Na content in all three species. The relatively low Na concentrations in *M. azedarach* in the sodium nitrate treatment indicate that this species may have an effective exclusion mechanism for this ion. Levels of Cl were consistently higher in the ammonium-fed leaves, but effects on Ca, Mg, K and P were different depending on species (Table 5.7). Effects on cation excess also depended on species. Ammonium-fed *M. azedarach* and *P. radiata* had markedly lower cation excess in leaves than nitrate-fed plants, while N source had little effect on values in *Eucalypt* (Table 5.8). In *M. azedarach* this seemed to reflect Ca concentrations, while in *P. radiata* Na appeared to have a major influence (Table 5.7).

Table 5.8 Excess cations in *Melia*, *Eucalyptus* and *Pinus* grown in an acid soil with N supplied as ammonium or nitrate (Expt 3)

Soil		Treatment	pH at transplanting	Species		
				<i>Melia</i>	<i>Eucalyptu</i> s	<i>Pinus</i>
Excess cations (cmol _c kg ⁻¹)						
Leaves + petioles						
Book	Book	Basal with N as nitrate	3.70	112	49	64
		Basal with N as ammonium + nitrification inhibitor	3.70	54	49	23
				N source, species and interaction effects: sig <u>P</u> <0.001 l.s.d between pairs of means: 21.2, <i>P</i> =0.05		

Correlations between cation excess and mineral content of leaves.

Regression analysis using all the data from experiments 1 to 3 above, showed that the strongest relationship between cation excess (ash alkalinity) and elemental content was with Ca concentration (Figure 5.1). Weaker positive relationships were shown with Mg. There was no relationship with K, the other major cation (Figure 5.2).

Figure 5.1. The relationship between ash alkalinity and % Ca in tissue for plants of *Melia azedarach*, *Eucalyptus globulus* and *Pinus radiata* grown under a variety of conditions described above (Cation excess = $32.5 + 45.9 \text{ Ca}$; $r^2 = 0.81$).

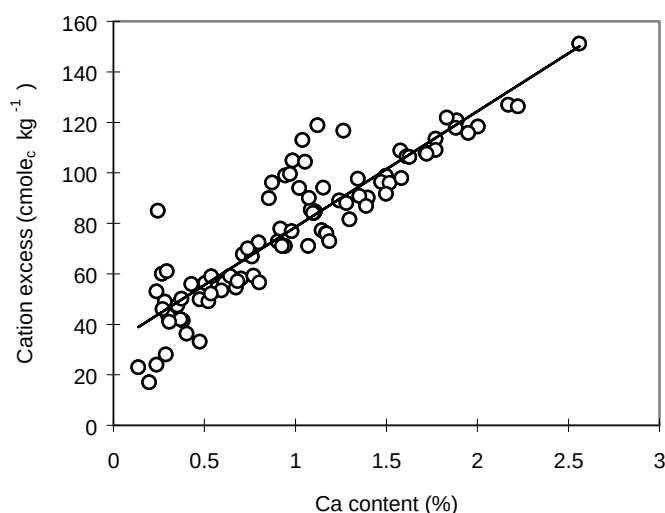
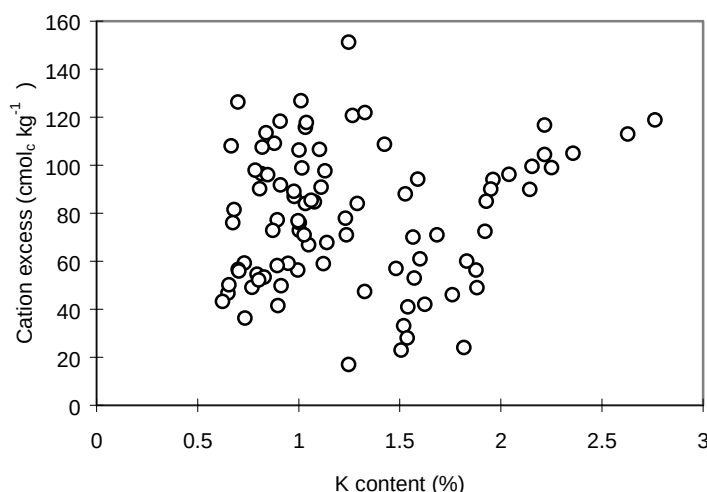


Figure 5.2 The relationship between ash alkalinity and % K in tissue for plants of *Melia azedarach*, *Eucalyptus globulus* and *Pinus radiata* grown under a variety of conditions described above ($r^2 = 0.01$).



It is noteworthy that the strong relationships between Ca and ash alkalinity found here with growing leaves of 3 species grown in a wide range of conditions designed to alter the balance between cation and anion uptake are similar to those described earlier (Figure 1.1) in the report with a wide range of samples of litter from different species grown in many locations.

Supplementary information on effects of nutrient supply on ash alkalinity of pasture legume species.

Data is presented from earlier field trials with pasture legumes to compare with the present data collected from trees. In these trials pasture legumes had been grown with rates of lime, P or K on responsive soils, with the aim of measuring responses to fertiliser nutrients or amendments and relating response to nutrient content of the foliage. The relationships were to be used for diagnosis. For the present purpose, ash alkalinity (measured by titration) is given below for trials with rates of lime, potassium and phosphorus. (Table 5.9).

Table 5.9 Effects of lime and fertiliser on ash alkalinity of pasture legumes.

