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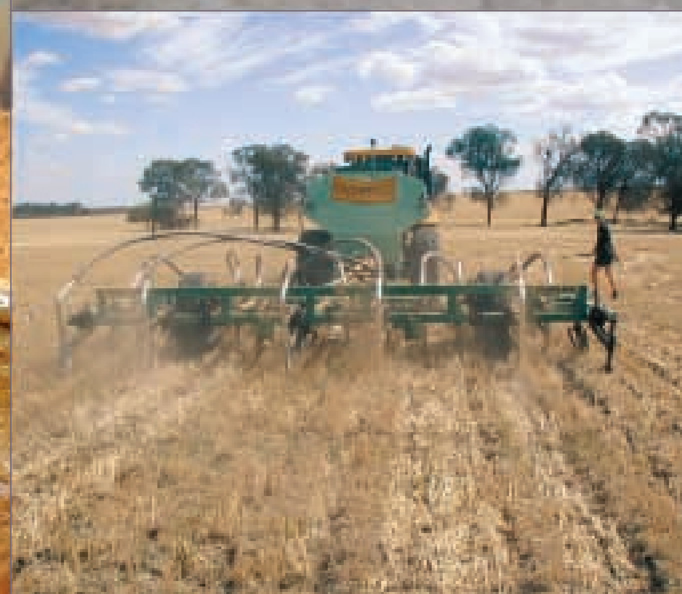
Subsurface Acidity



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Subsurface Acidity

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Productive agriculture increases the concentration of hydrogen ions in soil, which acidifies the soil.

Aluminium is a component of many soil constituents, including clays and oxides, and is also present on the surfaces of soil organic matter. As the concentration of hydrogen ions in soil increases, soil pH decreases, and aluminium starts to dissolve from the soil constituents, increasing the concentration of aluminium ions in soil solution.

As the concentration of aluminium ions in the solution increases, the aluminium in the soil solution becomes increasingly toxic to plant roots, reducing root growth. The smaller amounts of plant roots explore a smaller volume of soil, decreasing the ability of the roots to take up water and nutrient elements from soil, thereby reducing shoot and grain yields of plants growing in the soil.

Roots of different plant species differ in their tolerance to aluminium. Wheat, subterranean clover and annual ryegrass have a high tolerance, whereas canola, barley, annual medic and lucerne are very sensitive.

There are two major ways agricultural production increases the concentration of hydrogen ions in soil solution: the nitrogen cycle in soil, and removal of plant material (hay, grain) from paddocks.

Figure 1: *Eleven day old barley seedlings grown in acid subsoil from Perenjori. Seedlings on the left have grown in soil that has had lime applied to the soil and seedlings on the right have grown in the same soil without lime and a pH of less than 4.5.*

Summary

Subsurface acidity occurs when pH in the 10 to 35 cm zone of soil is less than 5.0.

Subsurface acidity is a major cause of decreased grain production in most WA soils and is amended by adding sufficient lime to the topsoil to raise the pH of the topsoil to 5.5 or greater.

Causes of soil acidity

The nitrogen cycle and the removal of plant material (hay or grain) are the primary causes of soil acidity.

Decreasing soil pH increases the amount of aluminium ions in the soil solution.

Aluminium is toxic to root growth.

Mineralisation

Soil organisms process soil organic matter changing it physically and chemically releasing nutrient elements to soil solution which can be taken up by plant roots.

Retention of ammonium and nitrate ions by soil

Soil constituents (sand, clay, oxides, organic matter) have both positive and negative surface charge sites.

Most soils have many more negative than positive charge sites.

Ammonium ions are positively charged and so are retained by negative surface charge sites present on soil constituents and so do not leach in soil. Most negatively charged nitrate ions are not retained by soil and leach.

If there are not enough negatively charged sites to hold onto the ammonium ions then the ammonium ions will leach away from the root zone.

