Causes and management of subsoil acidity

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Abstract
Subsoil acidity is widespread and its amelioration is costly and often practically infeasible. This paper summarises our recent research on cause and management of subsoil acidity. Acid production by plant roots due to excess cation uptake plays a major role in the development of subsoil acidity, particularly under legume-based agriculture. The deposition and decomposition of plant residues do not cause subsoil acidification but contributes to the development of subsoil acidity profiles through the liming effect on the topsoil. Nitrification from ammonium-based fertilizers or organic N of the residue and subsequent leaching of nitrate contribute mainly to topsoil acidification. In contrast, the uptake of leached nitrate in deeper layers may decrease subsoil acidity. Management of subsoil acidity is briefly discussed.

Key words
excess cation uptake, nitrate leaching, residue decomposition, subsoil acidification,

Introduction
At least 50 million ha of surface soil and 23 million ha of subsoils in Australia are acidic (Wahlquist, 2002). Surface soil acidity is commonly ameliorated with liming. However, amelioration of subsoil acidity is particularly difficult. Liming is often inefficient in ameliorating of subsoil acidity because of the slow movement of lime down soil profiles. Although heavy top dressings with lime may increase an amelioration effect on subsoil (Whitten 1997), such high rates may have adverse effects on some crops in the rotation (e.g. lupin, McLay *et al.* 1994) or cause deficiencies of certain nutrients. Deep placement of lime for amelioration of subsoil acidity is often considered economically unfeasible. Therefore, preventing or minimizing subsoil acidification on potentially acidic soils will be at least as important as amelioration of currently acidic soils. To achieve this, it is essential to understand the processes of subsoil acidification.

Although the cause of subsoil acidification is not fully understood yet, recent studies suggest that acid production by plant roots, due to excess cation uptake, plays an important role in the development of subsoil acidification. This paper summarises our recent research on possible causes of subsoil acidification, especially under legume-based agriculture. Management of subsoil acidity through managing cation/anion uptake is briefly discussed.

Excess uptake of cations over anions
Plant roots take up nutrients from soil solutions to meet their needs for growth. 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, 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. In most cases, plants take up more cations than anions, leading to a net acidification.

The form of nitrogen plays a prominent role in the cation-anion balance. NH_4^+-fed plants are characterized by a high cation/anion uptake ratio, and thus NH_4^+ nutrition leads to a strong acidification. In contrast, NO_3^--fed plants have a low cation/anion uptake ratio, and NO_3^- nutrition may result in an alkalization. By comparison, legumes when relying on N_2 fixation, take up more cations than anions, and hence release H^+ and acidify their rhizosphere. Tang et al (1997) showed a close linear relationship between the amount of H^+ released and the excess of cations over anions taken up by N_2-fixing plants of various legume species.

Plant species differ substantially in acid production and their capacity to acidify soils (see Tang and Rengel, 2003). Legumes generally cause more soil acidification than non-leguminous species. This may be attributed to the followings. First, legumes have a great excretion of protons due to great excess cation uptake during N_2 fixation. Second, they generally have a poor ability to take up soil NO_3^- during growth.

Additionally, legume residues contain high N, resulting in large amounts of NO_3^- produced during residue decomposition.

Deposition in soil profiles of acid produced due to excess cation uptake 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 plants of lupin and subterranean clover tended to increase with depth, and relatively uniform decreases of soil pH occurred in the soil profile. Where nutrients were applied only in the top10-cm layer, 50-70% of the roots of N_2-fixing plants were distributed in that layer, and pH was decreased most in the top layer. The decrease of pH in various soil layers was proportional to the root length density (Figure 1). In the field, deeper-rooted legumes cause subsoil acidification to greater depths than shallower-rooted legumes. For example, Loss *et al.* (1993) observed more soil acidification in deeper layers of soil profiles under lupin-wheat rotation than under pastures. The results suggest that excess cation uptake by plant roots is important in subsoil acidification.

