SOIL ACIDITY

1. pH

In solution some water (H_2O) molecules disassociate to form hydrogen (H^+) and hydroxyl (OH^-) ions.

$$H_2O \rightarrow H^+ + OH^-$$

pH is the negative logarithm of the hydrogen ion concentration [$-\log(H^+)$] in the solution. The pH scale ranges from 1 to 14, where pH 7 is **neutral**, pH less than 7 is **acidic** and pH greater than 7 is **alkaline**. At a pH of 7, there are an equal number of hydrogen (H^+) and hydroxyl (OH^-) ions.

The presence of dissolved compounds (solutes) in the water can change the balance of hydrogen and hydroxyl ions. In acid solutions hydrogen ions dominate, in alkaline solutions there are more hydroxyl ions.

Being a logarithmic scale, for each unit change in pH, there is a ten-fold increase (or reduction) in the hydrogen ion concentration. At a pH of 5.0, there are ten times more hydrogen ions than at a pH of 6.0, and one hundred times more than at a pH of 7.0.

2. MEASURING SOIL pH

Soil pH can be measured in a 1:5 soil:water suspension (pH_w) or in a 1:5 0.1 M $CaCl_2$ (calcium chloride) solution (pH_{Ca}). pH_{Ca} results are usually 0.2 to 1.0 unit lower than pH_w, depending on the soil type and its clay and organic matter content, Cation Exchange Capacity (CEC) and composition of the cation suite, aluminium % and the soluble salt content of the soil. The difference is wider in alkaline soils in which free lime is present. Generally the higher the salt content the closer the two pH values.

3. pH$_w$ IN SOILS

The general pH_w range for soils is 4.5 to 8.5. Lower values, down to 3.5, are usually associated with peaty soils or severely leached acid soils. Higher values, up to 9.5, are associated with high levels of exchangeable sodium, magnesium and free calcium carbonate (lime).

The optimum pH_w for most plants is 6.0 - 7.5, although some plants prefer more acid soils, e.g. pineapples, and others prefer alkaline conditions, e.g. lucerne.

The soil pH is not a constant value, it will fluctuate to some extent throughout the year, depending on seasonal conditions, the soil's moisture status and microbial processes in the soil.
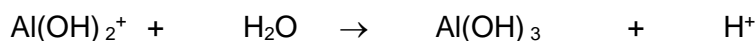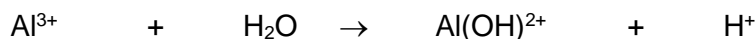
4.   BUFFERING CAPACITY

Lime (calcium carbonate) neutralises soil acidity (H^+ ions) by the following reaction:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2$$

As well as the hydrogen ions present in solution (as measured in soil solution pH determinations), some hydrogen ions are adsorbed onto soil colloids. These hydrogen ions may be released from exchange sites on soil colloids where there place is taken by calcium ions (Ca^{2+}) derived from the lime. Consequently, the concentration of hydrogen ions in the soil solution (and its pH) remains relatively unchanged.

This ability to resist change in soil solution pH and return to its original state is referred to as the soil's buffering capacity. Soils differ in their buffering capacity. The lower the buffer capacity of the soil, the greater the magnitude of the change in pH in response to an application of lime. These soils need less lime to achieve a desired change in pH. Soils with a high clay or organic matter content (high CEC) have a high pH buffer capacity. Large quantities of lime will be required on these soils to change the pH.

The presence of soluble forms of aluminium in acid soils has a major influence on the soil's acidity, its buffering capacity and the need for lime. Aluminium reacts with water to form hydrogen ions, as depicted in the following equations:

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+$$

$Al(OH)_3$ is insoluble, and does not contribute to acidity or cause aluminium toxicity.

5.   "BUFFER pH" TESTS

While useful in assessing the suitability of soil for plant growth, soil pH tests do not reliably indicate the amount of lime required to raise the soil pH to a more acceptable level. Extractable calcium, magnesium, aluminium and manganese concentrations should be considered in determining lime requirements.

In Queensland, a "Buffer pH" test is used to estimate on the amount of lime required to raise the soil pH to a more acceptable level in crops other than sugarcane. The test takes into consideration the reserve acidity or buffering capacity of the soil.

This Buffer pH Test has not been evaluated in the other Australian States.