Treatment	Pasture species				Treatment
	Sub clover	Balansa clover	Murex medic	Lucerne	mean
Ash alkalinity (cmol _c /kg)					
A. Lime trial - Roslyn					
0	101	76	90	114	95
0.5 t/ha	117	78	87	158	110
1.0 t/ha	119	80	88	161	112
2.0 t/ha	133	102	85	162	120
3.0 t/ha	134	109	93	160	124
Species mean	121	89	89	151	
Lime effects sig $P < 0.001$; Species sig $P < 0.001$; Interaction sig $P < 0.01$					
B. K trial - Ballanya					
0	106	147	91		115
25 kg/ha	98	125	89		104
50 kg/ha	92	118	82		97
100 kg/ha	88	115	84		96
200 kg/ha	87	105	78		90
300 kg/ha	89	107	83		93
400 kg/ha	86	111	88		95
Species mean	92	119	85		
K level effects sig $P < 0.001$; Species sig $P < 0.001$; Interaction not sig.					
C. P trial - Ginninderra					
0	123	133	137		131
8	119	123	128		124
16	121	124	122		117
32	106	132	112		117
64	110	135	107		118
128	100	132	102		111
Species mean	112	130	119		
P level effects sig $P < 0.01$; Species sig $P < 0.001$; Interaction sig $P = 0.05$					

The data for pasture legumes in our earlier study is not inconsistent with that from trees in the present work. As with the trees, lime increased ash alkalinity. The application of K tended to decrease ash alkalinity, an effect similar to application of ammonium which is also a univalent

cation. P depressed ash alkalinity in 2 of the 3 species possibly due to increases in tissue P. This gives us greater confidence in data from studies in model systems. It is also worth noting that the ash alkalinity values found in these pasture legume is within the range of the values found in the senescent leaf litter samples.

Uptake of cations from different parts of the soil profile.

Small seedlings of *Melia azedarach* and *Eucalyptus globulus* were transplanted to root boxes filled with an acid soil in the upper 20 cm and the same soil amended with lime in the lower 20 cm. Pairs of boxes had either the upper or the lower layer 'labelled' with 44 ppm strontium as strontium chloride (Pinkerton and Simpson, 1979). The intention was to estimate cation absorption from a layer related to the root length in the layer, using Sr content of shoots and Sr/Ca ratio as a measure.

Seedlings grew very poorly in this experiment. Examination of the roots showed that there were few laterals and that few roots grew through the soil, most grew down the side of the container and coiled around the bottom. No conclusion could be drawn from this work.

In a second attempt, seedlings tap roots were cut to encourage branching, soil was packed in small increments to ensure bulk density was the same throughout the box and the watering regime was altered. By these means better growth was obtained. However, insufficient time remained to germinate more seedlings and set up repeat experiments during the life of this project. It is hoped that this work will be continued later this year.

Rhizosphere pH

Plants of *Melia azedarach* and *Eucalyptus globulus* were raised in potting mix in plastic pots. At 3 months old, the bottoms of the pots were sliced off and the root mass trimmed. The pot with the roots so exposed was then placed in a hole cut to size on top of a plastic root box. The box was supported in a cradle held at 15 ° from vertical. The pot was then sealed into the box with silicone in a position which allowed the plant to remain vertical, while the roots could grow along the lower face of the box. This lower side was removable so that the roots could be viewed and pH measured using an indicator dye technique (Haussling M. *et al.*, 1985).

The most notable features of the pH change in the rhizosphere (Table 5.10) were:

- pH was lowered all along the roots of both species compared to the soil away from the root
- the drop in pH was not uniform with Eucalypt in particular showing a particularly acid localised zone of about 3 cm in length extending upwards from about 2 cm behind the apex. It is not known if this drop in pH is due to proton or organic acid excretion and its nature is worth further investigation.
- having regard to semi-quantitative measurement employed, it appeared that the rhizosphere of Eucalypt roots was more acid than of *M. azedarach* roots. While this is intuitively unexpected because of the lower ash alkalinity of the eucalypt, this species grew more vigorously and the effect on soil pH could be explained by the higher ash alkalinity per plant (see Tables 5.3 and 5.4).

Table 5.10. Soil pH adjacent to roots of *M. azedarach* and Eucalypt plants.

Soil away from root	Soil adjacent to Eucalypt root		Soil adjacent to <i>M. azedarach</i> root	
pH 6.2	basal region	pH 5.5-6	basal region	pH 5
	between 3 and 5 cm from tip	pH 4-5		
	apical 3 cm	pH 5.5-6	apical 5 cm	pH 5.5-6

These experiments taken together indicate that the supply of soil nutrients can have a substantial effect on cation excess and thus ash alkalinity of leaves. Accordingly, litter from the same species may differ in its effect on an acid soil depending on where it was grown. The distribution of Ca and other ions between stem and leaf differs between species. The balance between leaf and stem or twig material is likely to be a factor in determining ash alkalinity of litter.