Soil bacteria rapidly convert ammonium ions to nitrate ions

In moist soil bacteria convert ammonium ions, derived, from soil organic matter or fertiliser, to nitrate and hydrogen ions.

Fertiliser nitrogen

Fertiliser nitrogen is applied in 4 forms; urea, ammonium ions, nitrate ions, or both ammonium and nitrate ions.

Urea is rapidly converted to ammonium ions in soil. Ammonium ions from fertiliser or mineralised from soil organic matter are converted by soil bacteria to nitrate and hydrogen ions.

Excess hydrogen ions cause the soil to acidify.

The nitrogen cycle

Soil organic matter is the dead remains of plants and soil organisms (insects, earthworms, fungi, bacteria, protozoa, algae) growing in the soil.

In addition, animals grazing pastures or crop stubbles deposit faeces and urine onto soil, which contribute to soil organic matter. Soil organic matter is a source of nutrient elements and energy for soil organisms. While accessing the elements and energy present in organic matter, the organisms physically and chemically change it, and eventually release the elements as ions into the soil solution. This process is called mineralisation.

The nitrogen present in the organic matter is released (mineralised) into the soil solution as ammonium ions. The ammonium ions have a positive charge. Soil constituents possess both positive and negative surface charge sites.

In most soils, there are far more negative than positive surface charge sites. Ammonium ions in soil are retained by the negatively charged sites on the surfaces of soil constituents. Consequently, ammonium ions usually do not leach. However, ammonium ions may leach from sandy soils with relatively few negatively charged surface sites. When water is draining vertically and laterally through such soils and there is a large amount of ammonium ions in the soil, then, due to insufficient negatively charged sites on the surface of the sand to retain all the ammonium ions, they can leach.

In moist soil, the ammonium ions that are mineralised from soil organic matter are rapidly converted by bacteria present in soil to produce nitrate and hydrogen ions. The nitrate ions have a negative charge and are not strongly retained by soil and are readily leached in most soils, particularly in sandy soils common in Western Australia.

Fertiliser nitrogen is applied to soil as (1) urea, (2) ammonium ions (ammonium sulphate, monoammonium phosphate [MAP], diammonium phosphate [DAP]), (3) nitrate ions (potassium or calcium nitrate), or (4) both ammonium and nitrate ions are applied in the same fertiliser (ammonium nitrate). In moist soil, urea is rapidly converted to ammonium ions. Regardless of whether ammonium ions are derived from organic matter or from fertiliser, ammonium ions in soil are rapidly converted by soil bacteria to nitrate and hydrogen ions and these hydrogen ions may acidify the soil (see later).

Plant roots take up nitrogen from soil as either ammonium or nitrate ions derived from both soil organic matter and fertiliser applied to soil. Nitrogen is taken up by plant roots from soil as either a positive or a negative ion.

Plant roots need to maintain electrical neutrality either side of root membranes when they take up either ammonium or nitrate ions, and in the process the soil can be acidified.

Water in plants can be converted to positive hydrogen ions and negative hydroxide ions. When the plant roots take up positive ammonium ions from soil, positive hydrogen ions produced from water in the root are excreted into the soil.

The positive ammonium ions entering the root equal the positive hydrogen ions leaving the root. The positive charge of the ammonium ions now in the root are balanced by the negative hydroxide ions in the root derived from the water used to produce the hydrogen and hydroxide ions in the root. The positive hydrogen ions are excreted from roots to balance the negative ions in soil that previously balanced the positive ammonium ions in soil. The soil is acidified by the hydrogen ions excreted from roots to balance the ammonium ions taken up from soil by roots.

Likewise, when nitrate ions are taken up from soil by plant roots, to maintain electrical neutrality, hydroxide ions derived from water in roots are secreted from the roots into the soil. The hydroxide ions secreted from roots equals the nitrate ions taken up by the roots from the soil. Once in the root, the charge of the negative nitrate ions is balanced by the positive charge of hydrogen ions produced when water in the root is converted to hydrogen and hydroxide ions. Once in the soil, hydroxide ions excreted from roots react with hydrogen ions in soil to produce water. This accounts for the hydrogen ions produced in soil when ammonium ions were converted by soil bacteria to nitrate and hydrogen ions. The net result is no increase in soil acidification.