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6.   EFFECT OF pH ON NUTRIENT AVAILABILITY IN SOILS

Often it is not low (or high) pH that is the growth-limiting factor in soils, but one or more secondary effects that are pH dependent. In very acid soils, the availability of some nutrients e.g. phosphorus (P), calcium (Ca), magnesium (Mg) and molybdenum (Mo) is very low, so uptake by plants is reduced. Other elements, e.g. aluminium (Al), manganese (Mn) and iron (Fe) are readily available and may reach toxic concentrations at low pH.

When plants respond to lime treatment of acid soils, the plant response is normally due to the combined effects of alleviating aluminium or manganese toxicity and overcoming phosphorus, calcium, magnesium or molybdenum deficiencies.

As the pH rises above 7.5, the availability of phosphorus, boron, copper, iron, manganese and zinc decreases, so over-liming should be avoided.

In sandy soils low in organic matter, small lime applications, as little as 1 t/ha, may induce temporary deficiencies of micronutrients at critical stages of growth. This is one reason why lime should be applied well ahead of planting in annual crops, to allow the soil pH to stabilise before planting.

7.   ACID SOIL INFERTILITY

7.1   Hydrogen ion concentration

Acid soil infertility is rarely due to hydrogen ions as such, except below pH 4.2 where root uptake of other cations may be stopped or reversed. At very low pH, plant tissue itself may be damaged. Usually the cause is from one or more related factors, discussed herein.

7.2   Aluminium Toxicity and Phosphorus Deficiency

Aluminium is one of the most abundant elements in the earth's crust, but most of it is in forms that are not available for plant uptake. In neutral and alkaline soils, the solubility of aluminium is too low to be toxic to plant growth. In acid soils with pH values below 5.5, the solubility of aluminium increases sharply and more than half the cation exchange sites may be occupied by aluminium, which can be taken up rapidly by plants.

Concentrations of aluminium in the soil solution greater than 1 mg/kg Al will often reduce yields. The primary effect of aluminium toxicity is direct injury to the root system. Root development is restricted, and the roots become thicker and stubby, showing dead spots.

Aluminium tends to accumulate in the roots and impede the uptake and translocation of calcium and phosphorus to the tops, which may produce or accentuate calcium and phosphorus deficiencies. Aluminium toxicity symptoms in plant tops are often characterised by symptoms similar to those of phosphorus deficiency (dark green leaves, stunted growth, purpling of stems).

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Aluminium also reacts with and reduces the solubility of phosphorus in the soil, restricting its uptake and utilization by plants.

7.3   Manganese Toxicity

Like aluminium, manganese is quite abundant in soils, but is mostly unavailable for plant uptake. Manganese is an essential micronutrient, and plant deficiency can occur in alkaline and recently limed soils.

Manganese (Mn) is very soluble at pH values below 5.5. When grown on acid soils high in manganese, plant uptake can be high. Levels as high as 1 000 mg/kg Mn in dry matter are not uncommon.

Manganese toxicity is characterised by brown spots in older plant organs and by uneven distribution of chlorophyll. The toxicity is often accompanied by iron deficiency symptoms. Manganese toxicity is more likely to occur under anaerobic (waterlogged) conditions where Mn^{4+} is reduced to Mn^{2+}, the form taken up by plant roots.

7.4   Calcium or Magnesium Deficiency

Although aluminium (Al) and manganese (Mn) toxicities are often the cause of poor plant growth in acid soils, it may also be attributable to calcium (Ca) or magnesium (Mg) deficiencies. In the tropics, it is not uncommon to find acid soils that are low in calcium and magnesium without having aluminium problems.

Plants vary in their susceptibility to aluminium toxicity and calcium deficiency. Sugarcane, for example, is quite tolerant of high exchangeable aluminium but may respond to calcium, whereas other crops grown in the same field may exhibit symptoms of aluminium toxicity.

7.5   Molybdenum Deficiency

As pH falls below 6.0, the availability of molybdenum (Mo) decreases markedly. Where soils already have a low total molybdenum content, there is likely to be insufficient molybdenum for healthy plant growth.

Molybdenum is particularly important where legumes are being grown. The *Rhizobium* bacteria in the nodules on the legume roots have a tenfold higher requirement for molybdenum than the host plant. In legumes, the foliar symptoms of molybdenum deficiency are the same as those for nitrogen deficiency.

