Section

3

3. Nutrients and Nutrient Cycles

3.1 Background

Nutrient Cycles

A conceptual nutrient cycle summarises our current knowledge of the forms, amounts and fate of nutrients in soil/plant/animal systems. Those responsible for the recommendations of nutrient inputs to farming systems must have a good understanding of the fate of those nutrients. This is particularly important in understanding the nutrient requirements of farming systems and avoiding excessive amounts or forms of nutrients that may have a negative impact on the wider environment. Questions of particular interest for these nutrients are:

- What are the amounts and forms of nutrient present in the system?
- What is the form of nutrient that is available to plants?
- What is the source, process and rate of replenishment for the plant available form?
- What are the forms and rates of processes that lead to nutrient loss from the system?
- What are the forms and rates of processes that lead to nutrient gain to the system?

An ability to answer these questions will assist us in:

- Determining fertiliser requirements.
- Understanding the impact of fertiliser use on the environment.

3.2 Phosphorus in Soils

Key Learning Objectives

After studying this section you should be able to explain:

1. The amounts and forms of P present in the system.

2. The form of P that is available to plants.

3. The source, process and rate of replenishment for the plant available form of P.

4. The forms and rates of processes that lead to P gains or losses in the system.

5. The forms and solubilities of P in the common phosphate fertilisers used in New Zealand

6. The reactions and fate of different phosphate fertilisers added to soil with respect to:
    - P availability to plants
    - Soil acidity in the immediate area near the fertiliser granule

Introduction

Although P is the 4th macronutrient rated in order of the amount needed by plants, next to N, K and S, P is second only to nitrogen in limiting primary production in most temperate terrestrial and aquatic ecosystems. Loss of P from agricultural land to aquatic systems has been identified as a key cause of deterioration in surface water quality. In most soils, the native amounts of P and the rate of P supply to plant roots will not support the rapid plant production required of agricultural production systems. In general, P is seen as a very important plant nutrient of which soils are in short supply.

Role of P in Plants and Soil Organisms

Phosphorus is always present as the oxyanion, orthophosphate or its polymers in inorganic and organic compounds e.g. adenosine di- and triphosphate (Figure 3.2.1). P has a central role in the energetics and productivity of the biosphere in combination with the organic group adenosine. The energy associated with forming and breaking the bond between phosphate groups of adenosine triphosphate is universally used to store energy in the short term, and then provide energy for life reactions throughout the plant and animal kingdoms. Solar energy capture by plants is limited when P supply to the plant is low because adenosine triphosphate synthesis is constrained. Phosphate groups and their bonds to nucleobases are also important components of the genetic code DNA and RNA.

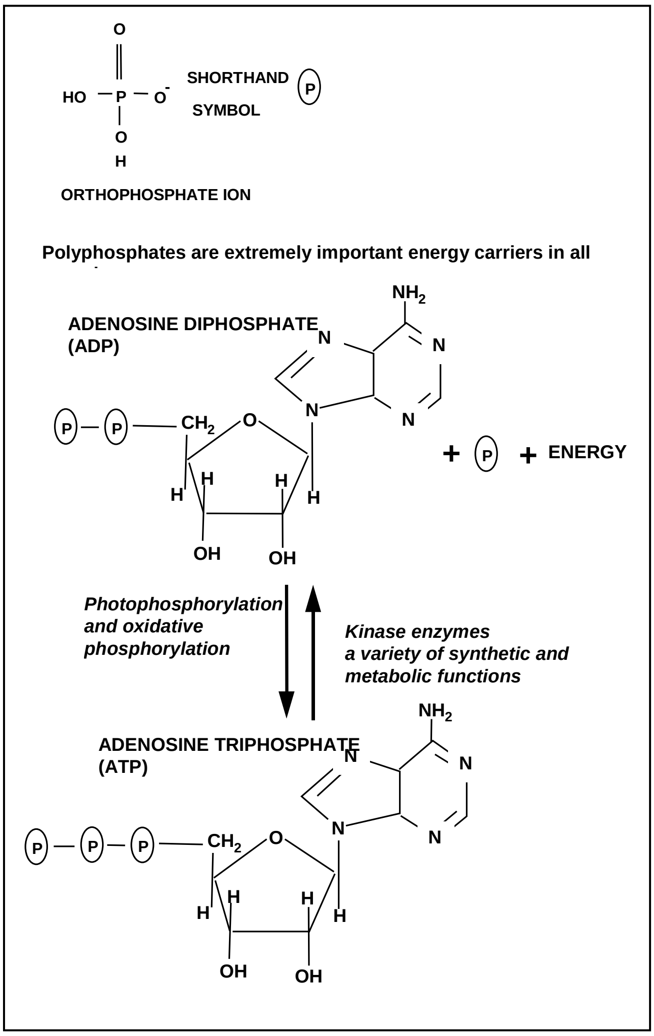

Figure 3.2.1 The orthophosphate ion and important organic phosphates ADP and ATP

Transformations of P in Soils

Soils represent the only significant reserve of P for plant growth (Figure 3.2.2). P in soils was originally derived from minerals formed within igneous rocks.

Phosphate must be in the soil solution before it can be adsorbed by plant roots, however, the concentration in solution is normally very low $<10^{-5}$ M and inadequate to sustain plant growth. Thus, it is important to understand how the solution P is replenished.

