Chapter 13

Subsurface soil acidification in farming systems: its possible causes and management options

Caixian Tang, Chandrakumara Weligama and Peter Sale

Department of Agricultural Sciences, La Trobe University, Melbourne Campus, Bundoora, Vic 3086, Australia

1. Abstract

Subsurface soil acidity is widespread and its amelioration is costly and often practically infeasible. This paper summarises recent research on the causes and management of subsurface soil acidity in farming systems. The development of subsurface soil acidity depends largely on acid production by plant roots due to excess cation uptake, particularly under legume-based agriculture. The deposition and decomposition of plant residues do not cause subsurface soil acidification but contribute to the development of subsurface soil acidity profiles through their liming effect on the topsoil. Nitrification from ammonium-based fertilizers or from organic N in plant residues, and subsequent leaching of nitrate, contribute mainly to topsoil acidification. In contrast, the uptake of leached nitrate and denitrification in deeper layers may decrease subsurface soil acidity. Various application methods and liming materials have been studied for their effectiveness in ameliorating subsurface soil acidity. These include application of lime, gypsum and organic materials, and growing acid-tolerant crops. Biological amelioration through managing excess anion (nitrate) uptake has been tested in the field and is a promising method to ameliorate subsurface soil acidity. The major challenge for the biological amelioration method is to synchronize nitrate movement and root capture in the subsurface soil for maximal alkalization and minimal nitrate leaching loss.

Key words: Biological amelioration, C cycle, cation-anion uptake, N cycle, crop residues, subsoil acidity

2. Introduction

Approximately 50% of the world's potentially arable land area consists of acid soils (pH≤5.5) (Kochian et al. 2004) and many soils have acidity below the plough layer (Sumner 1995). Topsoil acidity is commonly ameliorated with liming. However, lime movement down into the subsurface soil is slow, especially in variable charge soils and hence surface application of lime is often inefficient at ameliorating subsurface soil acidity. Although heavy top dressings with lime may have an ameliorating effect on subsurface soil acidity (see below), such high rates have adverse effects on some crops in the rotation (McLay et al. 1994a) or cause lime-induced deficiencies of nutrients such as Mn and Zn. Deep placement of lime into acid subsurface soil through injection and/or ripping is generally considered to be uneconomic.

Unfortunately, subsurface soil acidification (below the plough layer) is a continuing process under many farming systems, especially legume-based systems. Soil acidification can occur in soil profiles to a depth of more than 80 cm (Williams 1980; Coventry and Slattery 1991; Dolling and Porter 1994; Conyers et al. 1996; Moody and Aitken 1997; Noble et al. 1997b). In many soil profiles, acidification rates are greater in the subsurface soil than in the topsoil. For example, in the central wheatbelt of Western Australia, soil pH increased with increasing soil depth at uncleared (native vegetation) sites, whereas at cleared (farmed) sites the lowest pH occurred in the 10 to 30 cm layers. In southern New South Wales, even fertile red earth soils are showing the development of an acidic layer below the normal plough depths (Conyers et al. 1996).

Subsurface soil acidity is associated with toxicities of aluminium and manganese, and deficiencies of calcium and phosphorus. It primarily decreases root elongation, resulting in a poor root system and hence a decrease in the uptake of nutrients and water, particularly for acid-sensitive crops (Tang et al. 2002). Moisture in the topsoil is often depleted late in the growing season as temperatures and growth rates increase. Plants are therefore forced to rely on the supply of water and nutrients from deeper soil layers. However, the poor root systems of crops grown with subsurface soil acidity will limit reproductive growth and final grain yields.

There are several excellent reviews on the general topic of soil acidification and the management of soil acidity (e.g. Helyar and Porter 1989; Bolan and Hedley 2003; Coventry et al. 2003) which do not cover much on subsurface soil acidity and will not be the focus of this chapter. Instead, the chapter will review current knowledge on possible causes of subsurface soil acidification, especially under legume-based farming systems. It will then discuss management options for subsurface soil acidity with an emphasis on the biological amelioration through managing cation/anion uptake. This chapter does not attempt to review causes of subsurface soil acidification as a result of natural weathering processes (see Sumner 1995) or acid precipitation (see Alewell 2003).

3. Causes of subsurface soil acidification

Soil acidification in farming systems is attributed to a number of processes. The major causes in farming systems are the removal of alkalinity in farm products in the carbon cycle, and release of protons during N_2 fixation and nitrate leaching in the nitrogen cycle. Subsurface soil acidification, on the other hand, appears to be mainly caused by spatial separation of acid and alkali produced in these cycles (Figure 1). Tang and Rengel (2003) described the processes which contribute to this separation and to the development of acidity in deeper soil layers. In the carbon and nitrogen cycles, the acid produced by the roots due to excess uptake of cations over anions is distributed through the rooting zone, with the amount and distribution of the acid being proportional to the root length distribution. Plant residues in the carbon cycle however, are mainly oxidised in the surface soil. This oxidation of organic anions present in the residues is an acid-consuming process (increases pH), and thus the acidity generated by roots is neutralised in the topsoil, but still remains in the subsurface soil. In the nitrogen cycle, mineralization and nitrification mainly occur in the topsoil. When these processes are accompanied by nitrate uptake in the topsoil, then there is no change in topsoil pH. However, if nitrate is leached from the topsoil, then there will be a surplus of protons in the topsoil (Figures 1 & 2) resulting in topsoil acidification. The leaching of nitrate originating from the topsoil is unlikely to cause subsurface soil acidification. In contrast,

uptake of nitrate by roots and denitrification in subsurface soil layers may reduce the net production of acid by the roots. These processes are discussed in detail below.
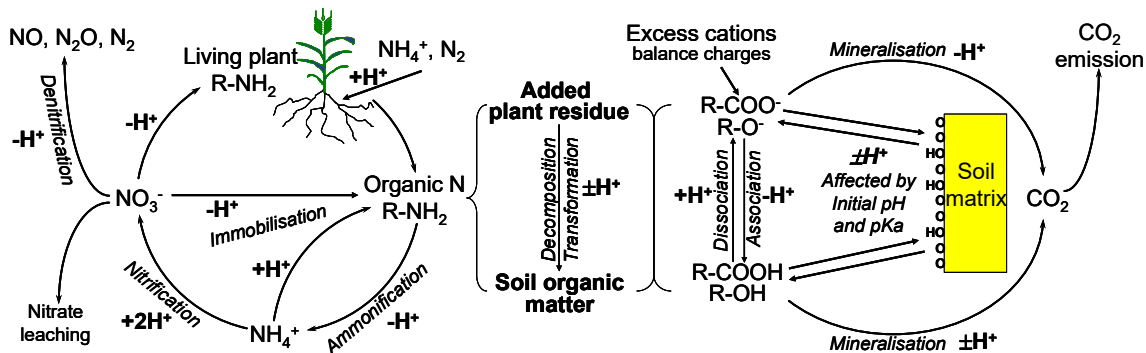
Figure 1. A simplified diagram illustrating the production and consumption of protons (H^+), in the nitrogen (left) and carbon (right) cycles. $\mathbf{+H^+}$ indicates acidification (decrease in pH); $\mathbf{-H^+}$, alkalization (increase in pH) and $\mathbf{\pm H^+}$, unknown effects.

