SOIL ACIDITY AND LIMING

Much of New Zealand's overseas income is still derived from agricultural production. To maintain the fertility and structure of our soils, and to make the most efficient use of the nutrients they contain, large amounts of crushed limestone (agricultural lime, $CaCO_3$) have been applied to our soils each year since the 1890s. In 1993, 1 025 662 tonnes of lime were applied. As most New Zealand soils contain adequate supplies of the nutrient calcium, this lime was added not to supply calcium but to raise soil pH. Many New Zealand topsoils are naturally acid, whereas most plants grow best in a near neutral soil. In New Zealand soils, the main benefits from the addition of lime are the increased availability of phosphorus and molybdenum, the prevention of aluminium and/or manganese toxicity, and the encouragement of more productive pasture species (e.g. white clover and ryegrass) at the expense of lower fertility species. The limestone used in agriculture was formed during Oligocene times, some 25 to 38 million years ago. Fortunately limestone outcrops occur in most parts of New Zealand from Northland to Southland, so it is not expensive to transport it to farmers.

INTRODUCTION

The population of our planet will be nearly six billion by the year 2,000. Depending on the rate at which birth rates fall to zero over the next 50 years, the United Nations has predicted that the world population could be between seven and 15 billion by the year 2100. Food needed to sustain these people comes largely from the plants and animals supported by the planet's soils, since globally food from the sea is relatively insignificant.

Soils are formed when climate (rainfall and temperature) and organisms (vegetation, micro-organisms and humans) interact with rocks and other forms of soil parent material on slopes of varying relief over time. The planet's soil resources are finite and diminishing as deserts expand through overgrazing and salinisation, while more intensive use of fertilisers, herbicides and pesticides increases soil vulnerability to erosion, and expanding urbanisation buries highly productive soils.

Pressures on existing arable land, and our insatiable need for paper continue to threaten the planet's forests. Once a forest is felled, it no longer absorbs water and returns it to the atmosphere by evapotranspiration, stores carbon in plant tissues, or holds soil in place. Soil erosion and the amount of carbon dioxide in the atmosphere both increase. The Worldwatch Institute estimates that topsoil is being lost at a global rate of 0.7% per year, and claims that this rate is accelerating. This erosion rate apears to be some five to ten times the formation rate for producing fertile soil from fresh parent material.

New Zealand has always been an efficient producer of agricultural products. Recent trends have seen moves towards more sustainable agricultural practices, and more concern regarding the proper use of fertilisers and other agricultural chemicals.

The pH of natural topsoils of New Zealand soils ranges from less than 4.0 to more than 6.0. The ideal pH for growing many agriculturally and horticulturally important plants is between 6.0 and 7.0. If the pH of a soil is significantly lower than this, agricultural lime(stone) is added to neutralise the acidity and raise the pH. This article discusses the causes of soil acidity, its effect on plant growth, and its control by liming.

WHY DO SOILS BECOME ACID?

Soil is not simply an amorphous mass of dirt, but a well structured ecosystem. About half its volume is solids, with the remainder consisting of pores (capillaries) of various sizes. The larger pores provide drainage, while the smaller ones store plant-available water. Ideally about half of the available pore space in a soil contains water while the remainder contain air. The water held in the soil is known as the soil solution. Thus soil consists of a mixture of organic and inorganic solids, and these are in contact with both water and air. This means that a variety of chemical processes can potentially occur in soil, including mineral hydrolysis, decomposition of organic matter, removal of water-soluble material and oxidation of sulphates. Each of these processes is described below, and their effect on pH discussed. The pH effects of fertiliser and acid rain are also covered.

Mineral hydrolysis

The rocks and rock debris that form the parent materials from which our soils are derived contain quartz (SiO_2) and various aluminosilicate and ferromagnesium minerals. As the parent materials weather to form soils, these minerals may dissolve in or be hydrolysed by water. Orthoclase, a member of the feldspar group of rock-forming minerals, is the pink colored mineral often found in granites (e.g. those from Karamea). Kaolinite is a phyllosilicate clay mineral. In the presence of water, orthoclase hydrolyses to kaolinite:

$$\underset{\text{orthoclase}}{2KAlSi_3O_8(s)} + 11H_2O(l) \rightarrow \underset{\text{kaolinite}}{Al_2(Si_2O_5)(OH)_4(s)} + 4Si(OH)_4(aq) + 2K^+(aq) + 2OH^-(aq)$$

Hydrolysis reactions, such as the one above, form clay minerals (e.g. kaolinite), and release ions and molecules into soil solution. The potassium ions released in the above reaction may be absorbed and utilised by growing plants or other organisms, adsorbed on to the negatively charged surfaces of humus or phyllosilicate clay colloids in the soil, or leached into the ground water and eventually make their way to the sea or to a lake.