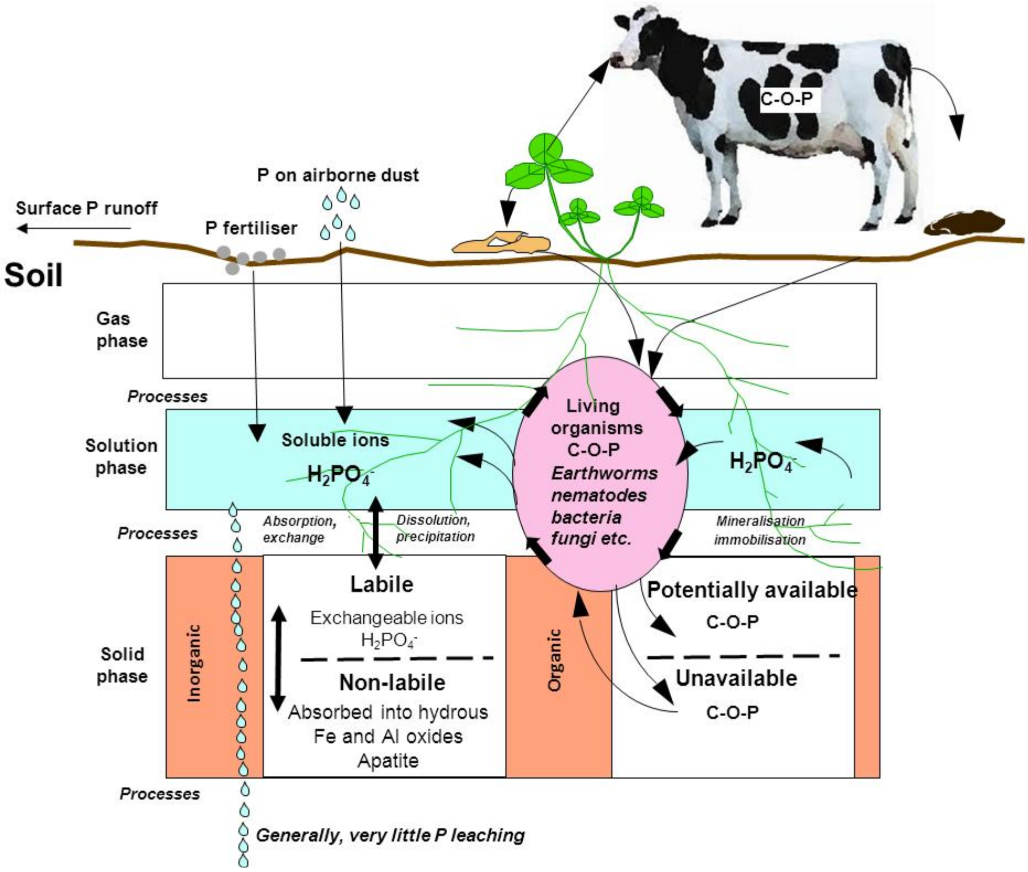

Figure 3.2.2 The P cycle in soils

To understand how the concentration of P in soil solution (solution phase) can be replenished, we must consider three chemical equilibrium between the solution and solid phase P in soils (Figure 3.2.2).

(i) Orthophosphate in solution ⇔ Primary P minerals
(ii) Orthophosphate in solution ⇔ P adsorbed on soil surfaces, amorphous Fe and Al hydrous oxides (Labile).

↑↓

Precipitated secondary minerals and
absorbed into hydrous oxides of Fe and Al in soil
(Non-labile)

We must also consider biological transformations:

(iii) Orthophosphate in solution ⇔ Soil organic P

Role of Primary Minerals

In most soils of temperate regions (phosphorus content 0.02% - 0.5%, topsoil average 0.05% or 1000 kg P/ha) primary P minerals (those found in igneous rocks) are only present in the sand fractions. In geological time they weather to produce soluble P and in turn secondary P minerals. The most common primary P minerals are the apatites. For example:

Fluorapatite Present in igneous deposits and the enriched phase of the secondary mineral carbonatites. Rich deposits of this unreactive P rock are mined and acidulated to make fertiliser.

$Ca_{10}(PO_4)_6F_2$

Apatite can also occur in more highly substituted secondary minerals. For example:

Francolite A carbonate substituted apatite - formed in sedimentary rocks in which CO_3^{2-} replaces some PO_4^{2-}. It is used as reactive phosphate rock (RPR) for direct application to pastures and in fertiliser manufacture.

$Ca_{10}\ [PO_4]_6\text{-}x\ (CO_3)x\ (F,OH)_2 + x$

During the natural weathering of soil parent materials over thousands of years, the apatite decreases as secondary minerals are formed and vegetation causes the formation of organic P.

In New Zealand, only a few recent alluvial soils contain significant amounts of natural apatite. In a chronosequence of New Zealand Soils (Walker and Syers, 1976) apatite had disappeared from the upper 60 cm of the soil profile in 22,000 years (Figure 3.2.3). Notably, apatite weathering is more complete in the top soil because there is more H^+ generation, more organic acids and chelates and a greater sink for Ca^{2+} (e.g. increased CEC and plant uptake).

$$Ca_{10}\ (PO_4)_6F_2 + 12H^+ = 6H_2PO_4^- + 10Ca^{2+} + 2F^-$$

Fluorapatite and hydroxyapatites are unreactive and dissolve too slowly (geological time) in most soils (pH 5-6) to provide sufficient plant available P for rapid plant growth. Francolites, however, can dissolve in mildly acidic soils (pH < 5.5) to provide sufficient P for plant growth (e.g. RPR use on legume based pastures).

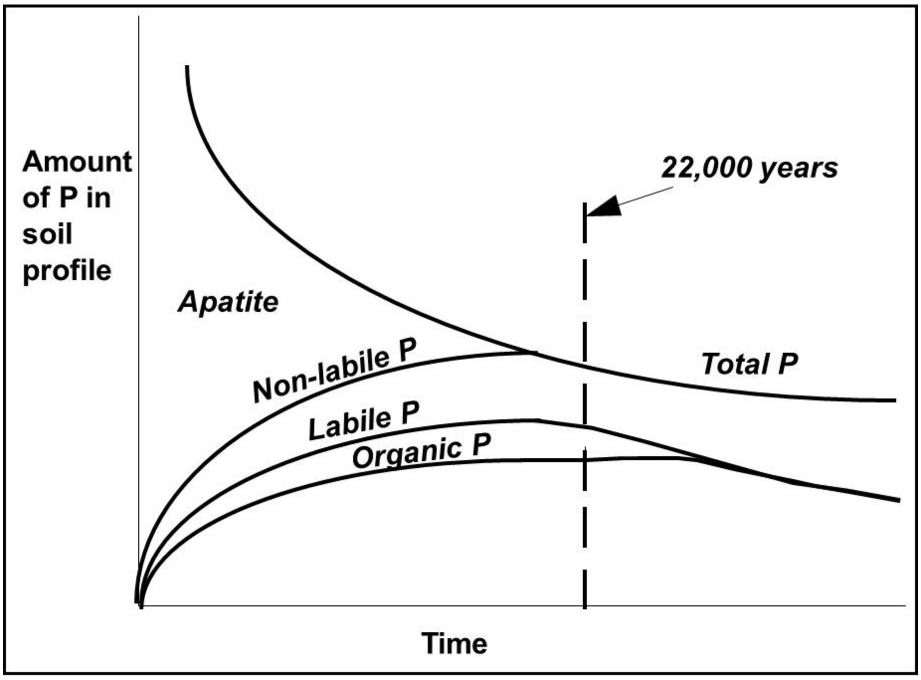

Figure 3.2.3 Transformation and loss of P during the weathering sequence of soils showing that the amount of apatite in soils decreases over time with soil weathering and the amount of organic P increases as plants and soil biology start to inhabit the newly formed soil and then stabilises. The amount of P adsorbed on to hydrous oxides of Fe and Al (labile) increases to a point and then decreases as plant demand for P increases and the amount of P absorbed in to the hydrous oxides of Fe and Al or precipitated (non-labile) increases over time.