3.1. Excess uptake of cations over anions

Plant roots take up nutrients from soil solutions to satisfy their growth requirements. The uptake of cations across the plasma membrane is associated with H^+ extrusion while uptake of anions is associated with OH^-/HCO_3^- release (or H^+ consumption). If plants take up more cations than anions, then there is an overall net extrusion of H^+ around the roots. If plants take up more anions than cations, there is a net alkalization along the roots (Marschner 1995; Paul et al. 2003; Tang and Rengel, 2003; references therein).

The form of nitrogen plays a prominent role in the cation-anion balance (see detailed discussion below). NH_4^+ nutrition leads to an excess uptake of cations over anions and to strong acidification, whereas NO_3^- nutrition results in a rhizosphere alkalization. By comparison, legumes that are actively fixing N_2, take up more cations than anions, and hence release H^+ and acidify their rhizosphere (van Beusichem 1981; Jarvis and Hatch 1985; Loss et al. 2003b; Tang and Rengel 2003). A close linear relationship was found between the amount of H^+ released and the excess of cations over anions taken up by N_2-fixing plants from various legume species (Tang et al. 1997).

Plant species differ substantially in their acid production and their capacity to acidify soils (Tang and Rengel 2003; references therein). Legumes generally cause more soil acidification than non-leguminous species. This may be attributed to the following likely causes. The first is that legumes excrete large amounts of protons due to excess cation uptake during N_2 fixation. Second, legume residues contain high N, resulting in large amounts of nitrate produced during residue decomposition. Finally, legumes generally have a restricted rooting system, with a poor ability to take up soil nitrate during growth, and this can lead to nitrate leaching from the root zone and to acidification due to a net proton surplus (Figure 1).

Tropical legumes generally have lower excess uptake of cations over anions than temperate legumes, and thus have a lower acidifying effect on the rhizosphere and the bulk soil (Andrew et al. 1973). In addition, the products of N assimilation in tropical legumes appear to be

ureides (allantoin and allantoic acid, which have high pK_a values) and are unlikely to be dissociated to donate protons at physiological pH values in the cytoplasm and the xylem (Bolan et al. 1991).

The release of acid produced by excess cation uptake from the soil depends on the distribution of the roots and nutrients, the pattern of nutrient uptake and H^+ extrusion along the roots. In an experiment using 1-m soil columns (Tang et al. 2000), where nutrients were applied uniformly throughout the column, root length density of NH_4^+-fed lupin and subterranean clover plants tended to increase with depth, and relatively uniform decreases of soil pH occurred in the soil profile. Where nutrients were applied only in the top 10-cm layer, then 50-70% of the roots of N_2-fixing plants were distributed in this layer and the soil pH decreased most in this top layer. The decrease of pH in different soil layers was proportional to the root length density (Tang et al. 2000). In the field, deeper-rooted legumes appear to cause subsurface soil acidification to greater depths than shallower-rooted legumes. For example, Loss et al. (1993a) observed more soil acidification in deeper layers of soil profiles under a deep-rooted lupin-wheat rotation than under shallow-rooted clover-based pastures. The results do suggest that excess cation uptake by plant roots plays an important role in subsurface soil acidification.

3.1. Role of plant residues

The accumulation of organic matter has been suggested as one of the causes of soil acidification. Two reasons for this explanation have been proposed: (i) organic matter forms soluble complexes with cations such as Ca and Mg and thus facilitates the leaching loss of these cations, and (ii) organic matter contains functional groups which can be a source of H^+ ions after dissociation (Brady and Weil 2002; Bolan et al., 2003). Organic matter is also thought to lower soil pH by releasing H^+ ions that are associated with organic anions, by the mineralisation of its N and the subsequent nitrification or by an increased cation exchange capacity and corresponding increase in exchangeable acidity (Williams 1980).

However, in many soil profiles the most acidified layers were below 10 cm, even though organic matter generally accumulated in the top 10 cm of the soil (Williams 1980; Dolling and Porter 1994). Indeed, in some farmed soils, the pH increased in the topsoil compared to the nearby uncultivated bushland soils (e.g. Dolling and Porter, 1994). Similarly, in a field survey, Griffin et al. (2003) examined the impact of land use on soil organic carbon and pH across various agro-ecosystems in Western Australia. It was found that soil pH was consistently lower at soil depths of 10-100 cm at sites that had been farmed for many years, compared to the corresponding uncleared 'native vegetation' sites. It was also shown that the organic carbon in the topsoils from uncleared bush sites tended to be less than those from farmed sites, but the reverse occurred in the subsurface soil, where the organic carbon in uncleared sites was generally greater than that in farmed sites. This indicates that organic matter accumulation may not be always associated with soil acidification.

The addition of organic matter to soil has been found to increase, decrease or have no effect on soil pH (Ritchie and Dolling 1985; Yan et al. 1996; Tang and Yu 1999; Tang et al. 1999; Marx et al. 2002; Paul et al. 2003; Xu et al. 2006b). These conflicting accounts of the effect of organic matter on soil acidification have probably resulted from differences in (i) composition of organic matter present in or added to soil, (ii) soil characteristics and (iii) decomposition resulting from different experimental conditions, such as temperature, water regime and leaching, that were used in the different experiments.