The above reaction releases hydroxide ions, and thus would decrease, rather than increase, the acidity of the soil. You can easily demonstrate that hydrolysis of rock-forming minerals releases hydroxide ions. Simply grind a small piece of rock with water in a mortar and pestle, and then add a few drops of phenolphthalein. The phenolphthalein invariably turns red. As hydroxide ions are released in these hydrolysis reactions, weathering of rock minerals is not a source of soil acidity.

Breakdown of the soil biomass

The decomposition of plant litter (known as mineralisation) leads to the release of a variety of chemicals. Initial decomposition leads to the production of carbon dioxide and of organic acids. In addition, organic forms of nitrogen, phosphorous and sulphur are converted into simple inorganic species that can be utilised by plants.

All of these processes can increase soil acidity. The excess carbon dioxide forces the carbonic acid dissociation equilibria to the right, releasing hydronium ions:

$$CO_2(g) + 2H_2O(l) \leftrightarrows H_3O^+(aq) + HCO_3^-(aq)$$
$$HCO_3^-(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CO_3^{2-}(aq)$$

The organic acids directly decrease soil pH, while hydrogen ions are released in some of the mineralisation reactions involving nitrogen, phosphorous and sulphur:

$$\text{proteins} \xrightarrow{\text{heterotrophic micro-organisms}} NH_4^+(aq) \text{ or } NH_3(aq)$$

$$2NH_4^+(aq) + 3O_2(g) + 2H_2O \xrightarrow{\textit{Nitrosomonas}} 2NO_2^-(aq) + 4H_3O^+(aq)$$

$$2NO_2^-(aq) + O_2(g) \xrightarrow{\textit{Nitrobacter}} 2NO_3^-(aq)$$

These pH reducing effects are very dependent on the exact nature of the organic matter decomposing, so soils around pine trees can be much more acidic than grassland soils.

Leaching

Where soils are near neutral or alkaline, Ca^{2+}, Mg^{2+}, K^+ and Na^+ cations, known collectively as the exchangeable bases, balance most of the negative charges present on the surfaces of humus and the phyllosilicate clay minerals. As these exchangeable base cations are in dynamic equilibrium with the cations present in the bulk of the soil solution, it follows that they are also the dominant cations present in the soil solution. When more rain falls on this soil than is removed by evaporation or plant transpiration, it runs through the soil, removing water-soluble material. In particular, it removes the mobile Ca^{2+}, Mg^{2+}, K^+ and Na^+ cations from soil solution, and replaces them with $H_3O^+(aq)$ and $Al^{3+}(aq)$ ions. Both of these species are acids, although this we don't usually think of cations like Al^{3+} as being acids. However, $Al^{3+}(aq)$ is a hydrated cation, $Al(H_2O)_6^{3+}(aq)$, and as such is a polyprotic acid with a pK_{a1} value of 5. This is comparable to that of acetic acid. The first proton is lost as follows:

$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \leftrightarrows Al(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$$

Further hydrolysis can then occur:

$$Al(H_2O)_5(OH)^{2+}(aq) + H_2O(l) \leftrightarrows Al(H_2O)_4(OH)_2^+(aq) + H_3O^+(aq)$$

$$Al(H_2O)_4(OH)_2^+(aq) + H_2O(l) \leftrightarrows Al(H_2O)_3(OH)_3(aq) + H_3O^+(aq)$$

$$Al(H_2O)_3(OH)_3(aq) + H_2O(l) \leftrightarrows Al(H_2O)_2(OH)_4^-(aq) + H_3O^+(aq)$$

As these hydrolysis reactions liberate $H_3O^+(aq)$ ions they will lower soil pH.

Alkaline soils (pH > 7.0) usually occur in dry regions where very little leaching occurs. In such soils, $Ca^{2+}(aq)$ ions from limestone cannot be leached away, and neither can the carbonate anions. By itself, this $CaCO_3$ does not cause soil pH to rise above 8.3. However, in very arid areas not even the highly mobile $Na^+(aq)$ and $K^+(aq)$ ions leach from the soil, so these can accumulate on the soil surface. When this occurs, soil pH may exceed 9.0.