Secondary Phosphate Mineral Forms (Mildly Acidic Soils, Sorbed and Precipitated or non-labile P)

Over geological times, as apatite minerals dissolve slowly in the natural acids produced by soil bacteria, fungi and plant roots, other soil ferromagnesium minerals and micas weather to form reactive iron and aluminium oxides on their surfaces. Phosphate released to soil solution from apatites will react strongly with these oxides to form secondary phosphate minerals.

It is generally accepted that surface adsorption of solution P (Figure 3.2.4) occurs before less exchangeable forms of phosphate minerals are formed, whether by absorption of P by an amorphous retaining component (e.g. Al or Fe oxides), or by precipitation of phosphate minerals (Al, Fe) $PO_4.H_2O$. Surface adsorbed P may be desorbed back into solution if the solution P concentration drops. This P has been termed labile. Phosphate absorbed into hydrous oxides or precipitated cannot be released into soil solution unless a chemical reaction occurs. This is non-labile P (Figure 3.2.5). Amorphous, hydrous oxides of Fe and Al are considered to be mainly responsible for P sorption (adsorption + absorption) in most soils and lake sediments. The sorption reaction involves Ligand exchange

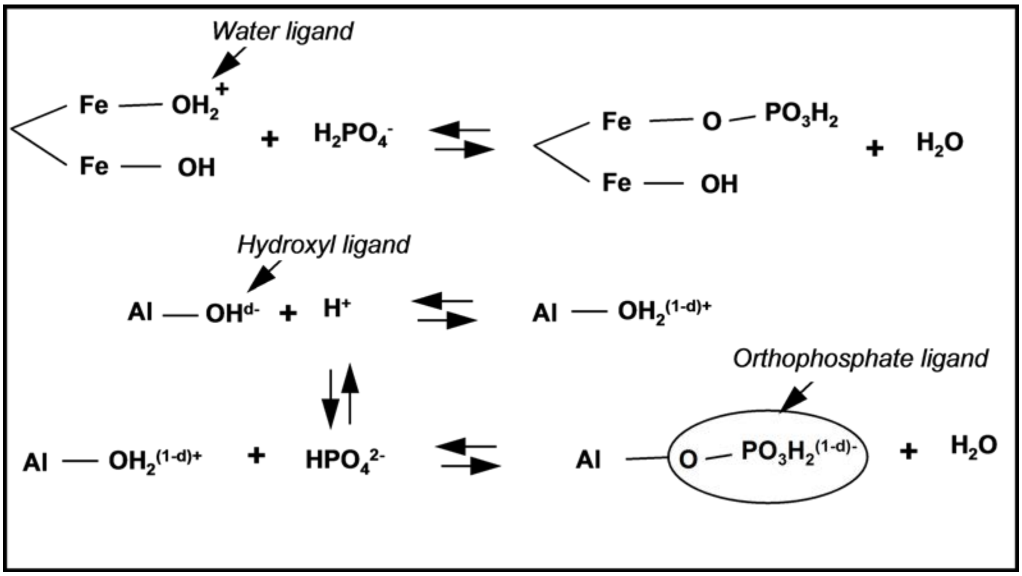

Figure 3.2.4 Ligand exchange reactions involved in P adsorption and fixation.

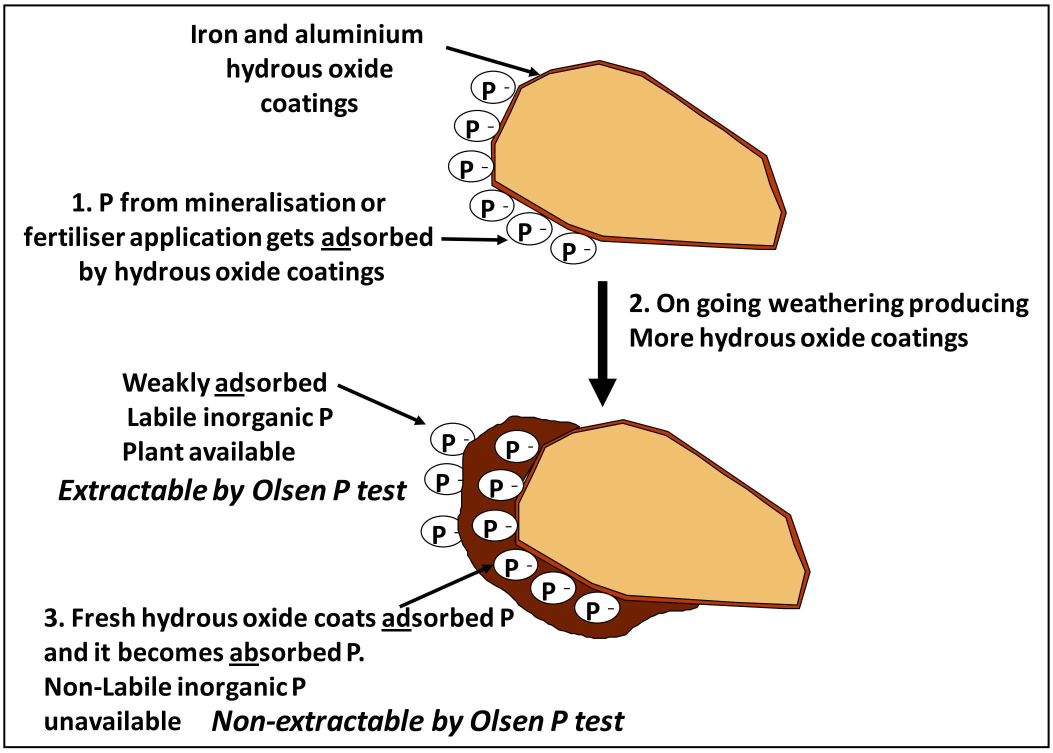

Figure 3.2.5 Adsorption of phosphate by soil mineral particles and the concept (1-3) *of P absorption (fixation) by hydrous oxides of iron and aluminium on soil mineral surfaces.*