Our recent studies have shown that addition of plant residues increased the pH of acidic soils. Furthermore, the amounts of alkalinity produced in the soil correlated positively with concentrations of excess cations and total nitrogen in the added residues, and negatively with the initial pH of the soil (Tang and Yu 1999; Xu et al. 2006b). Thus, the amount of alkalinity produced in soil decreased with an increase in the initial pH of the soil. The studies also demonstrated that the effects of the plant residue on alkalinity production were less under sterile conditions than under non-sterile conditions, and changes in soil pH were related to CO_2 release, and the dynamics of NH_4^+ and NO_3^- in the soil. Xu et al. (2006b) suggested that there were at least four components responsible for soil pH changes after plant residues were added to the soil: (i) mineralisation of organic anions (balanced by excess cations) from added plant residues, (ii) ammonification (organic N $\rightarrow$ NH_4^+) of the residue N, (iii) nitrification (NH_4^+ $\rightarrow$ NO_3^-) of mineralised residue N, and (iv) association/dissociation of protons from organic compounds. Processes (i) and (ii) result in an alkalization of the soil while Process (iii) acidifies the soil. The influence of Process (iv) on soil pH change depends on the initial pH of the soil and the pKa of the organic compounds present. The overall effect of plant residue addition on soil pH therefore depends on the extent of each of these processes.

From above studies and those published earlier, it is suggested that the deposition and subsequent decomposition of plant residues do not necessarily cause subsurface soil acidification. Rather they contribute to the development of the pH variation in soil profiles through their effect on the topsoil. The addition of plant materials to acidic soils generally increases soil pH. While the extent of proton excretion from roots during plant growth is proportional to the root distribution, the oxidation of organic anions during decomposition of the shoot residue mainly occurs in the topsoil since residues are generally not incorporated into deeper layers. Thus, the decomposition of shoot residues neutralises the acid created during plant growth in the topsoil. In some soils where subsurface soil acidification has occurred, an increased soil pH with time of farming has been observed in the topsoil (e.g. Dolling and Porter 1994). Root residues usually have lower concentrations of excess cations than shoot residues and have a lesser "liming" effect (Tang and Yu 1999; Tang et al. 1999). Therefore, root residue decomposition will not fully neutralize the acidity created along the roots in the soil profile and this acidity, produced during growth, will persist in the subsurface soil layers.

3.3. Nitrification and nitrate leaching
Nitrification and the subsequent leaching of nitrate have often been suggested as a major cause of soil acidification. However, such processes do not appear to be a cause of subsurface soil acidification. Mineralization and nitrification of plant residue N have been shown to occur mainly in the topsoil due to the relative immobility of NH_4^+ and deposition of plant residues on the soil surface. For example, 64% of N mineralisation and 50% of nitrification in the soil profile of a loamy sand, and 78% of N mineralisation and 41% of nitrification in a sandy clay loam occurred in the top 5-cm soil layer (Murphy et al. 1998). More recently, Dear et al. (2009) showed that while NH_4^+ was mainly concentrated in the topsoil of two Red Kandosols over the growing season, the concentration of NO_3^- decreased in the topsoil and increased below 30 cm, with annual pasture legumes. Thus, acidification caused by nitrification, and the subsequent leaching of nitrate, occurs mostly in the topsoil. There will be no net acidification in the topsoil if plant roots utilize all of the nitrate generated *in situ*. Nitrate uptake enhances excess anion uptake, and thus decreases extrusion of H^+ or increases extrusion of OH^-/HCO_3^-. However, if the nitrate is leached, then the topsoil will acidify because of the net increase in H^+ ions (Figure 2) and because the leaching of nitrate is accompanied by the leaching of cations other than H^+ ions (Di and Cameron 2005). If plant

roots take up the leached nitrate below the topsoil layer, it is expected that alkalization (or less acidification) will then occur in the subsurface soil. These processes are illustrated in Figure 2.
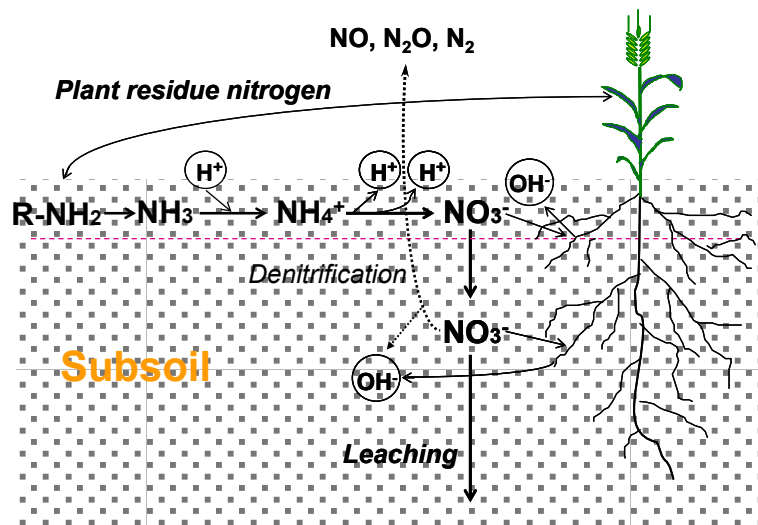
Figure 2. Schematic illustration of nitrogen transformations, and nitrate leaching and uptake, in relation to acidification in the soil profile.

The hypothesis that nitrification in the topsoil, and the subsequent leaching of nitrate into the subsurface soil, can decrease subsurface soil acidification, was tested in two column experiments with a sandy soil by Tang et al. (2000). These experiments examined the effect of nitrate and ammonium addition to the topsoil on subsurface soil acidification under wheat and the N_2-fixing legumes, lupin and subterranean clover. Nitrate leaching was achieved by adding excess water to the surface of the columns 18 days after sowing. In the first experiment, the addition of $Ca(NO_3)_2$ to the topsoil layer increased nitrate concentration in soil profiles but did not affect the growth of shoot and roots, or the N concentration in shoots of either species. It caused alkalization or reduced acidification at all depths, compared to the treatment without $Ca(NO_3)_2$.

In the second experiment, the addition of $(NH_4)_2SO_4$ to the top 10 cm significantly increased NO_3^- concentration in all layers with NH_4^+ being mainly retained in the top 20-cm layer. Compared to the plants receiving no $(NH_4)_2SO_4$, lupin grown with $(NH_4)_2SO_4$ in 0-10 cm of the column, caused more acidification in the top 10 cm but less acidification in 10-40 cm of the column. Similarly, subterranean clover grown with added $(NH_4)_2SO_4$ in the 0-10 cm layer caused more acidification in the top 10 cm and less acidification in the 20-50 cm layer. Growing wheat with $(NH_4)_2SO_4$ in the topsoil decreased soil pH in top 20 cm but slightly increased soil pH in the deeper layers (Tang et al. 2000). Clearly, leaching of nitrate from topsoil is unlikely to cause subsurface soil acidification. In contrast, the uptake of nitrate by the roots reduces net acid production in subsurface soil layers. Further research is needed to validate the results under field conditions.