Discussion

Ash alkalinity of leaf litter

There were substantial differences between species in the composition of cations in the leaf litter. Calcium levels ranged from 5 mg/g in *Eucalyptus regnans* to 40 mg/g in some samples of *Melia azedarach*. Acacia, *P. radiata* and eucalypt species were mostly low in Ca (the exception being *E. nitens* sample 25 collected from an sewage irrigation trial in Tasmania). Elm, poplar and *M. azedarach* had higher levels of Ca. K also varied substantially between species but there was also variation between samples within a species (Table 1.1). While in the majority of the litter samples Ca was the most abundant cation, often several fold higher in concentration than K. However in a few samples K was significantly higher than Ca (eg *Fraxinus oxycarpa* and *Eucalyptus triflora*). In other samples, mainly from the FM group which had been irrigated with sewerage effluent the values for Ca and K were of a similar order. It is of interest that while all 4 samples of poplar litter (#5, 10, FM15 and FM21) had high Ca concentrations, high K was found only in the two from the effluent irrigation site. *Eucalyptus triflora* appeared to be an accumulator of Na and Cl (Table 1.1), in agreement with Marcar (1989).

The ash alkalinities found in the leaf litter samples varied over the range ~45 cmol_c kg⁻¹ (*P. radiata*) to 250 cmol_c kg⁻¹ (*M. azedarach*). This is comparable to that of agricultural plants reported by Pierre and Banwart (1973)(maize stalks, 44 cmol_c kg⁻¹ : soybean leaves 250 cmol_c kg⁻¹), and as with the litter samples few of the materials measured by these authors exceeded 200 cmol_c kg⁻¹. Values as low as 6 cmol_c kg⁻¹ occur in cereal grains. The values for pasture plants (Jarvis and Robson, 1983 and Table 5.9) fall within that range. The large differences in the ash alkalinity between the litter samples of the different species could be due partly to nutritional factors (Tables 5.4, 5.6, 5.8) and time of the season (Table 5.2) which were identified as having some effect. Ash alkalinity was low in new leaves early in the season and increased with time. Species differences were maintained throughout, indicating that genetic factors were important. Under comparable conditions, ash alkalinity of *M. azedarach* litter was substantially higher than litter from eucalypt or *P. radiata* (Table 1.1; 5.2, 5.4, 5.6, 5.8).

Ash alkalinity is an indirect measure of organic anion content of the tissue. The litter has a

neutralising value in proportion to the content of organic anions which oxidise and consume protons (Helyar and Porter, 1989). For purposes of comparison of potential neutralising power of litter, calculation of ash alkalinity in terms of carbonate equivalent ($1 \text{ kmol OH}^- = 50 \text{ kg CaCO}_3$) suggests that *P. radiata*, *Eucalyptus globulus* and *M. azedarach* which have litter ash alkalinities of about 45, 100 and 250 and would require respectively 44, 20 and 8 t litter to equal 1 t CaCO_3 .

The high correlation between Ca and ash alkalinity (Figure 2.1 and 5.1) suggests that either could be used to predict the neutralising value of the litter. Calcium and Mg, which have stronger affinities for exchange sites, will increase the base saturation of the soil more effectively than K and Na. The levels of these divalent cations may be important indicators of the quality of leaf litters for improving the fertility of soils.

Amelioration of an acid soil by decomposing leaf litter

This study has demonstrated the potential role of leaf litter in raising pH of an acid soil. In a soil incubation experiment the addition of leaf litter material increased soil pH_{Ca} (Table 2.1; Figure 2.2) and lowered extractable Al (Table 2.1).

It is often assumed that at pH_{Ca} values below 4.5 phytotoxic levels of Al may exist in the soil solution. In this work there appears to be a general but imprecise relationship between Al in CaCl_2 and pH since at equivalent pH values there was often a spread of measured Al concentrations (Figure 2.1). This suggests that the solubility of Al in the litter treatments is not entirely controlled by the same mineral phase as in the lime treatments. Indirect evidence of this can be inferred from a plot of monomeric Al concentration measured in 0.01 M CaCl_2 extracts against pH (Noble *et al.*, 1996 Figure 4). The pH/monomeric Al relationship for *Melia azedarach*, *Betula pendula*, and *Brachychiton populneus* were very similar to those of lime while that for *Liquidambar styraciflua*, *Quercus robur* and *Pinus radiata* were markedly different (Noble *et al.*, 1996). This would suggest that organic complexes with Al play a greater part in controlling the level of monomeric Al in solution in the case of the latter group of species over the period of incubation. However, the formation of organic complexes with Al may be transient in that with time these complexes break down releasing Al back into solution. In studies evaluating the Al complexing ability of water-soluble fractions extracted from leaf litter, *Quercus robur* and *Pinus radiata* complexed significantly larger amounts of Al than species such *Melia azedarach*.

Other workers have shown that soil pH can be increased following the application of organic material such as lucerne, cowpeas, leucaena and Guinea grass (Hoyt and Turner, 1975 ; Hue and Amien, 1989). Various reasons for such a pH increase have been advanced, eg. release of NH_3 from decomposing organic material or production of OH^- by dissolution of solid Mn and Fe oxides in reducing conditions or by ligand exchange occurring through the replacement of the terminal OH^- of Al or Fe hydroxy oxides by organic anions. In the present experiment it is unlikely that the dissolution of Mn and Fe oxides contributed to the pH increases since the incubation conditions would not have favoured reduction and exchangeable Mn concentration decreased with increasing rate of organic matter addition (not shown).