There is also another possible outcome when soil bacteria convert ammonium ions to nitrate and hydrogen ions: the nitrate ions are leached and are **not** taken up by plant roots. When this occurs, the hydrogen ions produced when ammonium ions were converted by soil bacteria to nitrate ions acidify the soil.

Plant roots usually take up most nitrogen they require from soil as nitrate ions rather than as ammonium ions, so leaching of nitrate ions produced from ammonium ions in soil is a major cause of soil acidification.

Plant Roots

Plant roots need to be electrically balanced either side of the root membrane.

Plant roots can take up nitrogen as either ammonium (positively charged) or nitrate (negatively charged) ions.

If the plant takes up a positively charged ammonium ion it excretes a positively charged hydrogen ion to maintain the electrical balance. This exchange leaves more hydrogen ions in the soil water to balance the negative ions in the soil.

Extra hydrogen ions means the soil has acidified.

If the plant takes up a negatively charged nitrate ion it excretes a negatively charged hydroxide ion to maintain the electrical balance. This exchange leaves more hydroxide ions in the soil water to balance the positive ions in the soil. When ammonium ions are converted by soil bacteria to nitrate and hydrogen ions and the nitrate ions are taken up by plant roots, the hydroxide ions, secreted from roots into the soil, consume the hydrogen ions so there is no acidification of soil. However, if the nitrate ions are leached, then the hydrogen ions produced when soil bacteria convert ammonium to nitrate ions remain to acidify the soil.

Positive & Negative ions

Positively charged ions are known as cations.

Some common cations are ammonium, sodium, potassium, calcium and magnesium.

Negatively charged ions are known as anions.

Some common anions are phosphate, sulphate, molybdate, borate and chloride.

Plants take up more cations than anions.

When a plant takes up a cation it must secrete a cation to maintain the electrical balance either side of the root membrane.

Hydrogen is the cation that plant roots mostly secrete into the soil to allow the roots to take up excess cations. If grain or hay are removed from the paddock these hydrogen ions acidify the soil.

Measuring Soil pH

Soil pH is the universal measure of the level of soil acidity.

In Western Australia soil pH was measured in water until 1992.

Since 1992 soil pH has been measured in a weak salt solution of calcium chloride.

pH measurements taken from wet and dry soils can vary if we measure the pH in water because the soil has a “background” salt concentration.

By using a mild salt solution (calcium chloride) to measure the soil pH the results are more stable and less affected by the amount of soil water and salt in soil samples at the time of sampling.

Product removal

Plant roots take up nutrient elements from soil solution as either positively charged ions, called cations (ammonium, sodium, potassium, calcium, magnesium), or as negatively charged ions, called anions (phosphate, sulphate, molybdate, borate, chloride). Plants usually take up more cations than anions.

To maintain electrical neutrality either side of the root membrane, plant roots secrete hydrogen ions, produced from water in the roots, into the soil. The charge of the hydrogen ions secreted from the roots equals the positive charge of the excess cations taken up from the soil.

The excess positive charge of the cations now in the roots is balanced by the negative hydroxide ions remaining after water was converted to hydrogen and hydroxide ions and the hydrogen ions were excreted from the roots.

The positive charge of the hydrogen ions secreted into the soil balances the negative charge of anions left in the soil when the excess cations were taken up by the roots.

If there is no removal of plant material grown in the paddock, then as plant remains are returned to the soil to become soil organic matter, there is no net loss of nutrient elements, and acidification of the soil is negligible.

When hay or grain is harvested or grazed and removed from the paddock, the excess cations taken up from soil into the hay, grain or pasture are also removed.