3.4. Acid movement
The downward movement of H^+ and soluble Al, and NH_4^+ may contribute to subsurface soil acidification (Hue and Licudine 1999) but the magnitude of the downward movement is unknown. It is expected that such acid movement would be small because of the high affinity

of H^+ and Al^{3+} ions for negatively charged surfaces of soil colloids. In many soil profiles, pH is also higher in topsoil than in the subsurface soil so that little acid is able to move downward via mass flow or diffusion. Another consideration is that although the highest concentration of acids (lowest pH) is generally present in the subsurface soil layer, there is no evidence that this high concentration of acid moves lower over time. For example, the lowest soil pH in a deep yellow sand always remained between 10-30 cm irrespective of the years of farming (Dolling and Porter 1994). If the acid had moved deeper in the profile, this low soil pH should have moved into the lower layers with time. Further studies are required to verify this view.

4. Current methods for ameliorating subsurface soil acidity

Various application methods and liming materials have been studied for their effectiveness in ameliorating subsurface soil acidity. Some of these methods will be briefly discussed below. The first method that should be mentioned is surface liming. It may partially ameliorate subsurface soil acidity while direct liming into acidic subsurface soil has generally produced a quicker and greater yield response. Field trials have demonstrated yield advantages in growing acid-tolerant wheat varieties in soil with subsurface soil acidity (Scott et al. 2001). Modelling work has indicated that growing acid-tolerant wheat partially eliminates the adverse effects of acidity on crop yields in soils with severe subsurface soil acidity and almost fully eliminates the effect in soils with shallow/moderate subsurface soil acidity (Tang et al. 2003a).

4.1. Application of ground limestone
The surface application or otherwise shallow incorporation (0-10 cm) of lime is the most common practice to combat soil acidity in agriculture. Short-term yield responses to surface liming of soils with acid subsurface soils are often lacking or vary greatly, depending on application rate, lime quality, crop species, rainfall, acidity profile, soil type and the severity of acidity (Conyers and Scott 1989; Conyers et al. 1991; Scott et al. 1997; Whitten et al. 2000; Tang et al. 2003). Normally, the response to lime application by plants starts slowly and diminishes over the time (Mahoney and Uren 1982). The impact of liming is mainly restricted to the depth of its application because lime is a relatively insoluble material. The alkalinity-producing products in the form of OH^-, HCO_3^- and CO_3^{2-}, move slowly in soil profiles (Farina 1997, Scott et al.1997; Conyers et al. 2003). Furthermore, the increase in the surface soil pH by liming is likely to increase the negative charge (CEC) thereby increasing the retention of Ca, especially in variable-charge soils. Therefore, the effect of surface-applied lime on increasing subsurface soil pH can be limited with realistic lime application rates (2 t ha^{-1}) (Conyers and Scott 1989; Scott et al. 1997).

Many reports have therefore stated that surface liming gives no yield increase under different crops and soil types with subsurface soil acidity (Helyar 1991; Conventry 1992; Farina 1997). This problem can be partially overcome by applying high rates on the soil surface or incorporating lime into deep soil layers (Pinkerton and Simpson 1986; Conyers et al. 2003). Application of large doses of lime cannot be justified due to problems associated with over-liming including trace element deficiencies (Porter 1984; Bolland et al. 2001; Tang et al. 2003b). On the other hand, lime application is becoming a costly endeavour in many countries due to the transportation cost (Conyers et al. 1996). In addition, the cost of liming can be much higher compared to the returns from liming in low rainfall areas (Helyar et al. 1988). Nevertheless, a limited number of studies have showed that surface liming may partially ameliorate subsurface soil acidity in the long term (e.g. Sumner 1995; Whitten et al. 2000; Tang et al. 2003a).

Direct liming into the acidic subsurface soil layer through injection and/or ripping results in quicker and greater yield responses than surface lime applications (e.g. Coventry 1991; Sumner 1995; Scott et al. 1997). However, deep incorporation of lime is impractical due to lack of suitable machinery and high energy cost (Sumner et al. 1986; Scott et al. 1997).

Liming increases mineralisation and nitrification in acidic soils and hence can increase the likelihood of NO_3^- losses from leaching (Ridley et al. 2001). This in turn reduces the effect of the lime application on increasing the pH in the topsoil because NO_3^- leaching contributes to topsoil acidification. However, if the leached NO_3^- ions are taken up by the plants in the subsurface soil, then it is likely that the plant roots in the deeper soil layers will release OH^- and therefore counteract subsurface soil acidification and reduce subsurface soil acidity (as shown in Figure 2).

4.2. Application of gypsum

Surface-applied gypsum has been recognised as an economically viable, alternative method for combating subsurface soil acidity (McLay et al. 1994a). Gypsum ($CaSO_4 \cdot 2H_2O$, Ksp 2.1×10^{-5}) is more soluble than lime ($CaCO_3$, Ksp 8.7×10^{-9}) and thus moves faster in soil profiles. Additionally, the increase in pH in the surface layer increases the retention of Ca (see above). Gypsum was previously used in agriculture because of its ameliorating qualities in sodic soils, its ability to act as a soil conditioner, and its high content of Ca and S enabling it to act as a source of nutrients for plants (Shainberg et al. 1989). Yield responses to gypsum addition to acid soils, in most cases, were due to either improvement of Ca status or to a decrease in bioavailable Al in subsurface soil, which in turn stimulated root growth (Sumner 1993; Farina et al. 2000). As a result, plants can have better access to water and nutrients in acid soils. The effect of gypsum lasts longer in heavy-textured than light-textured soils. In a loamy sand profile surface-applied gypsum can be leached out from the profile in 5 years (Sumner 1990).

There are a number of explanations for the ameliorating effect of gypsum in acid soils. The first explanation is that the sulphate ions displace hydroxide ions from soil surfaces into the soil solution, which in turn react with free Al^{3+} (Reeve and Sumner 1972). The second suggestion is that sulphate can form non-toxic $AlSO_4^+$ ion pairs or non-soluble aluminium hydroxy sulphate (Alva et al. 1988). Thirdly, leaching of gypsum can increase ionic strength in the subsurface soil, which in turn reduces Al^{3+} activity (Ritchie 1989). Displacement of Al from soil colloids and the subsequent leaching of Al from soil is another suggestion (Oates and Caldwell 1985).