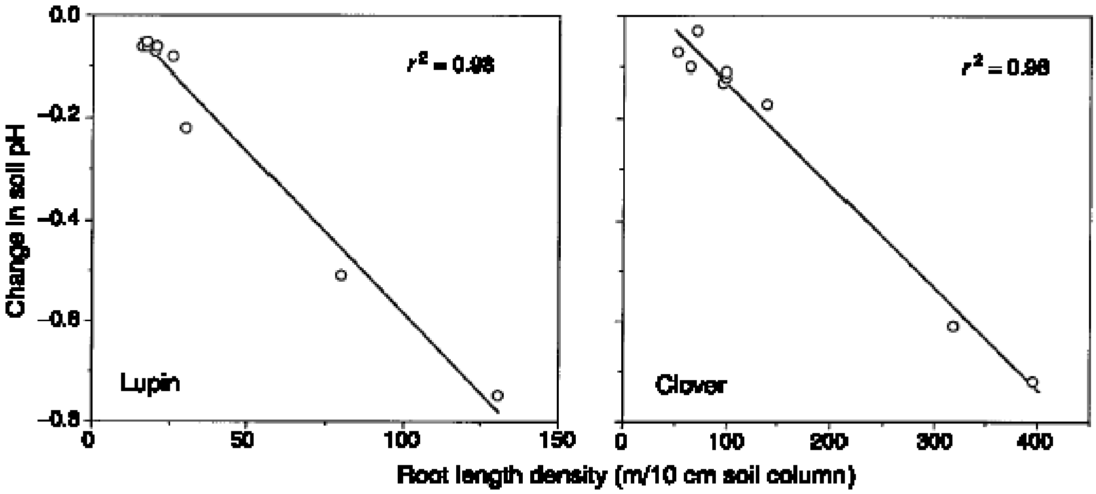

Figure 1. Relationship between decreases in soil pH of 10-cm sections and root length density of N_2-fixing plants of lupin and subterranean clover grown for 105 days in soil columns (Tang *et al.*, 2000).

Role of plant residues

The accumulation of organic matter has been suggested as being one of the causes of soil acidification. Organic matter is usually considered to lower soil pH by releasing H^+ that are associated with organic anions, by nitrification in an open system 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, whereas organic matter was generally accumulated in the top 10 cm of the soil (Williams, 1980; Dolling and Porter, 1994). By contrast, pH increased in the top soil after farming in some soils compared to the nearby uncultivated bushland (e.g. Dolling and Porter, 1994). In addition, organic materials are often used to ameliorate soil acidity.

Incubation studies examined the effect of applying plant organic materials differing in chemical composition on pH change of five soils with various initial pH (3.60-5.58 in 0.01 M $CaCl_2$) and organic matter content under sterile and non-sterile conditions (Tang *et al.*, 1999, Tang and Yu 1999). Addition of the plant materials at levels of 1-1.5% of soil weight increased the pH of all soils by up to 3.4 units during 100-d incubation under non-sterile conditions. The amounts of alkalinity produced in soil correlated positively with concentrations of excess cations and total nitrogen of the added materials, and negatively with the initial pH soils. Under sterile conditions (fumigated with chloroform), similar trends of soil pH changes and alkalinity production due to legume residues addition were displayed but the effects of residues on alkalinity production were less under sterile conditions than under non-sterile conditions (Figure 2). Direct shaking of soil with plant residues under sterile conditions increased the amount of alkalinity in the soils with initial pH of 3.60-4.54 but not in the soils with initial pH of 5.06 and 5.58.

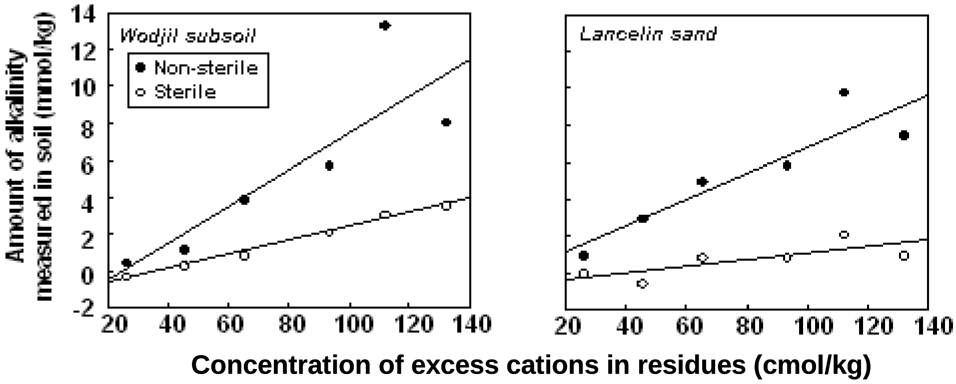

Figure 2. Relationship between excess cations in plant residues and alkalinity produced in Wodjil subsoil (initial pH 3.98) and Lancelin sand (initial pH 5.06) after 35 days of incubation under sterile and non-sterile conditions.