To balance the excess cations that were taken up, plants secreted hydrogen ions into the soil which acidify the soil.

Measuring soil pH

In Western Australia, soil pH is the universal soil test procedure used to indicate the extent of soil acidification in paddocks and whether lime needs to be applied to ameliorate soil acidity.

When soil is added to water, and then salt is added to the soil and water mixture, the pH decreases due to the salt. Soils contain a range of salts, including calcium, magnesium, sodium and potassium chlorides, nitrates and sulphates. The concentration of salts in the soil, particularly in the topsoil, can vary with the moisture content of soils at sampling. The concentration of these salts is usually lower in wet soils collected from the field after rain, and higher in dry soils collected when there has been no rain for some time i.e. during summer.

Soil pH was measured in water until 1992. To minimise the effect of salt concentration in soil on pH values, pH is now measured in 0.01 molar calcium chloride. All the pH values quoted in this publication were measured in calcium chloride.

Topsoil and subsurface acidity

In south-western Western Australia, about 75 per cent of the 18 million hectares used for agriculture were acidic to neutral in the top 10 cm when the soils were newly-cleared. Most of these soils were only marginally acid, at approximately 5.5-6.5. The remaining twenty five per cent of soils had marginally alkaline to alkaline soil pH values in the topsoil.

As a consequence of agricultural production, all the soils have acidified, but soil acidity has become a major problem for the 75 percent of soils that were originally acidic to neutral when first cleared. Subsequent research has shown that the top 35 cm (approximately) of these soils have acidified. However, for these soils, the greatest decrease in soil pH, and the greatest increase in the concentration of hydrogen and aluminium ions, occurred at between 10 to 35 cm.

When soil testing was first developed in Western Australia, it was used to determine the soil phosphorus in the top 10 cm of soil.

When newly-cleared, most Western Australian soils had negligible indigenous (native) soil phosphorus. Native plants had evolved to use these low levels of phosphorus very effectively. However, for most soils in the region the introduced plant species used for agriculture could not access the native soil phosphorus so fertiliser needed to be applied for profitable grain and pasture production.

Almost all of the phosphorus required for growing crop and pasture species in Western Australian soils has been added to the soils as fertiliser. Phosphorus is immobile in most Western Australian soils but, before herbicides were used to kill weeds, the phosphorus was mixed into the topsoil by ploughing and scarification to kill weeds. Consequently almost all of the soil phosphorus was found in the top 10 cm of soil.

WA Soil Acidity

When newly cleared, 75% of the 18 million hectares used for agriculture in the south-west of Western Australia were marginally acidic to neutral in the top 10 cm, and most were in the pH range of 5.5 to 6.5. The remaining twenty five per cent were marginally alkaline to alkaline.

With agricultural production all soils have acidified.

The 75% of soils that were already 5.5 to 6.5, in the top 35 cm at the point of clearing have now acidified to values between pH 3.7 to 5.0, with the largest decrease occurring in the 10 – 35 cm layer.

Soil testing and Phosphorous

Phosphorus soil testing was the first soil test used in Western Australia and the top 10 cm of soil was collected for the test. Only the top 10 cm of soil was used because phosphorus is immobile in most soils and all phosphorus in our soils for agriculture has been applied as fertiliser and was mixed into the top 10 cm of soil when soil was cultivated to kill weeds (before herbicide sprays where widely used) and sow crops. Subsequently, the top 10 cm of soil was also used to measure three other soil tests in Western Australia: soil pH, soil test potassium, and soil test sulfur. However, sampling to greater depth is required for all three of these new soil tests so the 10 cm sampling depth is inadequate.

Detecting subsurface acidity

Soil testing is used to detect if subsurface acidity is a problem.

The presence of subsurface acidity is determined in Western Australia by collecting separate soil samples from the top 10 cm of soil and then the 10 to 20 cm depth of soil.