Oxidation of sulphides
Soils do not usually contain high levels of sulphides: high sulphide levels are associated with the drainage of marine or estuarine sediments or the presence of mine effluent (either contaminated water or dumped solids that have susbsequently weathered). These sulphides result in localised areas of extreme soil acidity as the oxidation of sulphides to sulphate results in the release of acid. The equation below is for the oxidation of pyrite, which is typically found in mine effluent:

$$\underset{\text{pyrite}}{4FeS_2(s)} + 6H_2O(l) + 15O_2(g) \leftrightarrows 4Fe^{3+}(aq) + 8SO_4^{2-}(aq) + 4H_3O^+(aq)$$

Fertiliser application
The use of some fertilisers, including urea, ammonium sulphate and sulphur, will cause the pH of soils to become more acid. With urea, the initial hydrolysis reaction will cause the soil pH to rise, but the oxidation of the released ammonium ions to nitrate then causes soil pH to fall.

Acid rain
Acid rain can form wherever there are large cities with high concentrations of industry and vehicles. The burning of coal and petroleum products releases sulphur dioxide and oxides of nitrogen, which if not controlled are released to the atmosphere, where they form sulphuric and nitric acids. Once dissolved in rainfall, these acids may damage streams, lakes, ground water, buildings, vegetation and soils, and certainly decrease soil pH.

WHY DOES SOIL pH AFFECT PLANT GROWTH?

It would be logical to think that hydronium ion (H_3O^+) toxicity or calcium and/or magnesium deficiency were the obvious reasons why many plants grow poorly on acid soils. This was what the earliest researchers assumed. Later work soon showed that soil acidity had to be below about pH 3 before the hydronium ion concentration itself was toxic to most plant species. Calcium and magnesium deficiencies were found to be uncommon until soil pH drops below 4.0 to 4.5. So it must be some other pH-related effect that causes plants to grow badly in acidic soils.

Most metallic ions increase in concentration the lower the pH, as the acidic conditions cause the hydrolysis of the insoluble oxides in which they usually occur. This means that below pH 5.0 both aluminium and manganese reach toxic concentrations. The addition of lime reduces the concentration of both Al^{3+} and Mn^{2+} in the soil solution and thus improves crop yields.

Peat soils that do not contain inorganic mineral materials are unlikely to suffer from aluminium toxicity problems. The pH of such soils should not be raised above 5.0, or deficiencies of copper or other micro-nutrients may occur.

Unlike most other trace elements, the availability of molybdenum increases as the pH rises. However, it is still below optimum for most plants at pH 5.0, and indeed at this pH molybdenum deficiency may become the most important single factor limiting plant growth. Deficiency of this plant micro-nutrient may be corrected for by liming to raise soil pH to between 5.5 and 6.5, but for plants such as lucerne and peas which are very sensitive to molybdenum deficiency, this may well not be enough. In this case it is usual to use a molybdenum-enriched super phosphate fertiliser to correct the problem.

PREFERRED pH RANGES FOR PLANTS

In altering soil pH it is usually best to aim for a pH of from 6.0 to 6.5. Most commonly grown pasture plants, vegetables, fruits and ornamental shrubs, and their associated microorganisms, thrive in this pH range, because major plant nutrients are at least as available as at any other pH, and micro-nutrient deficiencies or toxicities are less likely to occur. Not all plants do prefer this pH range, however, and **Table 1** shows the preferred ranges for a number of common species.

Table 1 - Preferred pH ranges for a variety of plants grown in NewZealand

pH range	Flowers & Shrubs	Field Crops & Vegetables	Fruit
4.0 - 5.5	Hydrangea (blue)		Blueberry
4.5 - 6.0	Azalea, Erica, Rhododendron	Potato	
5.0 - 6.5	Broom, Holly, Magnolia	Oats, Parsley	
5.5 - 6.5	Clematis, Rose	Barley, Capsicum, Kumara, Ryegrass, Turnip, Wheat	Apple, Avocado, Cranberry, Melon, Strawberry
5.5 - 7.0		Carrot, White Clover	
5.5 - 7.5	Aster, Lupin	Corn, Cucumber, Pumpkin, Tomato,	Rhubarb
6.0 - 6.5	Most New Zealand Natives		
6.0 - 7.5	Chrysanthemum, Dahlia, Poppy	Asparagus, Broccoli, Broad Bean, Cabbage, Cauliflower, Lettuce, Marrow, Onion, Spinach	Apricot, Cherry, Grape, Hazelnut, Pear, Quince