A further study (unpublished) showed that changes in soil pH due to the addition of plant materials were related to CO_2 release, dynamics of NH_4^+ and NO_3^- in the soil. The results suggest that the decarboxylation of organic anions of added plant residues and ammonification of the residue N cause increase in soil pH whereas nitrification of mineralised residue nitrogen causes soil pH decrease, and that the association/dissociation of organic compounds also plays a role in soil pH change. Initial soil pH has a great impact on soil pH change by affecting nitrogen transformation, rate of decomposition and association/dissociation of undecomposed organic anions in the material. Depending on pH buffer capacity, the pH increase is generally greater in lower pH soils than in higher pH ones.

From the above studies and those published previously, it is suggested that the deposition and decomposition of plant residues do not cause subsoil acidification but contribute to the development of the soil pH profiles through the alkalization effect on the topsoil. The addition of plant materials to acidic soils increases soil pH. While the extent of proton excretion from roots during plant growth is proportional to the root distribution, 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 subsoil 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 less excess cations than shoot residues and have a lesser "liming" effect (Tang et al., 1999; Tang and Yu, 1999) Therefore, root residue decomposition will not fully neutralize acidity created along the roots in the soil profile and acidity produced during growth will persist in the subsoil layers.

Nitrification and nitrate leaching

Nitrification and subsequent leaching of NO_3^- has often been suggested as a major cause of soil acidification. However, such processes do not appear to be a cause of subsoil acidification. Mineralization and nitrification of plant residue nitrogen have been shown to occur mainly in the topsoil due to relative immobility of NH_4^+ and deposition of plant residues on the soil surface. For example, 64% of nitrogen mineralisation and 50% of nitrification in the soil profile of a loamy sand, and 78% of nitrogen mineralisation and 41% of nitrification in a sandy clay loam occurred in the top 5-cm soil layer (Murphy et al., 1998). Thus, acidification caused by nitrification occurs in the topsoil. There will be no net acidification in the topsoil if plant roots utilize all the NO_3^- 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 NO_3^- is leached, soil acidification will then occur in the topsoil because leaching of NO_3^- is accompanied by leaching of cations rather than H^+. If plant roots take up the leached NO_3^- below the topsoil layer, it is expected that an alkalization (or less acidification) occurs in the subsoil. These processes are illustrated in Figure 3.

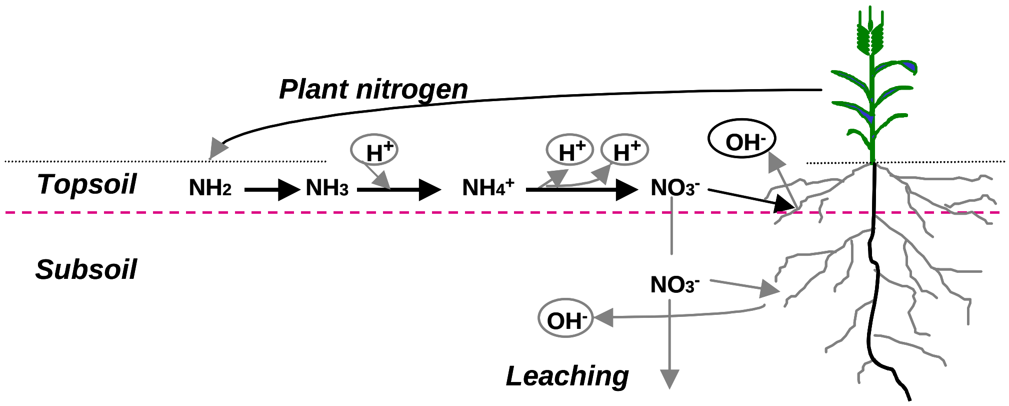

Figure 3. Schematic illustration of nitrogen transformations, nitrate leaching and plant uptake in relation to acidification in the soil profile.