8.   EFFECT OF pH ON SOIL MICROBIAL ACTIVITY

Plant root growth is not the only thing affected by soil pH. Soil microbial activity improves and organic matter decomposition increases when the soil pH is adjusted to the optimum for these processes. Several species of nitrifying bacteria, e.g. *Nitrosomonas* and *Nitrobacter*, are involved in the nitrification of ammonium ions, i.e. conversion to nitrate (NO_3^-). These species prefer neutral soil conditions so nitrification is reduced in acid soils.

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The activities of some of the symbiotic *Rhizobium* species associated with temperate legumes such as clovers, medics and lucerne are optimum at near neutral pH, while those found in symbiosis with tropical legumes prefer more acid soils, as long as they have sufficient magnesium and calcium. The fixation of molecular N_2 by free living organisms, e.g. *Azotobacter* is favoured by neutral pH.

9. SOURCES OF ACIDITY

Soil acidification is the natural and unavoidable cost of a productive agricultural system. It is likely to occur in high rainfall areas, and where irrigation is practised (unless the water is alkaline), the soil is cultivated, legumes are grown, nitrogen fertilisers are used and crop yields (and nutrient removal) are high.

Lime will need to be considered on a regular basis as part of a balanced fertiliser program unless the soil has a high buffering capacity and can resist changes in pH, or alkaline irrigation water is used. For example, lime is not required on heavy clay soils such as those found in the Wimmera, the central and north-west of New South Wales, and the Darling Downs; and in many irrigation areas in the Murray Darling Basin

Some of the more important processes involved in soil acidification are discussed below.
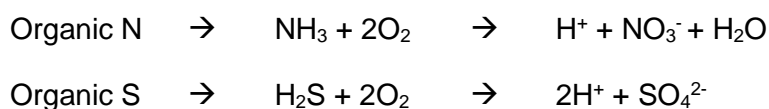
9.1 Mineralization of Organic Matter

When organic matter decomposes, carbonic acid (H_2CO_3) is formed. In turn carbonic acid may form carbon dioxide (CO_2), or dissociate to release hydrogen (H^+) ions. If hydrogen ions are formed, they can acidify the soil.

$$\text{Organic C} \rightarrow H_2CO_3 \rightarrow H_2O + CO_2$$
$$\rightarrow H^+ + HCO_3^-$$
$$\rightarrow 2H^+ + CO_3^{2-}$$
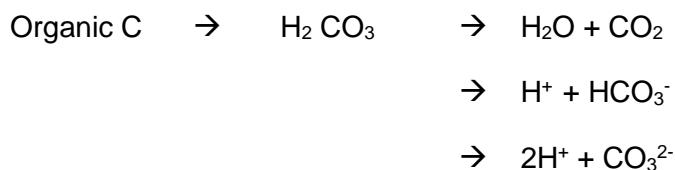
How much $CO_2 + H_2O$ or $H^+ + HCO_3^-$ is formed depends on the pH of the soil. As the pH increases, the equilibrium is shifted in favour of H^+ production. In alkaline soils HCO_3^- can even dissociate, producing another H^+ ion. Under acid conditions (pH less than 5.2) hardly any H^+ ions are produced as the equilibrium is shifted in favour of CO_2 production.

Microbial decomposition of organic matter also produces NH_3 and H_2S. Both these compounds can be oxidised in the soil to strong inorganic acids, i.e. HNO_3 (nitric) and H_2SO_4 (sulfuric), and so depress pH.

$$\text{Organic N} \rightarrow NH_3 + 2O_2 \rightarrow H^+ + NO_3^- + H_2O$$
$$\text{Organic S} \rightarrow H_2S + 2O_2 \rightarrow 2H^+ + SO_4^{2-}$$

The impact these processes have on soil pH is greatest in soils with a high organic matter content, and is the reason why peaty soils are typically very acid. Cultivation also has an

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impact, by aerating the soil and accelerating the breakdown of soil organic matter. Measures that increase soil organic matter levels, e.g. pasture improvement or the addition of organic wastes, can also contribute to soil acidification.