The oxidation of organic anions during decomposition of the leaf material is likely to make a major contribution to the increase in soil pH, through the consumption of protons (Helyar and Porter, 1989). In the present work, comparisons between the different leaf litters suggest the importance of ash alkalinity in determining soil pH after incubation (Figures 2.3 and 2.4). In

these Figures the ash alkalinity which was added in the leaf litter is plotted against final soil pH. Ash alkalinity is expressed as mg CaCO₃ assuming that 1 mole H⁺ requires 50 g CaCO₃ to be neutralised. The most effective litter was from *M. azedarach* (Fig 2.4) and the least effective from Liquidambar. On a calcium carbonate equivalent basis, the neutralisation capacity of *M. azedarach* litter was similar to that of lime. The other species had a lower neutralisation effect than would be predicted from their ash alkalinities. This may in part be related to the degree of decomposition of the litter as previously discussed. Differences in net mineralisation or immobilisation of N may have contributed to differences between species and treatments. Lime tended to increase the soil nitrate level compared to the control (Table 2.4), indicating net mineralisation of N resulting in a greater pool of protons to be neutralised. Leaf litter treatments markedly lowered soil nitrate indicating a net immobilisation of N during decomposition of leaf litter. This would have resulted in a net consumption of protons. However, the contribution of N-cycle processes to the change in pH would have been relatively small compared to that of organic anion decomposition. For example, calculations using the treatment with *M. azedarach* added at 32 mg g⁻¹ showed that the net effect of changes in soil nitrate and ammonium (relative to the control) would have been equivalent to adding 0.88 mg CaCO₃ per gram of soil. The ash alkalinity of the material was equivalent to 3.95 mg CaCO₃ (98% of the combined value). The corresponding values for *P. radiata* at the 32 mg g⁻¹ rate were 0.108 mg CaCO₃ equivalents for net changes in soil nitrate and ammonium compared to 0.59 mg CaCO₃ equivalents (85% of the total) for ash alkalinity.

The effects of leaf litter additions in our experiments could represent the situation where material is collected off-site. When leaf litter is deposited *in situ*, both the growing of the litter and its decomposition should be considered in relation to effects in the whole soil profile. Uptake of excess cations by roots during growth will result in acidification of the soil around the roots. The excess cations in the plant are balanced by organic anions which represent the ash alkalinity of the material. Differences between species in the ash alkalinity of senescent leaf material could be due to differences in the proportions of cations and anions taken up by the plant and in addition differences in the proportion of nutrients withdrawn from the leaves during senescence prior to abscission could also be important. Assuming uptake differences are significant, we would expect that the more alkaline the litter the more acid the soil around the roots. The cycling of nutrients through the soil/tree system and the redistribution of alkalinity in the soil profile through the deposition of organic anions on the surface will have important consequences for soil acidification (Helyar and Porter, 1989). The operation of the “biological pump” would be expected to have different consequences depending on the soil. On poorly buffered soils amelioration of acidity in the surface by leaf litter may be at the expense of undesirable acidification of the subsurface soil. In duplex soils with acid surface horizons and an accumulation of basic cations at depth in a neutral or alkaline B horizon, deposition of litter containing high levels of ash alkalinity on the soil surface would be entirely beneficial.

Aluminium complexing ability of leaf litter extracts

It was shown that the water soluble component of leaf litter from different species varied considerably in their ability to complex Al (Tables 3.1 and 3.2). More detailed studies with two contrasting species, *Melia* (*M. azedarach*) and chestnut were then undertaken and the extracts leached through soil columns to examine the effects on soil chemistry. Chestnut extracts were more efficient than *M. azedarach* extracts at binding Al in a non-labile form. In evaluating the influence of these water soluble extracts on potential Al phytotoxicity there are two aspects to be considered. Firstly, the concentration of phytotoxic Al in the soil solution

which effectively represents an intensity measurement, and secondly, the quantity factor which is of importance in amelioration and is predominantly described by the level of Al on the exchange component. The water extract of *M. azedarach* leaves had a higher pH than chestnut extract and raised the pH more and decreased exchangeable Al. This decrease in the case of *M. azedarach* was achieved by exchanging Al for Ca^{2+} , Mg^{2+} and K^{+} on the exchange complex. The Al displaced from the exchange complex was apparently precipitated as a solid phase within the column due to the increase in pH or removed in the leachate from the column (Table 3.6). In the case of the treatment with *Castanea sativa* leaf litter extract, Al was displaced from the exchange complex by K^{+} , Mg^{2+} and Mn^{2+} and transported out of the column largely as an organic complex (Figure 3.2). In both cases there appears to be competition between Al^{3+} and Fe^{3+} for binding sites and these sites were effectively saturated in the case of *C. sativa* treatment.

Lowering of phytotoxic Al levels by complexation with organic acids and other molecules in leachates from leaf litter may be transient and disappear once the organic molecules decompose. More permanent changes will follow from the increase in pH arising from the oxidation of organic anions in the added leaf litter as discussed earlier in this report. Water soluble extracts from decomposing litter of certain trees may play a significant part in the movement of alkalinity to depth and the neutralisation of phytotoxic Al in an acid soil.

Field observations of the effect of trees on soil acidification

The six comparisons described in Results section 4 show that the pattern of distribution of cations and pH_{Ca} with depth in the soil is different under tree plantations than under adjacent pasture (or ley farming) land use. With the exception of some parts of the *Q. suber* plantation, the pH in the planted area was higher than outside. Some of the most marked effects occurred in the distribution of exchangeable Ca^{2+} and to a lesser extent exchangeable Mg^{2+} , which again with the above mentioned exception were higher under the trees. The age of the plantations varied from 76 years for the *Q. suber*, where effects were most marked, to 16 years for the tagasaste, where effects were not as large.