To illustrate whether nitrification in the topsoil and NO_3^- leaching decrease subsoil acidification, two soil column experiments were conducted using a sandy soil. The first experiment examined the effect of NO_3^- addition, and the second examined the effect of NH_4^+ addition to the topsoil on subsoil acidification under nodulated lupins and subterranean clover, and wheat. Nitrate leaching was achieved by adding excess water to the surface of the columns 18 d after sowing. In the first experiment, the addition of $Ca(NO_3)_2$ in the topsoil layer increased NO_3^- concentration in soil profiles but did not affect growth of shoot and roots, and nitrogen concentration in shoots of either species. It caused less acidification at all depths compared to the -$Ca(NO_3)_2$ treatment.

In the second experiment, the addition of $(NH_4)_2SO_4$ in the top 10 cm significantly increased NO_3^- concentration in all layers but NH_4^+ was 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 $(NH_4)_2SO_4$ 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 (Figure 4). Clearly, leaching of NO_3^- from topsoil is unlikely to cause subsoil acidification. In contrast, the uptake of NO_3^- by the roots reduces net acid production in subsoil layers. Further research is needed to validate these results under field conditions.

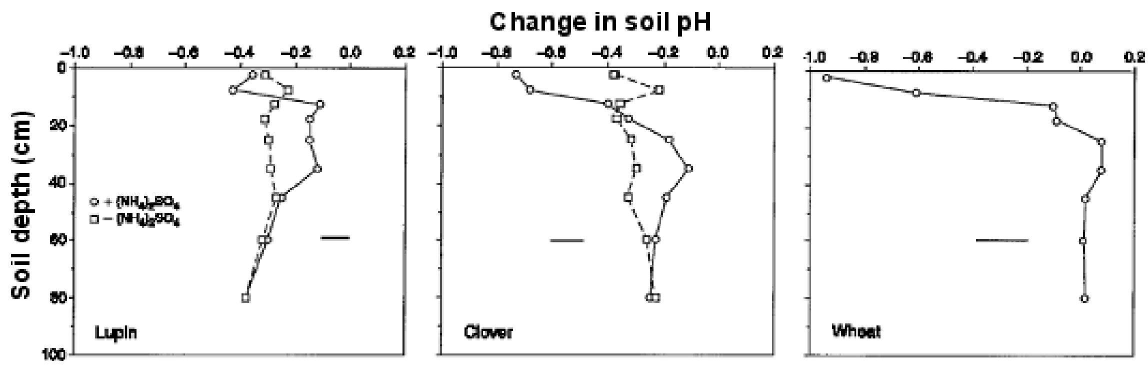

Figure 4. Effect of $(NH_4)_2SO_4$ addition in the top 10 cm on soil pH profiles after growing nodulated lupin, nodulated subterranean clover and wheat for 82 days. The pH change was the difference in pH of the soils with and without growing plants (Tang *et al.*, 2000).

Acid movement

The contribution of acid movement to the development of subsoil acidity is unknown. It is expected that such acid movement is small because of high affinity of H^+ and Al^{3+} on the surface of soil colloids. In many soil profiles, pH is also higher in topsoil than subsoil so that little acid is able to move downward via mass flow or diffusion. Further, although the highest concentration of acids (lowest pH) is present in the subsoil layer, there is no evidence that this highest concentration of acids moves down over time. For example, the lowest soil pH had always kept between 10-30 cm irrespective of years of cultivation in a deep yellow sand (Dolling & Porter, 1994). If the acid had moved downward in the profile, this lowest soil pH should have moved to lower layers with time accordingly. Further research is needed to illustrate this.