The ligands form part of the coordination shell of the surface metal ions. Virtually all anions of interest to plant growth react in this way except Cl^- and NO_3^-. These ligands are attached directly to the soil surface and are not part of the diffuse layer of anions attracted to a positively charged surface (non-specific adsorption) - they are much more strongly held (specific adsorption). Silicate H_4SiO_4 /$H_3SiO_4^-$, borate H_3BO_3/$H_4BO_4^-$ and molybdate

$H_2MoO_4/HMoO_4^-$ can all be involved in ligand exchange. Phosphate can be particularly strongly held by forming bidentate complexes with -Fe(OH) surfaces - when two Fe's have the correct spacing (Figure 3.2.6).

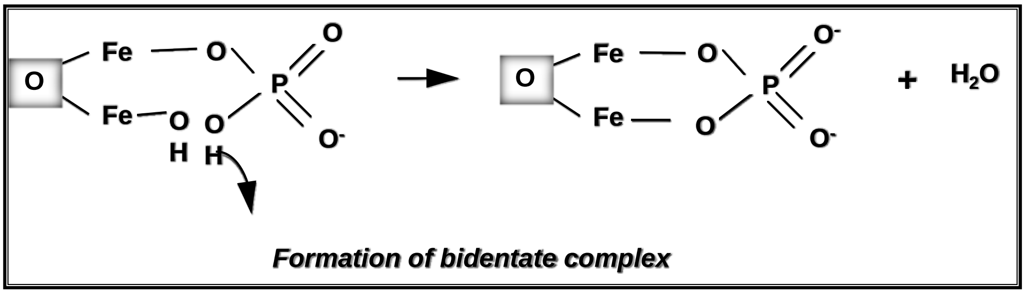

Figure 3.2.6 Formation of bidentate complex

Phosphate Sorption-Desorption (Phosphate Buffering)

Phosphate sorption and desorption control the soil solution P concentration in most agricultural soils. This is an important factor in determining how much P fertiliser will be available to the plant and how much P fertiliser is required to raise soil test levels to target values. A P retention soil test (also termed the Anion Retention Capacity) can be performed to provide advice on the relative ability of soils to adsorb P.

The equilibrium condition between the amount of P adsorbed on a soils surface and the P in the soil solution determines the ability of a soil to immediately replenish solution P which has been taken up by plant roots. For example consider Figure 3.2.7.

SOIL 1 (ALLOPHANIC SOIL, YELLOW-BROWN LOAM; HIGH P RETENTION):

(a) Requires high amounts of soluble fertiliser P addition to raise the amount of P sorbed on the soil surface to overcome the limiting value of the solution P concentration.
(b) Once fertilised, however, this soil may release more P to plants per unit decrease in solution P concentration.

SOIL 2 (BROWN SOIL, YELLOW-BROWN EARTH; MEDIUM P RETENTION)

(a) Requires lower P addition than Soil 1 to increase solution P concentration,
(b) However, P buffering capacity of soil is medium, therefore, removal of P by plants can quickly deplete the soil solution concentrations.

SOIL 3 (PALLIC SOIL, YELLOW-GREY EARTH; LOW P RETENTION)

(a) Requires much lower P addition than Soil 1 or 2 to increase solution P concentration,
(b) However, P buffering capacity of soil is low, therefore, removal of P by plants can quickly deplete the soil solution concentrations.

Volcanic loams (Allophanic soils), which tend to have high anion adsorption capacities, also tend to accumulate large amounts of organic matter and organic P. One hypothesis for this is that adsorption of organic ligands to the soil surface prevents their decomposition by microbial enzymes.