9.2   Respiration by plant roots

In the process of respiration, plant roots produce and exude carbon dioxide (CO_2) into the soil. This contributes to soil acidification in the same way as organic matter decomposition, i.e. by combining with water to form carbonic acid.

$$CO_2 \;+\; H_2O \;\rightarrow\; H_2CO_3$$
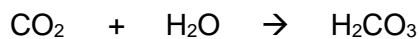
9.3   Nitrogen Fertilisers

The use of fertilisers containing or forming ammonium nitrogen (NH_4^+) can increase soil acidity. Anhydrous ammonia, urea and ammonium nitrate are approximately equal in the effect they have on soil pH (per kg of N), while ammonium sulfate is two or more times more acidifying per kg of N. Calcium nitrate does not acidify the soil.
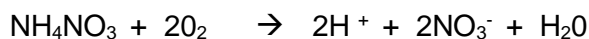
The mineralisation of urea, which is the most commonly used nitrogen fertiliser, is dependent on a naturally occurring enzyme known as urease. It starts with the conversion of urea to ammonium carbonate.

$$(NH_2)_2CO \;+\; 2H_2O \;\rightarrow\; (NH_4)_2\,CO_3$$

The ammonium is then nitrified in a two-stage process to nitrate (NO_3^-) by nitrifying bacteria (*Nitrosomonas, Nitrobacter, Nitrosolobus*). The full process can be summarised by the following equation:-
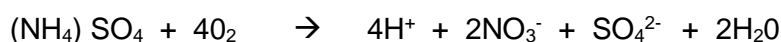
$$(NH_2)_2CO \;+\; 4O_2 \;\rightarrow\; 2H^+ \;+\; 2NO_3^- \;+\; H_2O \;+\; CO_2$$
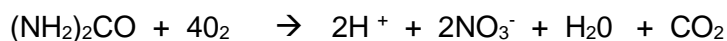
For ammonium nitrate (Nitram), the process is:

$$NH_4NO_3 \;+\; 2O_2 \;\rightarrow\; 2H^+ \;+\; 2NO_3^- \;+\; H_2O$$

For both cases, one H^+ ion is produced for each nitrate (NO_3^-) ion. In other words, the end product of the nitrification of urea and Nitram is nitric acid (HNO_3).

The ammonium sulfate reaction in the soil can be represented as follows:

$$(NH_4)\,SO_4 \;+\; 4O_2 \;\rightarrow\; 4H^+ \;+\; 2NO_3^- \;+\; SO_4^{2-} \;+\; 2H_2O$$

In this case, two hydrogen ions are produced for each nitrate ion. In effect, nitric acid (HNO_3) and sulfuric acid (H_2SO_4) are produced in the soil, the reason it is more acidifying.

Changes in soil pH as a result of the use of nitrogen fertilisers will be most noticeable on sandy or poorly buffered soils. Reductions in soil pH occur gradually, and will be most evident where nitrogen fertilisers are applied at high rates.

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Calcium nitrate, which is used as a non-acidifying nitrogen fertiliser in fertigation programs through drip and trickle irrigation systems in high value horticultural crops, simply dissolves to release nitrate ions. Hydrogen ions are not formed.

$$Ca(NO_3)_2 \rightarrow Ca^{2+} + 2NO_3^-$$
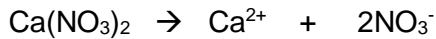
Calcium nitrate is too costly to use in broadacre crops and pasture.

9.4   Nitrogen Fixation by Legumes

The use of superphosphate and the introduction of legumes (clovers, medics) in pasture improvement programs has resulted in increased rates of soil acidification in many parts of Australia. This has incorrectly been attributed to the superphosphate, which on its own has little or no effect on soil pH.

Nitrogen fixation by *Rhizobium* bacteria in the root nodules of legumes is enhanced where superphosphate is used. The subsequent decomposition of nitrogen-rich plant residues can have the same effect on soil pH as nitrogen applied as fertiliser.

9.5   Soil Reactions involving Cations and their Loss through Leaching

The production of hydrogen ions by the processes described above is just part of the acidifying process.

On some soils, i.e. alkaline soils with a high cation exchange capacity, it will have little or no effect on soil pH. These soils often contain free calcium carbonate, which will neutralise any hydrogen ions that are formed. The dissolution of calcium carbonate and the weathering of soil minerals high in calcium and magnesium ensure that exchangeable levels of calcium and magnesium in the soil remain high. On other soils, there will be a gradual fall in pH and exchangeable calcium and magnesium levels, and an increase in exchangeable aluminium levels.