There is however conflicting evidence relating to the effect of gypsum on soil pH. Smith et al. (1994) found that the gypsum treatment (2.5 t ha^{-1}) reduced pH by 0.2 units in the 5-10 and 10-15 cm soil layers compared to the control. Probable displacement of Al^{3+} and H^+ from cation exchange sites by soluble Ca^{2+} appears to be a possible reason for the pH decrease. In contrast, the application of gypsum increased soil pH in other experiments (Sumner 1995). In these situations, the pH increase was attributed to the ligand exchange process in which the SO_4^{2-} ions replaced OH^- ions (Smith et al. 1994). The above two processes are likely to happen simultaneously and so the final pH in a gypsum-amended soil would be the net effect from both processes.

There are some implications for gypsum use as an ameliorant of acid soils. Gypsum application, especially at high rates can have adverse effects on the yield of some crops such

as lupins (McLay et al. 1994a) and can cause Mg and K to leach from the upper layers in sandy soils (McLay et al. 1994b). The application of gypsum can also be costly as more than 5 t ha^{-1} may be required to get a significant benefit (Farina 1997).

4.3. Application of plant residue and animal manure

The application of plant residues and animal manures to soil is considered to be a good agricultural management practice. This is because of the positive impacts on plant growth by providing plant nutrients (Bessno and Bell 1992; Naramabuye and Haynes 2006) and by improving soil structure. Organic acids are released during the decomposition process of organic materials. These acid ligands are known to be effective in binding toxic Al^{3+} (Hue et al. 1986). The organically-complexed Al species are less toxic to plant roots (Wong and Swift 2003). For example, in an experiment with highly acidic mine-spoil material (pH below 3.5) high rates of compost provided sufficient Al sorption capacity to keep the Al^{3+} activity in soil solution low enough for plant growth (von Wilert and Stehouwer 2003).

Apart from the effect of $CaCO_3$ in some animal manures, the addition of organic materials can also increase soil pH at least in the short term (Haynes and Naramabuye 2001; Wong and Swift 2003). This pH increase can be mainly due to decarboxylation of water-soluble organic anions in the materials (Yan et al. 1996; Rukshana et al. 2010). Other mechanisms that have been suggested to account for an increase in soil pH include: (i) adsorption of H^+ onto the surface of the organic materials (Hoyt and Turner 1975), (ii) production of OH^- ions by ligand exchange between the terminal OH^- on the sesquioxide surfaces and organic anions (Hue and Amien 1989), (iii) accumulation of NH_4^+ and hydrolysis of NH_3 during the decomposition of organic N (Hoyt and Turner 1975; Naramabuye and Haynes 2006), (iv) increase of soil base saturation through the replacement of protons and aluminium from exchange sites by cations added with organic matter (Bessho and Bell 1992), and (v) development of reducing conditions and associated denitrificaiton due to stimulated microbial activity during the rapid decomposition of the added organic matter (Hue 1992).

The composition and the degree of decomposition of organic materials may affect the amount of alkalinity released during decomposition (Noble et al. 1996, Tang et al. 1999; Tang and Yu 1999; Marschner and Noble 2000; Haynes and Mokolobate 2001; Xu and Coventry 2003; Xu et al. 2006a, b). For example, Noble et al. (1996) showed that the application of leaf litter neutralised soil acidity, and the extent of neutralisation was related to the content of their ash alkalinity. Similarly, Xu et al. (2006b) found that the amounts of alkalinity produced in soil correlated positively with concentrations of excess cations and total N in the added materials. The N concentration in organic materials influences whether the organic N is mineralized or immobilised which is crucial towards its effect on soil pH (Bolan et al. 1991).

Relatively little information is available on the movement down the soil profile of the alkalinity, released from the addition of organic materials. Lund and Doss (1980) showed that repeated applications of dairy manure at 135 t ha^{-1}year^{-1} for three years increased the pH and concentrations of exchangeable Mg and K in the subsurface soil of a Plinthic Paleudult. Similarly, Wright et al. (1985) found that the combined application of cow manure (44.8 t ha^{-1}) and dolimite (8.4 t ha^{-1}) to the topsoil increased subsurface soil pH and decreased exchangeable Al in a Typic Paleudult. However, in a soil column experiment, the presence of plant residues had little effect on the mobilization of the reaction products of surface-applied lime in the profile of an acidic Red Latosol (Moraes et al. 2007). Recently, Butterly et al. (2009) showed that the soluble fraction of residues is important for alkalinity release during the initial stages of decomposition. It is expected that the organic compounds in the soluble

fraction can move down in the soil profile before they are decomposed by microbes. Depending on residue and soil type, significant amounts of the alkalinity moved below the soil layer in which the crop residue was applied, within 3 months of the application (C Butterly and C Tang, unpublished).

An alternative strategy that should have potential in alleviating subsurface soil acidity is the practice known as subsoil manuring. This involves the deep incorporation of high rates of organic manures in subsurface layers to improve the physical properties of dense clay subsurface soils that restrict root growth, water uptake and crop yields in dry years (Gill et al. 2009). The marked improvement in macroporosity and hydraulic conductivity in subsurface soil layers with subsoil manuring, were attributed to the increased microbial activity associated with the breakdown of the organic amendment (Clark et al. 2007) and the breakdown of exudates from the increased mass of roots in the organic-amended subsurface soil layers. Not surprisingly, there were large increases in crop yields following this subsurface soil intervention. Given that the organic acids released from the decomposing organic amendments should alleviate any toxic Al species that might be present in acidic subsurface soils (Wong and Swift 2003) then one would expect that subsoil manuring would have an additional benefit of ameliorating subsurface soil acidity, if the subsurface soils being treated with the deep-placed manures, are also constrained by subsurface soil acidity.

4.4. Addition of coal-derived organic materials
The humic materials produced during oxidation of coal have been used for ameliorating soil acidity in general, and subsurface soil acidity in particular, in recent years (van der Watt et al. 1991; Noble and Randall 1998; Inoue et al. 2001; Imbufe et al. 2004; 2005). These materials are soluble in water and can leach down the soil profile in contrast to lime. The humic products are rich in carboxylic and phenolic groups, which provide reactive sites for cation exchange, bind phytotoxic elements, increase pH buffering and promote the penetration and retention of Ca in soils (Imbufe et al. 2004). Potassium humate is one of humic materials and is produced by the alkaline treatment of Victorian brown coal. It can effectively increase pH and levels of K, Mg and Ca in soil (Imbufe et al. 2004; 2005). In a column experiment, calcium fulvate increased soil pH to a depth of 100 cm in soils with a clay content of 6-32%, after columns were leached by two pore volumes of water (van der Watt et al. 1991). Use of coal-derived organic materials as an ameliorant of acid subsurface soils is promising. Further research is required to validate their effectiveness and economics in the broad-acre agriculture.