The differences in pH_{Ca} between these tree planted and unplanted sites could be interpreted as either an increase in pH under the trees or a decline in pH due to the pasture or ley farming over the period, and both effects may have contributed. Differences in pH found between paddock and roadside reserve in a survey conducted in the southern slopes region of NSW were interpreted as being due to acidification under farming (Chartres *et al.*, 1990). In Chartres's work the comparison was between land cleared for agriculture and land remaining in roadside reserves. In the present work, soils under trees planted on previously cleared agricultural land were compared with soils in the unplanted agricultural area (except for *M. azedarach* which was planted on a cleared roadside). We have no reason to doubt that acidification in the farmed areas would have continued after the trees were planted. At the very least, the cessation of agricultural production in the planted areas would have slowed acidification. The thesis that the trees have had a positive effect and actually raised pH and levels of cations on the surface is supported by observations at the *M. azedarach* site. Control samples were taken from the grazed pasture and the roadside away from the trees were similar to each other but different from the samples taken under the trees. Also at the Tagasaste site, the inter-row and row areas had been treated similarly and excluded from agriculture for all but the previous year, yet the pH_{Ca} and cation values of the inter-row samples were intermediate between the samples from the tree row and the farmed area indicating a greater effect near the trees, irrespective of the exclusion of agricultural activity.

The data taken as a whole suggests that trees have contributed to the redistribution of alkalinity. The concentration of alkalinity in the top 50 cm of soil under the trees must be occurring at the expense of acidification elsewhere. So far we have no evidence of lateral or vertical transfer of alkalinity. One possibility is that the acidification, having occurred in the rhizosphere along an extensive root system, the acid has diffused into a large bulk of soil where it is buffered and changes in pH are consequently difficult to measure. The converse is that the increase in pH in the surface is measurable because the alkalinity has been concentrated in a relatively smaller volume of soil. This work provides evidence for the redistribution of cations by trees and for the functioning of the biological ‘pump’. It is encouraging in that it shows that amelioration of acid surface soils by trees may be possible given suitable circumstances.

In an earlier review (Noble and Randall, 1998), commissioned by The Rural Industries Research and Development Corporation, we identified a number of gaps in our knowledge of the way trees affect soils. The work discussed above goes some way to filling those gaps. It provides a conceptual framework for further studies as discussed earlier (Noble *et al.*, 1996) and outlined below. It also gives some guidance for the management of tree plantings which is discussed under ‘Implications’, the following section.

On the basis of known information and these results, a scheme of the cycling of alkalinity and nutrients can be outlined which is relevant to the effects of tree growth on soil acidity. This is summarised in the cartoon below (Fig D1)

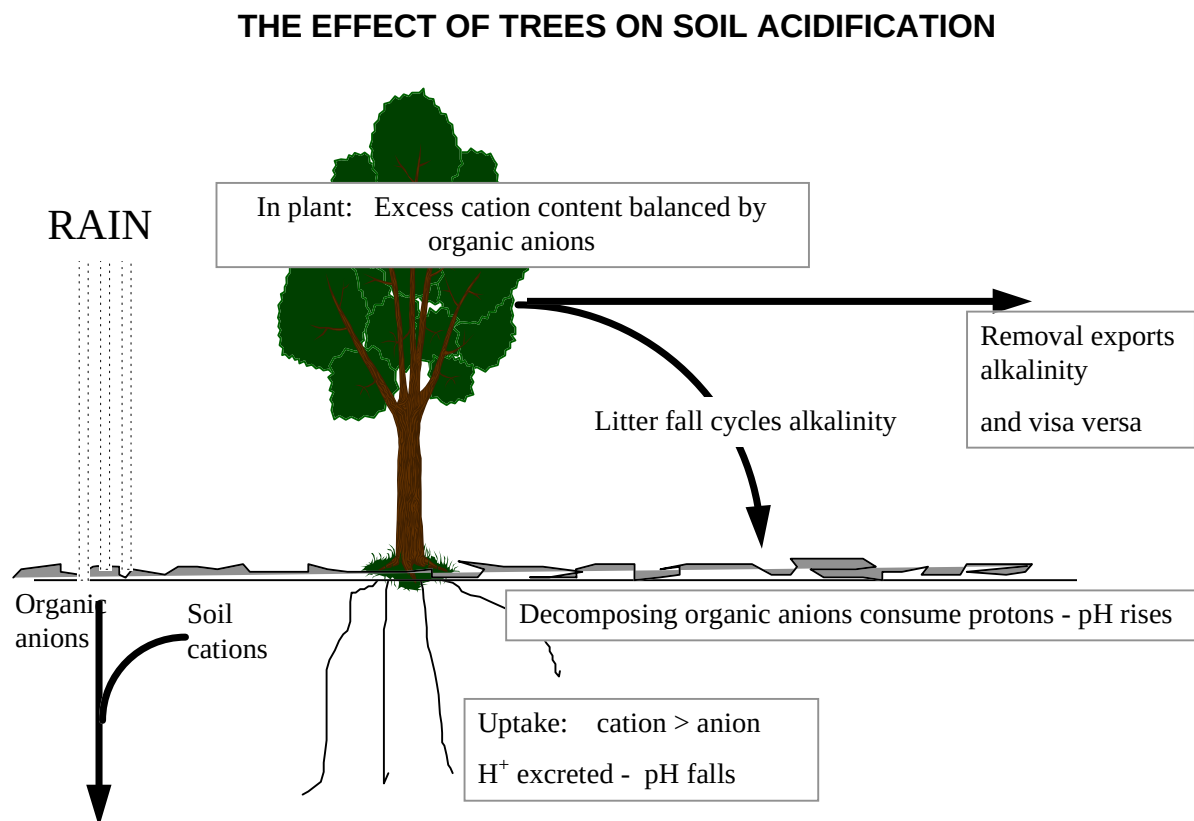


Figure D1. Illustration of some of the processes resulting redistribution of cations in soil

under trees in relation to soil pH.