In acid soils, hydrogen ions replace other cations on the exchange sites of soil colloids, and solubilise aluminium (Reverse process to that depicted in Section 4 on "Buffering Capacity"). Once calcium, magnesium and other cations have been displaced from the surface of soil colloids and become part of the soil solution, they are more subject to loss through leaching. Such losses gradually deplete the soil of calcium and magnesium. Leaching is most likely to occur on sandy soils and in high rainfall areas (and if excess irrigation water is applied).

Positively charged cations, such as calcium (Ca^{2+}), are not lost in isolation. They are accompanied by an equivalent anionic (negative) charge. The number of positive and negative charges is balanced.

On soils high in organic matter, where legumes are grown, and where nitrogen fertilisers are used, nitrate (NO_3^-) is formed in the soil. Nitrate is essential to plant growth, but it is also highly prone to leaching. When negatively charged nitrate is leached, positively charged cations or bases, e.g. Ca^{2+}, accompany it. The inefficient use of soil nitrate by plants, and its resultant loss through leaching, can accelerate the rate of soil acidification.

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The loss of calcium and magnesium with nitrate depletes the topsoil of these nutrients. If hydrogen ions are lost, they will contribute to subsoil acidification. In pastures, leaching losses and the rate of acidification are greater where shallow rooted annuals are grown than with deeper rooted perennial species.

9.6   Plant Uptake

In the same way that loss of cations through leaching can acidify the soil, so too can the uptake of nutrients by plants. It matters little how the cations are removed (through leaching or plant uptake). The higher the yield and the sale off farm of plant and animal products, the greater the demands placed on the soil and its nutrient reserves. Large amounts of nutrient are removed where hay and silage crops are grown.

NPK fertilisers are applied to increase crop and pasture yields. Plants take up considerable amounts of negatively charged anions such as nitrate (NO_3^-) and phosphate ($H_2PO_4^-$ and HPO_4^{2-}) and positively charged cations such as potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}). The higher the yield, in response to fertiliser (and irrigation), the greater the removal.

On soils prone to acidification, this drain on the soil's calcium and magnesium reserves will gradually lead to a fall in their exchangeable levels, and increased acidity. Lime is required as part of a balanced fertiliser program on these soils.

10.   CORRECTION OF SOIL ACIDITY

When added to acid soils, lime (calcium carbonate) dissolves to release calcium (Ca^{2+}) and carbonate ions (CO_3^{2-}).

$$CaCO_3 \quad \rightarrow \quad Ca^{2+} \quad + \quad CO_3^{2-}.$$

The calcium (Ca^{2+}) ions occupy exchange sites on soil colloids, displacing hydrogen (H^+), aluminium (Al^{3+}) and other cations such as iron (Fe^{3+}).

In solution, the H^+ ions are neutralised by reacting with carbonate (CO_3^{2-}) from the lime.

$$2H^+ \quad + \quad CO_3^{2-} \quad \rightarrow \quad H_2O \quad + \quad CO_2$$
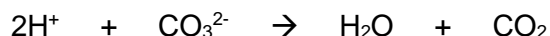
The displaced aluminium reacts with water to form more hydrogen ions, as depicted in the series of reactions in Section 4 on "Buffering Capacity". These hydrogen ions are in turn neutralised, and ultimately the aluminium (Al^{3+}) and iron (Fe^{3+}) are precipitated as insoluble hydrous oxides.

Soil fertility is improved as a result of the neutralisation of soil acidity, and the reduction in exchangeable aluminium levels. The rate and magnitude of change in soil pH depends on the fineness and purity of the lime, the rate at which it is applied; and the soil's buffer capacity, clay and organic matter content. Finely ground limestone mixed uniformly with a soil reacts more rapidly than coarse lime, less evenly spread.

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FURTHER READING

More information on the use of lime is contained in the Incitec Pivot Agritopic on "Lime and Dolomite".

WARNING

The information contained in this publication is for use as a guide only. The use of fertilisers and soil amendments are not the only factors involved in producing a top yielding crop or pasture. Local soil, climatic and other conditions should also be taken into account, as these could affect responses.

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