5. Biological amelioration through managing cation-anion uptake by crops

5.1. Impact of the form and uptake of N on rhizosphere pH
Nitrogen uptake has a marked influence on the cation–anion uptake balance and rhizosphere pH due to the high demand for N by plants (Marschner 1995; Mengel et al. 2001). This is because total N uptake can be responsible for 70 to 80% of the total ion uptake by plants (van Beusichem et al. 1988; Neumann and Romheld 2002). Moreover, plants can take up the N either in the cation (NH_4^+) or anion (NO_3^-) form. In addition, legumes assimilate N in its neutral gaseous N_2 form. Some plants even take up organic forms of N such as amino acids (Jones and Darrah 1994) and urea (Harper 1984). Therefore, the role of N in cation-anion balance depends on the form of the available N in the soil as well as the crop or pasture species. It follows that a predominant supply of nitrate would lead to a greater anion uptake than cations while a predominant ammonium and uncharged N (i.e. biological N_2 fixation)

supply would result in greater cation uptake than anions (Marschner 1995; Tang and Rengel 2003; references therein).

The metabolic assimilation of the N ions following the uptake into root cells produces H^+ or OH^- ions which in turn contribute to pH changes in the rhizosphere. For example, the assimilation of NO_3^- results in the production of OH^-, which is released into the rhizosphere during NO_3^- reduction in root tissue, in order to stabilize intercellular pH (Neumann and Römheld 2002). In contrast, assimilation of NH_4^+ by roots produces H^+ ions which can result in lower pHs in soil (Marschner 1995).

5.2. Factors affecting nitrate uptake

Nitrate uptake occurs via H^+ co-transport system which requires energy (Taiz and Zeiger 2006). This process depends on the trans-membrane H^+ gradient generated by the H^+-ATPase in the membrane. The pH decrease in the growth medium increases the H^+ gradient between the cell and external environment favouring NO_3^- uptake. However, the uptake of NO_3^- is regulated by the availability of NO_3^-. Indeed, a key factor for generating enzymes that are required for NO_3^- transportation and assimilation is the presence of NO_3^- in the environment (Taiz and Zeiger 2006).

Plants prefer to take up NH_4^+ compared to NO_3^- when they have access to NH_4^+ ions (Colmer and Bloom 1998). However, the diffusion coefficient of NO_3^- is much higher than that of NH_4^+ (Miller and Cramer 2004). In addition, NO_3^- ions are not adsorbed onto soil colloidal surfaces with negative charges and thus freely move in the soil profile. These two characteristics have contrasting consequences on nitrate availability and access to the root system. Nitrate can be more available to roots via diffusion or mass flow than ammonium, and this increases the possibility of its interception by roots. On the other hand, nitrate can be easily lost from the soil profile by leaching (Black 1992). As a result, the timing of root proliferation is important for interception and take up nitrate from the soil (Diggle et al. 1990).

Plant species differ greatly in their demand for N and in root morphology and root distribution in the soil profile. They therefore differ in their ability to intercept and to take up NO_3^- in the soil profile (see Tang and Rengel 2003). Generally, perennial species can take up more NO_3^- than annual species, and non-leguminous species take up more than legumes. In the field, NO_3^- leaching was much greater under the grain legume *Lupinus angustifolius* than under wheat (Anderson et al. 1998). Also, the concentrations of NO_3^- in soil profiles were higher under subterranean clover and yellow serradella than under the mixed culture of subterranean clover and perennial grass species at a low and medium rainfall site of south-eastern Australia (Dear et al. 2009). Genotypes within the same species may also differ in utilizing soil NO_3^-. For example, less NO_3^- was leached under deep-rooted than shallow-rooted genotypes of bentgrass (Bowman et al. 1998). Furthermore, growing acid-tolerant species and genotypes, compared to acid-sensitive ones, on acidic soils usually leads to increased root growth in these soils, particularly in acidic subsurface soils, and this will increase the capacity of roots to absorb NO_3^-. Selecting genotypes that intercept and take up more soil NO_3^- may provide an option for minimizing subsurface soil acidification and ameliorating subsurface soil acidity.

Nitrate availability in soil will influence root growth, which in turn affects NO_3^- uptake. Localised sources of NO_3^- are known to increase root proliferation in the soil where they occur (Robinson 1994). The enhanced root proliferation results from increased root elongation and initiation of lateral roots. The localised stimulatory effect of root growth by

NO$_3^-$ supply occurs due to specific signalling property of NO$_3^-$ ions themselves. It has also been suggested that the concentration of NO$_3^-$ in the plant affects the expression of the NO$_3^-$-inducible MADS-box gene (ANR1). This gene encodes "a component of the signal transduction pathway linking external NO$_3^-$ supply to increased rate of lateral root elongation" (Zhang and Forde 2000). Selection of varieties that can over-express the NO$_3^-$-inducible MADS-box gene would benefit rhizosphere alkalization through improved root proliferation and NO$_3^-$ capture and uptake in acid subsurface soils.

5.3. Excess nitrate uptake and subsurface soil alkalization

As discussed earlier, differences in anion/cation uptake by roots can lead to the release of protons or hydroxyl ions, resulting in acidification or alkalization in the rhizosphere (Tang and Rengel 2003). There needs to be an excess of anion uptake over cation uptake in order to increase rhizosphere pH. Therefore, a large amount of anions should be supplied to roots to encourage excess anion uptake in order to combat the acidity. Given that the magnitude of N uptake by plants, it follows that a large supply of nitrate anions, that will result in excess anion uptake (Mengel et al. 2001) and subsequent rhizosphere alkalization, will be required in the acidic soil layer. Root-induced rhizosphere alkalization can be extended to the bulk soil depending on soil pH buffer capacity (Hinsinger et al. 2003).