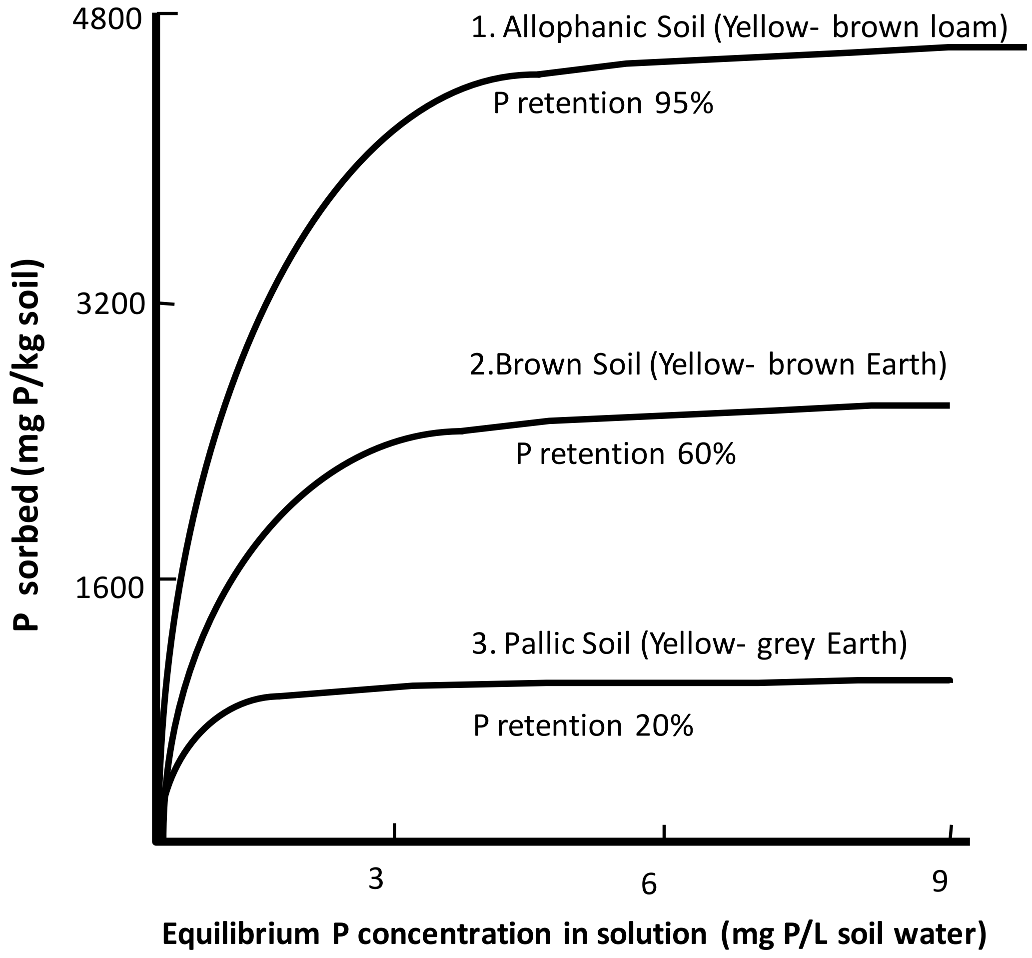

Figure 3.2.7 Phosphate sorption characteristics of 3 New Zealand soil orders (soil groups in brackets)

Under laboratory conditions, less P can be desorbed from a soil than is sorbed upon P addition. Reasons for this are that slow adsorption and precipitation reactions continue, preventing a proportion of the added P from being released to soil solution. In field soils, growth of roots and micro-organisms convert inorganic (Pi) to organic P (Po) which also immobilises plant available P.

Nature and Amounts of Organic P in Soils

All Po in soils is derived from either nucleic acids, phospholipid, sugar phosphoproteins, inositol polyphosphates (seed P) and other phosphoesters present in plant material, animal excreta and soil macro and micro-organisms. These simple compounds are easily decayed (mineralised) and in most cases the P becomes associated with high molecular weight humic and fulvic acids that are the products of organic matter decomposition. These large complexes are essentially insoluble in water. Such complexes are believed to retain Pi and Po by sorption and ion exchange reactions. Up to 50% of soil organic P can be attributed to such complexes.

Under what Conditions do Reserves of Soil Organic P Change?

The amounts of Po in soils vary enormously from soil to soil. The amount of Po in a soil results directly from the difference in organic P addition and organic P decomposition. Processes that lead to increases in soil organic matter also lead to increases in soil Po (immobilisation) (i.e. high plant growth rate and slow litter or dung decay; high anion retention may slow organic matter decay). Phosphate fertiliser is converted to Po in productive environments (e.g. grassland, where Po input as roots, shoots and animal excreta decay is high).

In New Zealand pasture soils, Po may make up 50-80% of the total P in the top 7.5 cm. Commonly, the ratio of organic N to Po is between 10:1 and 5:1. Experiments with plant litter have indicated that when the C:Po ratio exceeds 300:1, Pi from soil solution is also immobilised during decomposition. At ratios of 200:1 in litter, Po is likely to be mineralised to Pi. These criteria are only approximate rules and only broadly apply to field soil Po decomposition. The nature of the micro-site (i.e. moisture, aeration, microbial access to substrates) may be a more important factor controlling decay.

To release Pi back into soil solution, micro-organisms need to solubilise the water-insoluble organic complexes. This is achieved through the release of extracellular hydrolytic enzymes. Phytase and various phosphatases are common extracellular enzymes and can act directly to release orthophosphate from organic phosphates. In other cases more powerful enzymes are required to break the carbon back bone of such compounds.

Losses of P from the Cycle

P is mostly lost in organic products removed from the farming enterprise. Because P is strongly adsorbed by soils, little P leaching occurs. However, surface runoff and erosion of topsoil by wind and water removes organic and inorganic P dissolved in the runoff water and on fine soil particles (particulate P). Eroded soil represents the major transfer mechanism of P from terrestrial to aquatic systems in New Zealand (see Section 5.1), but the proportions of dissolved and particulate P may vary depending on landscape, soils, their management and climate.

Poor land management can accelerate this transfer. Disposal of P in sewage and manure effluents into waters cause the terrestrial P cycle to be uncoupled. The P entering streams increases aquatic plant, algal and bacterial growth, which causes pollution.

Effect of Liming on Soil P Availability

A number of common farming practices help in unlocking the reserve soil P pool and, thereby, enhance the uptake of P by plants. Liming is one of the important agricultural practices that have often been shown to influence the mobilisation of P in soils. Liming has been shown to reduce the amount of P fertiliser required to achieve a given yield. The reduction of P requirement results directly from an increased solubilisation of soil P and its subsequent uptake and/or indirectly from an increase in P uptake due to reduced Al and Mn toxicity. Liming has also been found to increase, decrease or have no effect (Haynes,1984) on the amount of P available for plant uptake, with P decreases likely to be due to the calcium in lime reacting with P to form calcium phosphates. The effects of liming on soil nutrient availability are discussed in more detail in Section 3.6.

Plant Availability of P

As a plant root takes up orthophosphate ions, the already low solution P concentration drops (Figure3.2.8). Replacement P must move to replenish the concentration at the root surface or the root must grow into soil with a higher P concentration. Movement of P can take place either by the soil solution moving (mass flow) during periods of net water uptake by the plant roots (as transpiration occurs during daylight hours), or, by P ions diffusing (diffusion) from a high concentration near the soil surface to the low concentration at the root surface.

We can show by calculation that the flow of water from soil to plant is not the main P supply process:

- If a crop uses 3 mm of soil water per day, this is equivalent to:
  (0.003 m x 10,000 m^2) 30 m^3 water per hectare.
- At a soil solution P concentration of 0.2 mg P/L (0.2 mg P/L ≡ 0.2 g P/m^3) this means that:
  6 g of P can be taken up per day in the transpiration flow (***Mass Flow***).
- A mature crop (95 days) of maize would require approximately 100 kg P/ha.
- Mass Flow will only supply 0.6 kg.
- As the maize root only intercepts <2% of the soil volume in the top 150 mm of the soil, ***interception*** can only provide <2% of the P in the soil solution per hectare.
- At a water content of 30% of the soil volume ($\theta = 0.3$), the total soil solution P per hectare to a rooting depth of 150 mm is a volume of:
  45 mm (or 450 m^3) and contains 90 g P. Two percent of this (<2 g) can, therefore, be intercepted by roots.