LIMING

The addition of lime has already been mentioned as one way to control soil pH and hence the levels of aluminium, manganese and, to a lesser extent, molybdenum ions in soil. Liming also stimulates biological activity in soils. By increasing the cycling of three important plant macro-nutrients, nitrogen, phosphorus and sulphur, it increases their availability to plants. By stimulating earthworm activity, liming can increase the infiltration of rainfall thus reducing the potential for runoff and erosion, while increasing plant-available soil moisture.

However, liming to increase soil pH above 6.5 may do more harm than good. It may reduce the availability of phosphate and cause deficiencies of micro-nutrients such as manganese (in wheat) and zinc (in pastures). Overliming may also increase the loss of sulphate if the excess calcium is leached. Liming to increase soil pH above 6.5 should only be undertaken for crops known to grow best at these pH values.

It is thus important to be able to accurately calculate the amount of lime to add to soil to achieve the desired results.

How much lime is needed to raise soil pH?
The amount of lime needed to raise the pH of a soil by a given amount (say 1 pH unit) depends on the amount of humus and clay the soil contains. This relates to the way that lime works. Lime ($CaCO_3$) dissolves slowly in the soil solution to release calcium and bicarbonate ions:

$$CaCO_3(s) + H_2O(l) + CO_2(g) \leftrightarrows Ca^{2+}(aq) + 2HCO_3^-(aq)$$

The bicarbonate neutralises the hydronium ions in the soil solution, while the calcium ions displace the hydronium and aluminium ions held by the negative charges on the surfaces of the humus and clay particles. Once displaced into solution, these hydronium and aluminium cations are also neutralised by the bicarbonate.

$$HCO_3^-(aq) + H_3O^+(aq) \rightleftharpoons CO_2(g) + 2H_2O(l)$$

$$\text{Soil colloid} \begin{array}{c|c} \ominus & H_3O^+ \\ \ominus & H_3O^+ \end{array} + Ca^{2+} \rightleftharpoons \text{Soil colloid} \begin{array}{c|c} \ominus & \\ & Ca^{2+} \\ \ominus & \end{array} + 2H_3O^+$$

The more humus and clay a soil contains, the greater its reserve acidity (i.e. aluminium content), and the greater amount of lime needed to raise the soil pH by a given amount. Organic and clay-rich soils containing humus and clays thus have considerable buffer capacity. It requires less lime to raise the pH of sandy soils.

ENVIRONMENTAL IMPLICATIONS

Unlike fertilisers, herbicides and pesticides, which may cause environmental problems if improperly used, lime is unlikely to cause damage to the environment. The only nutrient it adds to soils is calcium, and this is already present in large amounts in most soils and has no harmful effects. Lime is the cheapest substance available to neutralise the harmful effects of soil acidity.

AN EXPERIMENT - MEASURING SOIL ACIDITY

The availability of plant nutrients, and hence the growth of plants depends, among other factors, on soil acidity. Soil pH is obtained by vigorously stirring 10g of soil (that will pass through a 2mm sieve) in 25mL of distilled (deionised) water and leaving the suspension to equilibrate overnight. The pH of the suspension is then read using a calibrated pH meter. If one is not available, the pH can be estimated using either universal indicator or litmus paper that changes colour over a wide pH range (i.e. not the litmus paper that is simply blue in base and red in acid).

If you do not have access to this equipment, you may determine the approximate soil pH using a commercial coloured indicator solution. These are available from many garden shops. To use the indicator, mix a small quantity of soil (about as much as you can fit on a 5 cent coin) with enough indicator to moisten it, on a white plate. (A piece of white plastic, e.g. a spoon, is ideal). The indicator changes colour depending on the pH of the soil, and the pH is determined by comparing the colour obtained with that of the standards provided. White barium sulphate, $BaSO_4$ may be sprinkled over the moistened soil to make it easier to observe the colour obtained.

You may find it interesting to determine how the pH varies with depth by digging a hole and determining the pH at regular (say 10cm) depth increments. If you live near a forest, you could examine how trees affect soil pH by determining the pH of the litter layer and/or topsoil at 1 m intervals along a transect between two large trees.

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