Tree growth acidifies the soil in proportion to the excess of cation over anion uptake. This excess is balanced by the synthesis of organic anions and reflected in the ash alkalinity of the tree tissues. Tree growth also mobilises nutrients from the soil. Once in the tree the alkalinity and the nutrients are in transportable forms.

The net effect of trees on the soil will then depend critically on the fate of the tree and its litter. If the trees are burnt then alkalinity and nutrients in the ash remains at risk of being washed or blown away until it is incorporated into the soil. If leaf litter or timber is removed from or brought on to a site then there is a corresponding loss or gain of alkalinity or nutrients. If the material falls and decomposes on the site where it grew then there is no net loss or gain of nutrients.

But in the process of trees acquiring nutrients and dropping litter on the surface there may be a redistribution of minerals and alkalinity from the soil explored by the roots to the surface - the biological pump. This may be a lateral redistribution or vertically in the soil profile. Uptake of nutrients acidifies the soil around the roots. Organic material returned to the soil may decompose on the surface or may be first incorporated by earthworms. Oxidation of the organic anions will consume protons and raise the pH. The extent of the effects on soil pH will depend on the pH buffer capacity of the soil.

A further opportunity for redistribution within the soil profile occurs after the litter is deposited on the surface. Then soluble organic anions complexed with cations may be leached to deeper layers, the process continuing until the organic materials are oxidised. The oxidation process consumes protons and raises pH. The net result on the soil will depend on the magnitude of the above processes and where in the soil profile they occur

Many factors will thus determine the net effects of trees on soil pH. Apart from the characteristics of the soil, these include the rooting habits, growth rates and nutrient composition of the trees themselves, the quantities and composition of the litter produced, the fate of the trees and litter due to human or natural agencies and climatic factors which determine litter decomposition and leaching of litter products in the soil.

A basis for assessing the long-term impact of a tree species on soil chemical properties

Although some information exists to suggest that trees may promote the formation of podsolise through mobilisation of soil Al and Fe (Bloomfield, 1953)(Bloomfield, 1964)(McColl and Pohlman, 1986), there has been a paucity of information for predicting the influence of individual tree species on such soil formation processes and on soil chemical properties in general, and we lack methods for evaluating the long-term impact of trees on the soil resource base. In this project we have worked towards remedying this by evaluating a limited range of species for affects on soil acidification. Significant differences between species were found in ash alkalinity and in Al complexing ability of the water soluble fraction of the litter and these have been discussed above. We suggest that these two inherent characteristics of the litter material can be combined into an index for predicting some of the effects of these species on soil chemical properties (Figure D2). The rationale for this index is as follows.

Trees species producing litter with a high ash alkalinity can be considered as efficient in redistributing bases from the rooting zone to the soil surface through the process of ‘biological pumping’. In this way they have a potentially beneficial effect on the surface soil. There is clear evidence to suggest that this is the case in the field sites sampled.

In contrast, species whose litter contains compounds which have a high affinity for soil cations and can mobilise them through forming soluble complexes would allow leaching of cations from surface horizons and essentially promote podzolisation.

The quadrats in Figure D2 which are delineated by the median values for the group of tree species studied define four groups of species which are likely to have potentially different effects on soils.

Group 1 (top left): high ash alkalinity / low complexing ability; potentially leading to increased base status of the surface soil due to biological pumping.

Group 2 (top right): high ash alkalinity / high complexing ability; transfer of bases from depth to the surface is likely to be offset by high leaching with potential for podzolisation.

Group 3 (bottom left): low ash alkalinity / low complexing ability; transfer of bases from depth to the surface is likely to be relatively small, but the low complexing ability provides relatively low potential for podzolisation.

Group 4 (bottom right): low ash alkalinity / high complexing ability; little redistribution of bases to the surface to compensate for the high leaching potential giving strong potential for podzolisation.