Together mass flow and interception will supply < 0.601 kg P in 95 days. By default the rest of the plants P requirements (99 kg P/ha) must move by diffusion. A P ion diffusing slowly along the thin water film connecting soil particles and roots will be continually adsorbed and desorbed from the adsorption sites on the soil surface. Measurement of the P concentration in plant tissue can indicate if P supply is adequate for maximising plant production (Table 3.2.1).

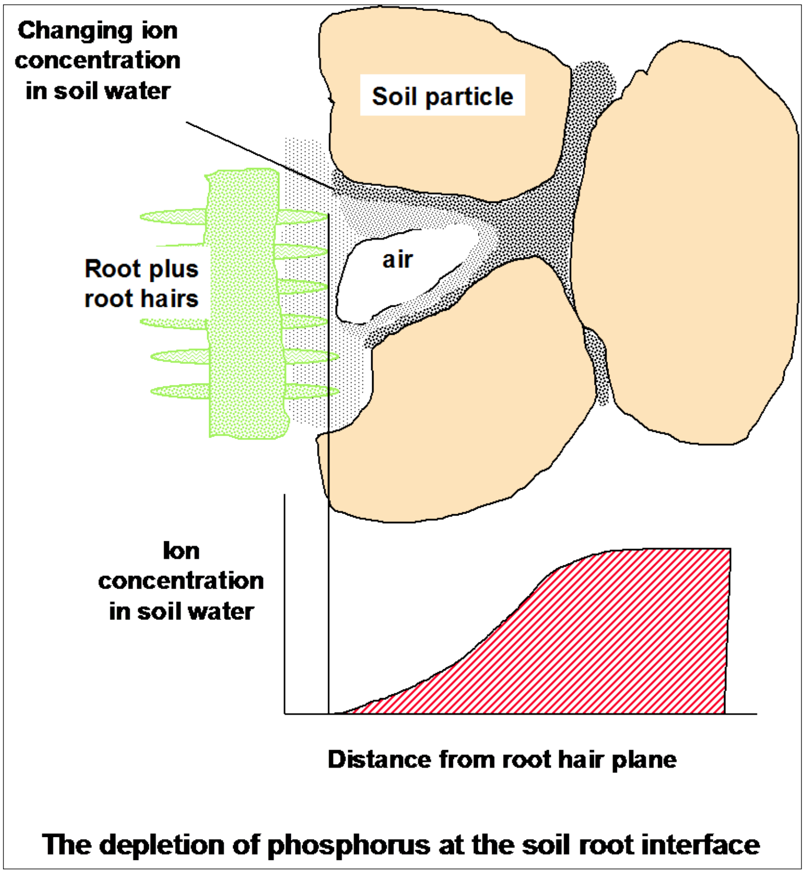

Figure 3.2.8 P diffusion to roots

Thus the travel time for P to reach roots in high sorbing (relatively less P ions in solution - more adsorbed on soil colloids) Yellow-brown loams (YBL) will be longer than in low P sorbing soil, Yellow-grey earths (YGE) (relatively more P ions in soil solution - less adsorbed on soil colloids). Thus more fertiliser P must be supplied to the YBL than the YGE to increase the soil solution P concentration and allow P to move faster to the plant root

Table 3.2.1 Guidelines for interpreting mixed pasture P (% of DM) herbage analyses.

Deficient	Low	High	Optimum
<0.30	0.30-0.34	>0.40	0.35-0.40

Source: New Zealand Fertiliser Manufacturers' Research Association (2009)

Measuring the Ability of Soils to Supply Phosphate to Plants

Phosphate available to plants in the short-term is either in soil solution or weakly adsorbed on the surface of soil particles (see Figure 3.2.8). Chemical extraction procedures have been developed which sample these two forms of soil phosphate. These procedures are discussed in more detail in Section 4.

The chemical principle of the soil test is to supply a sufficiently high concentration of anion that some of the non-specifically and specifically adsorbed (ligand exchange) P is desorbed into the extracting solution. The concentration of P in the extracting solution is then measured. The common test in New Zealand is the Olsen P extraction that uses 0.5 M $NaHCO_3$ at pH 8.5 as the extractant.

P in Fertilisers, Soil Amendments and By-Products

Fertilisers and other soil amendments that contain P are applied to soils to increase the pool of plant available P and overcome the P availability constraints to plant productivity. To be effective, these sources of P must cause an increase in the soil solution P concentration bathing plant roots. Traditionally single superphosphate is the most common fertiliser used in New Zealand.

COMMON P FERTILISERS

Phosphate fertilisers are broadly grouped into water-soluble (fast release), partly water-soluble (medium release) and water-insoluble (slow release) fertilisers. Water-soluble fertilisers are immediately available for plant uptake, whereas water-insoluble fertilisers are available over a long period. The release of P over a longer period is judged from the fertiliser's solubility in a solution of 2% citric acid (See Section 3.7). The important water-soluble P fertilisers include: single superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP) (Table 3.2.2). The important water-insoluble P fertilisers include: reactive phosphate rocks (RPR) and (historically) basic slag. Other fertilisers that contain both water-soluble and water-insoluble P components and have been manufactured from time to time include; partially acidulated phosphate rocks (PAPR) and superphosphate and reactive rock mixtures (e.g. Longlife super), and microbial phosphate (BioSuper).

Monocalcium phosphate (MCP) is the principal soluble P component present in SSP and TSP. Ammonium phosphate is the principal soluble P component in MAP and DAP fertilisers. In addition to P, SSP supplies sulphur (S), as gypsum, and MAP and DAP fertilisers supply nitrogen (N). Lime-reverted superphosphate contains most of its P as dicalcium phosphate [$CaHPO_4$], which is sparingly soluble in water. It is normally used most effectively in mildly acidic soils (pH<5.8). Similarly, mildly acidic soils are also suitable for direct application of reactive phosphate rocks (RPRs). The RPRs that are suitable for direct application to soils are those in which the carbonate is highly substituted for phosphate in the apatite structure:

$$Ca_{10}(PO_4)_{6-x}\,(CO_3)_x\,(F_2OH)_{2+x}$$

In New Zealand, such rocks are identified as having more than 30% of their total P soluble in 2% citric acid. Phosphate fertilisers should be compared based on their P availability and the amount of other nutrients present.