There is evidence that subsurface soil alkalization can occur following N fertilizer applications to the soil surface. This has occurred both in glasshouse experiments (Black 1992; Tang et al. 2000) and under field conditions (Adams and Pearson 1969; Noble et al. 2008; Tang et al. 2011). In soil-column experiments, Tang et al. (2000) showed that the columns receiving Ca(NO$_3$)$_2$ in the topsoil layer had pH 0.1-0.2 units higher in deeper soil layers than columns receiving no Ca(NO$_3$)$_2$, after growing N$_2$-fixing lupin and subterranean clover plants for 105 days. Although N$_2$ fixation itself causes soil acidification, a net alkalization occurred below 20 cm with lupins and below 30 cm with clover plants.

Similar findings were observed in a four-year field experiment where coastal bermudagrass was grown in an irrigated sandy loam soil. In this study, Adams and Pearson (1969) applied NH$_4$NO$_3$ at an annual rate of 896 kg N ha^{-1} year^{-1}. This resulted in a decline in soil pH of around 1.3-1.4 units in the surface 0-15 cm, and a decline of 0.3-0.5 of a unit in the 15-30 cm soil layers, compared to the initial soil pH. However, there was either no pH decline or an increase of about 0.3 units in 30-45, 45-60 and 60-75 layers. The effect of Ca(NO$_3$)$_2$ was also investigated (Figure 3), with the Ca(NO$_3$)$_2$ being supplied at rates of 448, 896 and 1344 kg N ha^{-1} to the surface 0-20 cm layer. Changes in pH and exchangeable Ca in the soil profile were measured after 4 years of N application. The alkalizing effect of Ca(NO$_3$)$_2$ was evident in all soil layers compared to the initial soil pH (Figure 3A). Exchangeable Ca data indicate an increased Ca movement in the deeper layers with increasing N rates. Calcium movement is generally accompanied by an anion, which most likely would be the NO$_3^-$ anion. Therefore, it appears that NO$_3^-$ leaching increased with increasing N rates which in turn led to increased NO$_3^-$ uptake by bermudagrass roots in deeper layers, resulting in alkalization in these soil layers. The increased movement NO$_3^-$ ions facilitated the movement of Ca to subsurface soils, thereby helping in mitigating subsurface soil acidity.
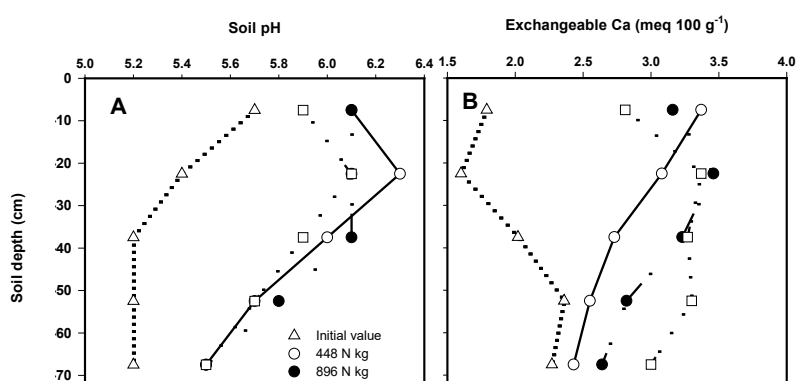
Figure 3. Effect of application rates of $Ca(NO_3)_2$ (kg ha^{-1} year^{-1}) to the surface on pH (A) and on exchangeable Ca (B) changes with soil depth after 4 years of application in a sandy loam soil (Adopted from Adams and Pearson 1969, with kind permission of Soil Science Society of America).

In another field study with Gamba grass (*Andropogon gayanus*), a significant pH increase was observed in 0-30 cm soil layer when N was supplied in the NO_3^- form compared to the control and the NH_4^+ treatments (Noble et al. 2008). The study was conducted in an acid sandy soil and the grass was given three different N treatments; these were no N, KNO_3 or $(NH_4)_2SO_4$ with the N applications totalling 287 kg N ha^{-1} over a three-year period. The supply of KNO_3 increased the pH by 0.2 to 0.3 units in the 0-30 cm soil layers after three years. This alkalization was a direct result of excess anion uptake by plants as there was a little possibility for denitrification in this lightly textured soil. In contrast, the supply of decreased pH by 0.4 units, the acidity likely resulting from plant uptake and nitrification of ammonium

Biological amelioration of subsurface soil acidity by managing the supply and uptake of nitrate from the subsurface soil, has recently been examined in more detail at two field sites using acid-tolerant and acid-sensitive wheat varieties. The results collated from the 2006 trials show the potential for ameliorating subsurface soil acidity using nitrate fertilizers (Tang et al. 2011). Similar yields and N-use efficiency were achieved with the supply of nitrate, compared to the supply of urea. Application of nitrate increased rhizosphere pH up to 0.5 units and the bulk soil pH to 0.3 units, to a depth exceeding 30 cm at both sites (Figure 4). The placement of nitrate fertilizer in the 10-15 cm soil layer increased subsurface soil pH more than the surface application. The treatment effects on the bulk soil pH became more significant in the second and third season. In contrast, the application of urea (as the most common N fertilizer) acidified the soil in the 5-10 cm soil layer by up to 0.4 units compared to the control, and up to 0.7 units in the 10-15 cm layer, compared to the nitrate treatment, after 3 years of treatment (Conyers et al., 2011). Nitrate application markedly increased nitrate concentration in soil profiles, particularly at the 10-20 cm depth (Figure 4), whereas urea application increased the NH_4^+ concentration. The majority of the nitrate was retained in the top 30-cm layers in the medium rainfall region. In the soil-induced process, the net effect of urea (ammonification followed by nitrification) is a decrease in pH, whereas nitrate source does not contribute to this process at all. More field work is required to assess the impact of nitrate leaching, and uptake from deeper soil layers, in different soils under different climatic conditions.
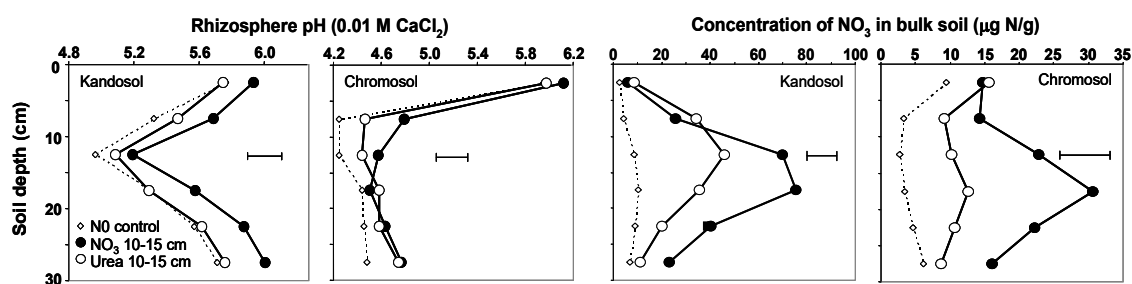
Figure 4. Changes in rhizoshere pH and NO_3 concentration in profiles of Kandosol and Chromosol soil under a wheat crop supplied with no N fertilizer, $Ca(NO_3)_2$ or urea at 10-15 cm. Bars are LSD values at *P*=0.05 (adopted from Tang et al. 2011).