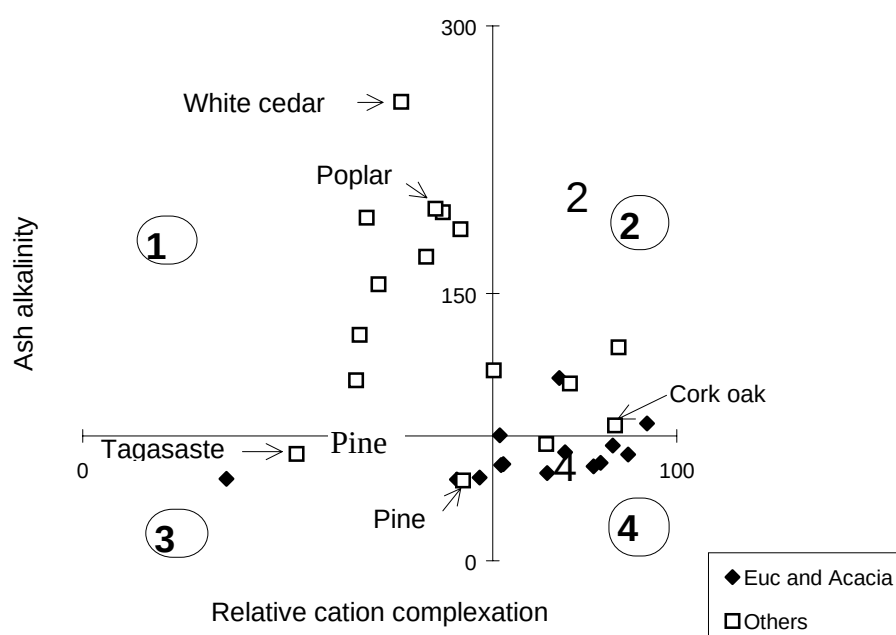


Figure D2 Cation complexing ability plotted against ash alkalinity. The relative complexing ability is based on data from a standard assay in which an aqueous extract of litter containing 34.8 mg organic carbon / L is incubated with 50 μ M Al at pH 4.0 and the labile (uncomplexed) Al is then measured (data derived from Tables 3.1a and b). The Al present in complexed form is expressed as a percentage of the initial Al. The axes intersect at the median values

The eucalypt and acacia species had generally low ash alkalinities. Because of relatively high complexing ability, the eucalypts fell mainly in group 4. The relative distribution between these four groups of the species which were studied in the field samplings accords with the effects observed. White cedar and poplar in group 1 showed an increase in cations in the soil beneath them. Radiata pine in group 3 showed relatively little effect on soil, while under cork oak (in group 4) there was evidence of podzolisation. The relatively small effect of tagasaste was consistent with the species being in group 3, although the relatively short time since establishment makes a conclusion here difficult. Unfortunately, there were no samples of river red gum included in the laboratory studies and therefore it could not be placed in Figure 2D.

Implications and recommendations

Once nutrients have been mobilised from the soil and taken up by plants they are in transportable forms and the fate of the tree and litter is critical in determining the effect of tree growth on the pH and fertility of the soil. In developing acidity budgets for tree plantings a knowledge of the ash alkalinity of litter, foliage, bark and timber would be required. In this study the focus has been on the quantification of this parameter in the leaf litter. The fact that we have shown that leaf litter from tree species can bring about significant amelioration of acidity, suggests that the planting of selected species on specific soil types (such as acid sodic soils) may be a viable option in the remediation of marginal lands affected by accelerated acidification. This is the first study that we know of that has attempted to match tree species to the remediation of acid soil problems.

This study has shown that tree species differ in

- ash alkalinity of their litter
 - mineral nutrient concentration, particularly calcium concentration of their litter
- and that ash alkalinity and Ca concentration are highly correlated.

Such factors could influence decisions when selecting between alternative species for planting on a particular site. Some examples could be:

Situation	Appropriate ash alkalinity (other factors being equal)
Planting on neutral to alkaline soils	High or Low
Planting on neutral to acid poorly buffered soil	Low
Planting on acid duplex soil with base-rich subsoil	High
Planting where removals of alkalinity are balanced by lime application	High or Low
Growing material off site for transfer to improve an acid soil	High
Planting on a site with high risk of litter loss by wind or water erosion	Low

It has further been shown that the ability of leachates from leaf litter to complex cations differs markedly between species. This has implications for lowering the levels of phytotoxic aluminium in acid soils under leaf litter while the soluble organic materials remain undecomposed. Long term effects will follow from the movement in soils of cations in organic complexes by leaching. This may accelerate the natural process of podsolisation, as demonstrated with *Q. suber* and *Castanea sativa*, which would result in a lowering in fertility status. This aspect should be borne in mind when considering specific species for possible revegetation programs.

An index which includes both ash alkalinity and cation complexing ability has been proposed. This needs further testing and if the results are consistent with our present data should enable

a rapid evaluation of species with respect to their potential long term effects on soils.

Field measurements have indicated that trees can make an appreciable difference to the acidity and exchangeable cation content of the soil which underlies them, within a few decades of planting. We have not made estimates of the rates of change which occur. However, we have identified some of the factors which will determine species differences. Given rates of growth and litter production and knowing ash alkalinity of the materials and pH buffer capacity of the soils, calculations of the potential effects on soil acidity over time could be made. This study represent the first attempt to characterise a number of indigenous and deciduous / temperate species for their chemical composition, ash alkalinity and Al/Fe complexing ability. This data set would assist in the decision making process in the selection of trees for specific purposes.

Intellectual property

No intellectual property was expected to arise from this project and none has.

Summary

This work has provided evidence for the role of tree plantings in the redistribution of alkalinity and also of nutrients in soils. Field studies showed that the soil under plantings of several tree species had a higher pH and exchangeable cation content than similar soil immediately adjacent under pasture or ley farming. However, at one site there appeared to have been a marked decline in pH and soil cation content under *Q. suber* (*Quercus suber*) trees. It is argued that while the soil under pasture may have acidified due to agriculture since the plantations were established, the trees themselves had influenced the properties of the underlying soil.

To further understand the mechanisms involved in the redistribution of nutrients and changes in soil acidity by trees, 56 samples of litter were collected and characterised for ash alkalinity, mineral composition and the ability of their soluble extracts to complex aluminium. The samples represented 33 species including exotic deciduous, exotic evergreen and indigenous species.