The samples are then sent to a soil testing laboratory to measure soil pH.

If the pH in the 10 to 20 cm sample is 5.0 or less, then subsurface acidity is present in the soil.

Ameliorating soil acidity

There are 3 key types of liming material in WA; limesand, limestone and dolomite.

Limesand and limestone comprise calcium carbonate ($CaCO_3$). Dolomite comprises 40 to 60 percent calcium and magnesium carbonate.

Lime is the cheapest and most effective treatment for soil acidity.

The carbonate in the lime consumes the excess hydrogen ions in the soil solution (water) and on the surfaces of soil particles (constituents) and the chemical reaction that takes place produces water and carbon dioxide so consuming the excess hydrogen ions.

As soil pH increases, aluminium toxicity decreases and plant root growth is increased.

Soil testing was eventually extended in Western Australia to include measurements of soil pH. As soil testing for phosphorus was originally conducted on the top 10 cm of soil, so the soil pH was only measured for the top 10 cm. Soil acidification in the top 10 cm of soil was eventually identified as a significant problem in Western Australia, and acidification in the top 10 cm is now called **topsoil acidity**.

Acidity, which develops between 10 to 35 cm in soil, is a much more important problem for cropping in Western Australia than topsoil acidity, and is called **subsurface acidity**. Subsurface acidity cannot be detected by sampling the top 10 cm of soil. To test for subsurface acidity, it is necessary to measure soil pH in the 10 to about 35 cm depth of soil.

Ameliorating soil acidity

Adding lime to soil is the usual treatment for soil acidity. There are many lime deposits in Western Australia, including limesand and limestone near the coast, and dolomite deposits found inland.

Lime is the cheapest and most effective treatment for soil acidity. The carbonate component of lime consumes hydrogen ions present in the soil solution and on the surfaces of soil constituents (where most hydrogen ions in soil reside) and in doing so raises soil pH.

The carbonate component of lime also reacts with aluminium in soil solution to form insoluble aluminium compounds. As soil pH rises (with applied lime), aluminium ions in soil solution react with other ions in the solution or on the surfaces of soil constituents to form insoluble compounds. Therefore, adding lime to soil decreases the concentration of aluminium ions in soil solution and plant root growth is no longer reduced by aluminium toxicity.

Ameliorating topsoil acidity

Lime is very insoluble. For lime to be effective at decreasing soil acidity it needs to be applied in a very fine form that is mixed through the soil. The very small particle size ensures that there are more lime particles with as much carbonate as possible exposed at the surface of the particles. Consequently, these carbonate ions will react with a greater volume of soil to consume hydrogen ions in the soil and decrease soil acidity.

Traditionally lime in WA has been applied to the soil surface and it is incorporated into soil during cultivation. Whilst this practice has proven effective in decreasing topsoil acidity it has to date only had moderate effects on subsurface acidity.

Ameliorating subsurface acidity

Research has shown that enough lime needs to be applied to the topsoil to raise topsoil pH to about 5.5 before there is significant downward movement of alkalinity from the limed topsoil to have any effect on subsurface acidity. It may take several applications of lime to the topsoil to achieve and maintain a pH value equal to or higher than 5.5, extending the time until the subsurface is ameliorated by this method to many years.

For sandplain soils with a subsurface acidity problem, we are looking at the feasibility of placing lime at depth during a deep ripping operation. This subsurface placement of lime is being applied to soil that already has had lime applied in a previous year to the topsoil so the topsoil pH is 5.5 or greater.

Sandplain soils develop a hardpan caused by vehicles (tractors, trucks, seeders, harvesters, spraying equipment, utes) being driven over the soil. The vehicles shake the topsoil, and during the shaking, the fine sand particles in the topsoil are shaken down the soil to fill pores in the subsoil creating a hardpan in the soil at about 10 to 35 cm depth.