Whereas water-soluble fertilisers are commonly used for capital (i.e. raising soil P status rapidly) and maintenance (maintaining soil P status) applications, partly water-soluble and water-insoluble fertilisers can be appropriate for maintenance application in soil that promote their dissolution. In cost comparisons of fertiliser required to supply P, calculations are based on estimates of the amounts of P that will be released to plants in one year. For fertilisers supplying soluble P this amount is estimated from the percentage of their total P soluble in 2% citric acid.

For RPRs the amount dissolving in one year is estimated using a description of its particle size and performance in a laboratory dissolution test (Watkinson, 1995). Fertilisers with high total nutrient content are cheaper by weight to transport and apply than low nutrient fertiliser. Fertiliser costs should be considered in terms of cost per unit nutrient applied (which includes raw materials, transport and spreading) and not in $/tonne of product applied.

Table 3.2.2 Common phosphate fertilisers currently being used in New Zealand.

Product Name	**Fertiliser component**	**P components**		**Other nutrients and important incidental components**			
(N-P-K-S)		***Soluble***	***Sparingly soluble***				
Superphosphate (SSP) (0-9-0-11.5)	SSP	MCP*		Gypsum*		F*	Cd*
Triple superphosphate (TSP) (0-20.5-0-1)	TSP	MCP			Ca	F	Cd
Triple superphosphate sulphur super (0-12.6-0-6.3)	TSP, SSP, Elemental S	MCP		Gypsum, Elemental S		F	Cd
Diammonium phosphate (DAP) (18-20.1-0-0)	DAP	$(NH_4)_2HPO_4$		NH_4-N		F	Cd
Cropmaster 15 (15.2-10-10-7.7)	DAP, ammonium sulphate, potassium chloride	$(NH_4)_2HPO_4$		NH_4-N	Soluble S, K and Cl	F	Cd
Reverted superphosphate	SSP, lime	MCP	DCP*	Gypsum		F	Cd
Serpentine superphosphate (0-6.7-0-8.5, 5% Mg)	SSP, serpentine	MCP	DCP	Gypsum	Magnesium sulphate*	F	Cd
Pasturezeal (3-9.6-0-10)	SSP, urea	MCP		Gypsum	urea	F	Cd
Reactive phosphate rock (RPR) (e.g. Ben Guerir phosphate rock) (0-13-0-0)	RPR		apatite	Carbonate	Ca	F	Cd
Reactive phosphate rock S	RPR, Elemental S		apatite	Elemental S, Carbonate	Ca	F	Cd
RPR,SSP, elemental S (0-10.6-0-3.9)	RPR, SSP, Elemental S	MCP	apatite	Elemental S, Gypsum	Ca	F	Cd

*MCP = Monocalcium phosphate $Ca(H_2PO_4)_2$, DCP = Dicalcium phosphate $CaHPO_4$, Gypsum $CaSO_4$, Magnesium sulphate $MgSO_4$, F = Fluoride Cd = Cadmiu

REACTIONS OF PHOSPHATE FERTILISER COMPOUNDS IN SOILS

Phosphate compounds that are used as fertiliser are broadly grouped into water-soluble (fast-release) and water-insoluble (slow-release) fertilisers. The important water-soluble P fertilisers include: single superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). The important water-insoluble P fertilisers include: PRs and basic slag. Partially acidulated phosphate rocks (PAPR) and superphosphate/reactive rock mixtures (e.g., Longlife super in New Zealand) contain both water-soluble and water-insoluble P components. Monocalcium phosphate (MCP) and ammonium phosphate (AMP) are the principal P components present in superphosphates (SSP and TSP) and ammonium phosphates (MAP and DAP), respectively. It is important to understand the reactions of these P compounds in soils in order to predict the effect of these on the (im)mobilisation of P.

Water-Soluble Compounds

When superphosphate fertilisers are added to soils, the dissolution of MCP results in the formation of slowly soluble dicalcium phosphate (DCP) with a release of phosphoric acid close to the fertiliser granules (Equation 1). Phosphoric acid subsequently dissociates into $H_2PO_4^-$ and hydrogen ions (protons – H^+). The protons reduce the pH around the fertiliser granules to a very low level (< 2 pH). When ammonium phosphate fertilisers are added to soil, they dissociate into ammonium (NH_4^+) and $H_2PO_4^-$ ions. The subsequent oxidation of NH_4^+ to NO_3^- results in the release of protons (Equation 2).

$$Ca\,(H_2PO_4)_2 + H_2O \rightarrow CaHPO_4^{\cdot}\,H_2O + H_3PO_4 \qquad \text{(Equation 1)}$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad \text{(Equation 2)}$$

The acidic solution around the fertiliser granules dissolves the Fe and Al compounds in the soil, resulting in the adsorption and precipitation of P. The pH around the ammonium phosphate fertiliser granules, however, is unlikely to be as low as that around superphosphate fertilisers, causing less adsorption of $H_2PO_4^-$ ions. The concentration of plant available P in soil solution decreases with time of contact of fertiliser granules in soils, the decrease depending on the amount of Fe and Al compounds in the soil. The retention of P by soils decreases the amount of P available for both plant uptake and leaching to groundwater. The acidity generated can also have important implications to the mobilisation of metals.

Water-Insoluble Compounds

When insoluble P fertilisers, such as RPRs are added to soil they need to be dissolved in soils for the P to become plant available. In soils, RPRs dissolve by using the acid produced in the soils (Equation 3). This is a major reason why RPRs can be effective as a nutrient source in acid soils (pH < 5.8). The rate of dissolution also depends on the chemical nature and the particle size of the PR. Dissolution rate increases with decreasing particle size. Sechura RPR (from Peru), and Gafsa RPR (from North Africa) are considered to be highly reactive. Once the RPR is dissolved, the P released undergoes similar adsorption and precipitation reactions as in the case of soluble P fertilisers.

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^- \qquad \text{(Equation 3)}$$

Fertiliser brands, such as the 'Microbial Phosphate' in New Zealand and 'Coastal super' in Australia contain a small amount of water-soluble P, RPR and elemental sulfur (S^o). Microbial oxidation of S^o in these fertilisers releases sulfuric acid. This results in the solubilization of PRs (known as 'biosuper' effect) and the mobilization of metals.