There were substantial differences between species in the composition of cations in the leaf litter. Ca was the predominant cation in most samples and levels ranged from 5 mg g⁻¹ in *Eucalyptus regnans* to 40 mg g⁻¹ in some samples of white cedar (*Melia azedarach*). There were also very large differences in ash alkalinities between leaf litter samples. At one extreme was radiata *Pinus radiata* needles with ~45 cmol_c kg⁻¹ ash alkalinity. At the other was *Melia azedarach* with up to 250 cmol_c kg⁻¹. This range is comparable to that of agricultural plants. Soil and nutritional factors as well as time of the season influenced ash alkalinity but the ranking of species was maintained over a wide range of conditions, indicating the importance of genetic characters. Ash alkalinity, measured by ashing and titration, was correlated with cation excess, calculated by difference between concentrations of cations and inorganic anions (cation excess = 0.95 titration - 8.8; $r^2 = 0.89$). In this set of samples, ash alkalinity and Ca concentration were highly correlated (ash alkalinity (cmol_c kg⁻¹) = 18.92 + 6.88 Ca (mg kg⁻¹); $r^2 = 0.98$), and Ca concentration could be a useful preliminary index of litter quality for amelioration of acid soil .

Incubation of litter with an acid soil for 8 weeks raised soil pH and exchangeable Ca. Ash alkalinity is an indirect measure of organic anion content of plant material. Organic anions are

synthesised to maintain charge balance between cations and anions in plant tissue. Litter would be expected to have a neutralising value in proportion to the content of organic anions, which when oxidising consume protons. There was a significant positive relationship between the amount of ash alkalinity added and soil pH after incubation but the slope of the line differed between species. On a calcium carbonate equivalent basis, *M. azedarach* litter was similar to lime in effect on soil pH. Litter from species such as liquidambar (*Liquidambar styraciflua*), and birch (*Betula pendula*) had a lower neutralisation effect than would be predicted from their ash alkalinities. This was attributed to differences in degree of decomposition of the material, and possibly the nitrogen content.

The water soluble extracts from litter of different species differed substantially in their ability to complex aluminium in solution. It is thought that the formation of organic-Al complexes in acid soil infiltrated with leachates from litter would lower the levels of phytotoxic Al in the soil and thus benefit plant growth. However, such effects are likely to be temporary pending the eventual decomposition of the organic materials. Detailed studies with chestnut (*Castanea sativa*) and *M. azedarach* litter extracts applied to soil columns showed that both the pH and the complexing ability of the litter extracts were important. *M. azedarach* extract displaced Al from the exchange complex and, because of its high pH, precipitated Al. Chestnut extract strongly complexed and leached Al.

We have proposed an index which includes litter ash alkalinity and cation complexing ability to allow classification of species for their potential long term effects on soil. If this index stands up to further evaluation it should prove useful in matching species to particular soils.

The study provides evidence for the operation of the “biological pump” in redistributing nutrients in soils. The mobilisation of nutrients into trees provides the opportunity for the redistribution of alkalinity in the soil profile through the deposition of organic anions in litter on the surface. This will have important consequences for soil acidification, depending on the fate of the litter. If the litter is lost from the site, the net effect will be acidification of the soil. We hypothesise that loss of litter contributed to the acidification which occurred under the *Q. suber* plantation mentioned above. If the litter decomposes in situ, then the pH and nutrient content of the surface soil will be raised. We suggest that this occurred at the other field sites examined. The operation of the “biological pump” would be expected to have different consequences depending on the soil. On poorly buffered soils amelioration of acidity in the surface by leaf litter may be at the expense of undesirable acidification of the subsurface soil. In acid duplex soils, if the roots can take up cations from a neutral or alkaline B horizon, the deposition of litter containing high levels of ash alkalinity on the soil surface would be without detriment to the subsurface. These are considerations when selecting trees for particular sites.

Publications arising from the work

1. Noble, A.D. and Randall, P.J. (1995) The amelioration of soil by trees. Review for the Rural Industries Research and Development Corporation.
2. Noble A D and Randall P J (1995) Ash alkalinity of the leaf litter of tree species and effects on pH and phytotoxic aluminium in an acid soil. National Workshop on the Effects of Agroforestry on Soil Fertility, Canberra, March 1995
3. Noble A D and Randall P J (1995) Do deep rooted perennial species have a role in the management of acid soils? Ash alkalinity of the leaf litter and neutralisation of soil acidity. National Soil Acidity Workshop, El Caballo, Western Australia, September 1995.
4. Noble A D and Randall P J (1996) Effects of tree leaf litter properties on soil acidity. IV International Symposium on Plant Soil Interactions at Low pH, Belo Horizonte, Brazil. March 1996. Poster presentation
5. Noble, A.D., Zenneck, I. and Randall, P.J. (1996) Leaf litter ash alkalinity and neutralisation of soil acidity. *Plant and Soil*. 179, 293-302
6. Randall, P J and Noble, A D (1998) The effect of trees on soil acidification. National Soil Acidification Conference 1998. Coolumb Qld.
7. Noble A D, Little I P and Randall P J (1998) A comparison of the influence of *Pinus radiata* (radiata pine) and *Quercus suber* (cork oak) and improved pasture on soil chemical properties. (submitted to Australian Journal of Soil Research))
8. Noble, A D and Randall, P J (1998) The role of leaf litter from a number of tree species in the neutralisation of soil acidity. (in review for Agroforestry Systems)
9. Noble A D, James T J and Randall P J (1998) Influence of water soluble extracts from leaf litter of the tree species *Melia azedarach* and *Castanea sativa* on chemical properties of an acid red podzolic soil. (in revision)

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