Plant roots cannot grow through the physical hardpan but water, and soil mobile elements, such as nitrate and calcium ions, can move through the hardpan. The hardpans reduce the ability of plant roots to explore soil and obtain water and nutrient elements below the hardpan. The most effective treatment is to deep rip the hardpan. The deep ripping allows the roots to grow down the sections of soil that have been deep ripped allowing access to water and nutrient elements below the hardpan.

The deep ripping research to ameliorate physical hardpans in Western Australian sandplain soils was undertaken in the 1980s before there was significant development of subsurface acidity in these soils. Subsurface acidity is now a major problem for many WA soils, including the sandplain soils. Subsurface acidity results in aluminium toxicity occurring in the 10 to 35 cm zone of soil. This is also the depth where a physical hardpan also frequently occurs, particularly in sandplain soils.

If the sandplain soil also has a subsurface acidity problem, then even if the soil has been deep ripped, aluminium toxicity in the 10 to 35 cm zone will reduce or prevent plant roots growing down the rip lines to deeper soil. The roots will only grow through the 10 to 35 cm zone when both the physical hardpan and aluminium toxicity in the zone have been ameliorated. The deep banding lime research on the sandplain soils has therefore included treatments in which:

Figure 2: *Cutaway soil profile over the top 20 cm of soil. The profile was treated with pH indicator solution and pH indicator powder. Note the purple areas that show where the lime has been placed during subsurface liming.*

1. The soil is deep ripped only, which only ameliorates the physical hardpan.
2. While the soil is being deep ripped, lime is also blown, with the aid of a modified air-seeder, into the deep ripped slots. This ameliorates both the physical hardpan and aluminium toxicity in the 10 to 35 cm zone.

This research uses existing farm machinery that has been modified to deep rip and place the lime at depth in the soil.

Time will tell if deep placement of lime while ripping previously limed sandplain soils with a topsoil pH 5.5 or greater proves to be an effective, profitable operation for cropping the sandplain soils. In the meantime, the proven technique for ameliorating subsurface acidity is to apply sufficient lime to raise topsoil pH to at least 5.5. This allows the alkalinity from the lime in the topsoil to move down into the subsurface to reduce the aluminium toxicity in the subsurface.

Duplex soils, which are sandy soils over loam or clay subsoils, have been shown to have poor soil structure in the loam or clay subsoils. Recent research has shown that when gypsum is applied to the subsoil, the structure of the loam or clay in the subsoil is improved.