Root proliferation in acid subsurface soils is important if the biological amelioration of subsurface soil acidity is to occur. Localised application of N and P can play a vital role in the stimulation of root growth either in the surface or subsurface soil layer, whereas localized applications of K had relatively little effect on root growth (Robinson 1994). A later study demonstrated that localised supply of nitrate and P together was required to maximise alkalization in an acid subsurface soil (Weligama et al. 2008). This alkalization resulted from an increased uptake of NO_3^- and stimulated root proliferation in the fertilizer-applied layer, which in turn enhanced shoot growth due to efficient exploration of resources in the acid subsurface soil. While nitrate supply alone increased root growth, P placement alone did not stimulate root proliferation in the acid soil (Weligama et al. 2008). The study suggests that P fertilizer should be applied together with nitrate to achieve maximal benefits in extra root growth and pH increase.

An alternative fertilizer strategy for ameliorating subsurface soil acidity was proposed by Noble et al. (1997). This involved providing the ingredients of $Ca(NO_3)_2$ in the soil surface layer by applying lime and an NH_4^+-based fertilizer (apart from nitrate fertilizers) at the surface. The subsequent nitrate leaching into the subsurface soil, and the uptake of nitrate from the subsurface soil layers, were thought to offer a feasible and practical method to address subsurface soil acidity. This proposal has been verified in a number of studies. Poss et al. (1995) reported an alkalization that occurred in subsurface soil of a red Kandosol in a semi-arid climate with mean annual rainfall of 539 mm. The soil was limed (2.5 t ha^{-1}) two years before the start of the experiment and urea was applied to the surface at 140 kg N ha^{-1}. The study showed that a net acidification of 1.8 kmol H$^+$ ha^{-1} occurred in the topsoil whereas a net alkalization of 0.9 kmol OH$^-$ ha^{-1} occurred in the 25-90 cm layer. Nitrate uptake by wheat roots and denitrification were postulated as possible reasons for the alkalization in the subsurface soil. Tang et al. (2000) showed that the addition of $(NH_4)_2SO_4$ in the top 10 cm of 1-m soil columns significantly increased NO_3^- concentration in all layers with NH_4^+ being mainly retained in the top 20-cm layer, and that growing wheat decreased soil pH in top 20 cm but increased soil pH in the deeper layers. Similarly, Black (1992) observed that the application of urine or a urea solution resulted in acidification in the 2-8 cm deep layer and significant alkalization in the 8-10 cm layer. Uptake of NO_3^- by plants was the most likely reason for the alkalization that occurred in the deeper soil layer. However, in another experiment, the supply of urea with surface liming was not successful in rhizosphere alkalization in the subsurface layer. One explanation was that the severe acidity of the soil reduced the population of nitrifying microorganisms resulting in limited nitrification (Weligama et al. 2010b).

There are several key requirements for optimizing the use of the biological amelioration in addressing subsurface soil acidity. These are that the crop should be tolerant of soil acidity, that a large amount of NO_3^- needs to be supplied to the surface soil, and that sufficient water or rainfall is supplied to the soil surface to leach the NO_3^- into the subsurface soil layers. However, there is a delicate balance required between the NO_3^- supply and the rain events that

supply water to the surface. Insufficient water supply with high NO_3^- will restrict deep root growth and plants may not be able to capture any of the NO_3^- that is subsequently leached. Similarly, insufficient NO_3^- supply and adequate water may also fail to produce sufficient deep roots to capture the leached NO_3^- (Weligama et al. 2010a). There also needs to be synchrony in timing, such that the root system has time to develop to capture NO_3^- from subsequent leaching events. The major challenge for the biological amelioration method is to minimize NO_3^- leaching loss, especially in sandy soils and in high rainfall environments. Modeling work is needed to study the feasibility of the biological method and how to maximize alkalization effects while at the same time minimizing NO_3^- leaching losses under different scenarios (e.g. Dunbabin et al. 2003).

6. Conclusions

There is strong evidence that root activity due to excess cation uptake is a major cause of subsurface soil acidification in many farming systems. Nitrification of ammonium, from the ammonification of organic N, and the subsequent leaching of the nitrate, appear to be the major causes of topsoil acidification. However, they are not likely to cause subsurface soil acidification. Subsurface soil acidification appears to be mainly caused by the spatial separation of acid and alkali produced by the C and N cycles. While much emphasis has been given to the amelioration of soil acidity, minimizing or preventing subsurface soil acidification should receive more attention. This may be achieved through selection of lower acid-producing species with less excess cations in their tissue, and managing cation/anion uptake in soil profiles.

Surface liming is currently the most common strategy to combat soil acidity, and may partially ameliorate subsurface soil acidity in long-term (Sumner 1995; Whitten et al. 2000, Tang et al. 2003b). Direct liming into the acidic subsurface soil produced a quicker and greater yield response, but is generally considered to be uneconomic. Field trials have demonstrated yield advantages of growing Al-tolerant wheat cultivars in soil profiles with subsurface soil acidity (Scott et al. 2001). The use of Al-tolerant cultivars now forms part of a different strategy to deep liming, known as biological amelioration, for combating subsurface soil acidity.

Biological amelioration operates by enabling roots in the subsurface soil to take up nitrate ions. The approach has been tested in the field and appears to be a promising method to counteract subsurface soil acidification and to ameliorate subsurface soil acidity. This is certainly the case where rainfall is low and profit margins from farming are small. Based on current N application rates of 30-150 kg ha^{-1}year^{-1}, with an N-use efficiency of 40%, the application of the N in the nitrate form would generate alkalinity equivalent to 42-214 kg lime ha^{-1}year^{-1}. This should be able to stop and reverse the acidification process (Porter et al. 1995). The major challenge for the biological amelioration method is to synchronize NO_3^- movement and root capture, in order to minimize NO_3^- leaching loss and maximise alkalization in the subsurface soil.

7. Acknowledgements

8. References

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