Causes of subsoil acidification

Soil acidification is attributed to many processes among which removal of alkalinity in farm products in the carbon cycle and NO_3^- leaching in the nitrogen cycle are major causes in farming systems. Subsoil acidification appears to be mainly caused by spatial separation of acid and alkali produced in these cycles. Figure 5 summarizes these processes that may contribute to the development of soil pH profile. In the carbon cycle, while the acid produced by the roots due to excess uptake of cations over anions during plant growth is distributed in the whole soil profile (rooting zones) (A), the plant residues are mainly oxidised in the surface soil (B). The amount of acid generated by plant roots is proportional to the distribution of root length. The oxidation of organic anions present in the residues is an alkalization process. However, the alkalization occurs mainly in the topsoil and thus the acidity generated by roots in the subsoil persists. In the nitrogen cycle, mineralization and nitrification mainly occur in the topsoil. The leaching of NO_3^- originating from the topsoil is unlikely to cause subsoil acidification. In contrast, uptake of NO_3^- by roots in subsoil layers may reduce net acid production by the roots (C). Finally, the downward movement of H^+ and soluble Al, and NH_4^+ may contribute to subsoil acidification (Hue and Licudine, 1999) (D). The magnitude of such downward movement is unknown but is expected to be minor.

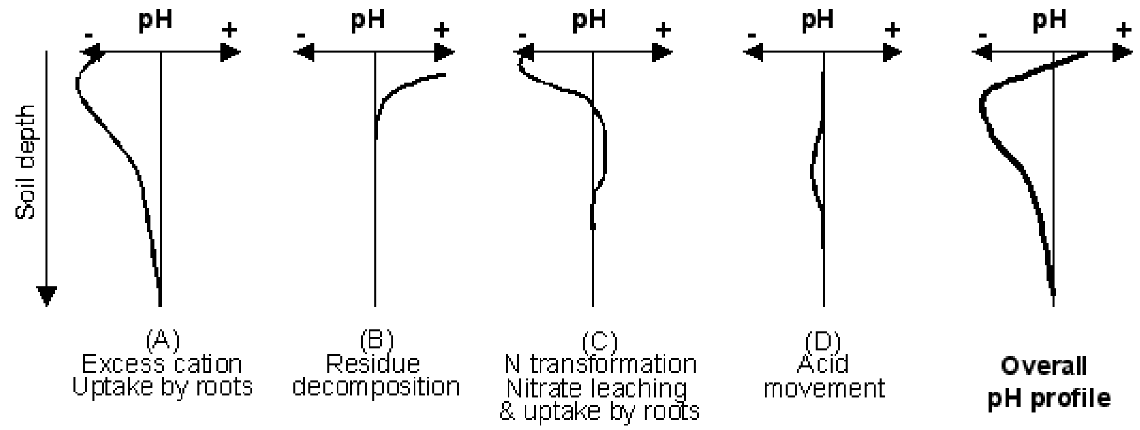

Figure 5. Possible causes of subsoil acidification. (-, + represent pH decrease and increase, respectively)

Conclusions

Surface liming is currently the most common strategy to combat soil acidity, and may partially ameliorate subsoil acidity in long-term (e.g. sandy loam in the region with 360 mm annual rainfall, Tang *et al.*, 2003). Direct liming into acidic subsoil produced a quicker and greater yield response. Field trials have demonstrated yield advantages of growing Al-tolerant wheat cultivars in soil with subsoil acidity (Tang *et al.*, 2002). Growing Al-tolerant wheat partially eliminates the adverse effects of acidity on crop yields in soils with severe subsoil acidity and almost fully eliminates the effect in soils with shallow/moderate subsoil acidity (Tang *et al.*, 2003b).

There is strong evidence that root activity due to excess cation uptake is a major cause of subsoil acidification. Nitrification from NH_4^+ or organic N and subsequent leaching of NO_3^- appear to be a major cause of topsoil but not subsoil acidification. Plant species differ substantially in uptake of excess cations over anions, their ability to produce acid and to uptake soil NO_3^- (Tang *et al.*, 1999b). Legumes, when they are fixing N_2, generally have greater uptake of cations over anions and have low capacity to take up NO_3^- once organic N is mineralised, and thus produce more acidity in soil profiles than non-legumes. Much emphasis has been given to the amelioration of soil acidity. Due to the difficulty and cost of ameliorating subsoil acidity, minimizing or preventing subsoil acidification should receive more attention. This may be achieved through selection of species with low excess cations in the products and low acid production, and managing cation/anion uptake in soil profiles.

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