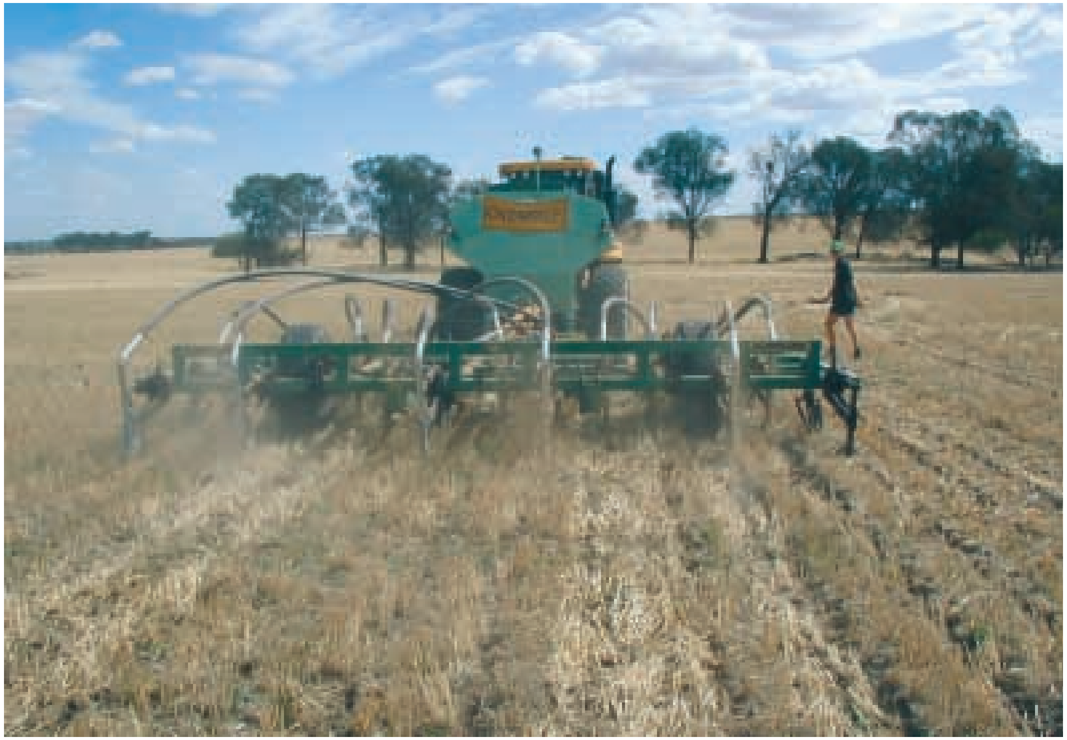

Figure 3: *Deep ripping and placement of lime at depth using grower scale machinery at Corrigin.*

As a result, more roots of crops can explore the subsoils for water and nutrient elements so increasing grain yields. However, gypsum only corrects the physical problem in the subsoil of the duplex soils. Most of the duplex soils also have a subsurface acidity problem in the 10 to 35 cm soil zone.

Research is being conducted to determine if applying both gypsum and lime to the subsoils of the duplex soils will further increase grain yields. The deep-placed gypsum improves the structure of the loam or clay subsoil, and the deep-placed lime reduces subsurface acidity.

Until the research is completed, applying sufficient lime to raise topsoil pH to at least 5.5 is a proven long-term management strategy for subsurface acidity in all soils, including the duplex soils.

Amending subsurface acidity

The present proven strategy is to add sufficient lime to the topsoil to raise the pH in the topsoil to 5.5 or greater.

This will ensure that alkalinity created by liming the topsoil will move down the soil to ameliorate subsurface acidity.

This downward movement of alkalinity raises the subsurface pH and decreases aluminium toxicity in the subsurface.

Removing aluminium toxicity increases plant root growth allowing the roots to explore a greater volume of soil.

Greater root volume increases the uptake of water and nutrient elements in the subsurface, increasing grain yields.

Conclusions and recommendations

For most soils used for cropping in Western Australia, subsurface acidity is the major soil acidity problem and it can greatly reduce grain yields.

It is therefore essential that farmers test the subsurface to assess if they have a subsurface acidity problem. If a problem is detected, this subsurface acidity will need to be ameliorated to maintain profitable grain production.

If subsurface acidity is allowed to continue to develop, then the problem becomes increasingly more difficult and expensive to ameliorate, and grain yields continue to decline.

To test for the presence of subsurface acidity, soil samples need to be collected at a minimum of two depths:

1. Top 10 cm.
2. 10 to 20 cm.

If the pH for the 10 to 20 cm depth is less than 5.0 then subsurface acidity is a problem. If the topsoil pH is less than 5.5, apply lime to raise topsoil pH to at least 5.5, and this will ensure alkalinity from the limed topsoil will move down from the topsoil into the subsurface to start reversing the aluminium toxicity in the subsurface.

Acknowledgements

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Further reading:

Farmnote 78/2000	"The importance of pH"
Farmnote 79/2000	"Soil acidity and barley production"
Farmnote 80/2000	"Management of soil acidity in agricultural land"
Farmnote 44/2002	"Tolerance of wheat varieties to soil acidity"
Farmnote 45/2002	"Lime and narrow-leafed lupins"
Farmnote 26/2002	"Treatment of compacted soils in the eastern wheatbelt"
Bulletin 4538	"Lime for high rainfall pastures (above 800 mm annual rainfall)"