ACIDIFICATION EFFECTS OF PHOSPHATE FERTILISERS IN SOILS

In legume based pastures, phosphate fertilisers produce acids by two processes, namely:

- fertiliser reaction and
- nitrogen fixation.

When SSP and TSP fertiliser granules dissolve in soil solution they release phosphoric acid which dissociates into phosphate ions and acidic hydrogen ions. In legume based pastures, phosphate fertilisers are added mainly to promote biological N fixation by the legumes by overcoming a soil deficiency of P. Irrespective of the P fertiliser sources, application of P to legume based pastures promotes N fixation and thereby indirectly causes soil acidification. Acceleration of N cycling caused by raising the P fertility status of the soil/legume/system generates considerably more acidity than the acidity produced directly by the dissolution of superphosphate fertiliser granules.

Part of the acid (H^+) produced during the solubilisation of superphosphates is neutralised by the release of OH^- during the adsorption of $H_2PO_4^-$ ions onto soil colloids (Equations 4 & 5).

$$\text{Fe-OH} + H_2PO_4^- \rightarrow \text{Fe-}H_2PO_4 + OH^- \qquad \text{(Equation 4)}$$

$$OH^- + H^+ \rightarrow H_2O \qquad \text{(Equation 5)}$$

Thus the change in the pH of the bulk soil with the addition of superphosphate fertilisers is comparatively less than that caused by the addition of ammonium fertilisers. The acidity produced by SSP dissolution can be calculated as follows:

40 kg P as SSP/ha produces = 0.64 kmol acid (H^+)

1 kmol (100 kg) of $CaCO_3$ neutralises = 2 kmol acid

40 kg P (or 0.64 kmol acid) requires = 32 kg lime

It is estimated that at an annual application rate of 40 kg P per hectare, approximately 32 kg lime ($CaCO_3$) is required to neutralise the acid produced by superphosphate fertilisers.

In the case of MAP and DAP fertilisers the oxidation of ammonium to nitrate results in the release of acidic hydrogen ions. The pH around the MAP and DAP fertiliser granules, however, is unlikely to be as low as that around SSP and TSP fertilisers causing less adsorption of P ions. Most of the acidity is produced by MAP and DAP generating nitrate ions (see Section 3.4). It is estimated that at an annual application rate of 40 kg P, approximately 104 and 148 kg lime is required to neutralise the acid produced by MAP and DAP fertilisers, respectively. The presence of N in ammonium phosphate fertilisers enhances the uptake of P.

LIMING VALUE OF ROCK PHOSPHATES

In addition to supplying P and Ca, RPR can also have a liming value. The liming action of RPR can occur through two processes. Firstly, most RPRs contain free calcium carbonate ($CaCO_3$) that can act as a liming agent in its own right. Secondly, the dissolution of RPR in soils consumes acids and thereby reduces the soil acidity.

It is estimated that a liming value equivalent to 3.2 kg $CaCO_3$ is derived per kg of P dissolved from the RPR. From the amounts of P and free $CaCO_3$ in the RPR it may be possible to calculate its total liming value. For example, the total liming value of a tonne of North Carolina phosphate rock (NCPR), which contains 13.1% P and 11.7% $CaCO_3$, is about 500 kg $CaCO_3$ (liming value from dissolution = 422 kg $CaCO_3$, availability dependent on dissolution rate; liming value from free $CaCO_3$ = 70 kg, immediately available).

Since the free $CaCO_3$ in the RPR dissolves reasonably fast it can give an immediate liming value. Whereas the phosphate component in RPR dissolves at a variable but generally slow rate in soils and hence the liming value from the dissolution of RPR occurs over a long period of time. Unless the RPR dissolves in soils, there is no benefit of adding RPR either as a P source or as a liming material.

PHOSPHATE FERTILISERS CONTAMINANTS

The two main unwanted elements present in P fertilisers are cadmium and fluoride. The issues relating to fertiliser contaminants are discussed in more detail in Section 6.

SUPERPHOSPHATE POISONING OF ANIMALS

Superphosphate poisoning of cattle sometimes occurs when they are allowed to graze a recently top-dressed paddock. When SSP, TSP and RPR fertilisers are applied after a light rain, the dust particles tend to stick onto the leaf blades and a subsequent spell of fine weather results in the dry deposition of fertiliser particles on the leaves. Allowing cattle to graze the paddocks at this stage is likely to result in the intake of large amounts of fertiliser causing superphosphate poisoning.

Fluoride in phosphate fertilisers is considered to be the main toxic component and phosphate plays only a secondary role in superphosphate poisoning. Although RPR is less soluble than SSP and TSP fertilisers, when ingested by the animals, the RPRs dissolve readily in the acidic conditions of the animals' digestive system releasing both phosphate and fluoride.

In most cases, superphosphate poisoning has been reported when the animal is allowed to graze soon after fertiliser application. The ingestion of fertiliser is exacerbated when the pasture is short and the stocking rate is high.

Treatment of superphosphate poisoning of dairy cattle requires an immediate removal of the herd from the recently fertilised pasture. If this is not possible, offer the cattle plenty of supplementary feed so that the amount of fertiliser they are ingesting is diluted. Drenching the affected animal with calcium chloride is recommended in severe cases. Proper veterinary advice is required for the rate and frequency of drenching.

Superphosphate poisoning can be prevented by withholding stock from recently top-dressed pastures until at least 25 mm of rain has fallen. This requires staggered fertiliser application so that some unfertilised paddocks are always available for grazing. Alternatively, fertiliser can be spread on one half of the paddocks that have been most recently grazed and the other half can be top-dressed after a minimum period of 2 weeks or 25 mm rainfall has occurred.

SOIL AMENDMENTS AND BY-PRODUCTS AS P SOURCES

Slags and P supply

Three sources of slag products have been used in New Zealand. The conventional basic slag imported from Europe (Belgian slag), the fluidised bed boiler (Foremost Green) and the Glenbrook steel ash (Kobmax). While the first one is used primarily as a source of phosphate, the last two are used as liming materials. The European basic slag used to rank next to superphosphate as the world's leading phosphate fertiliser. Most of the slags are rich in Ca and Mg and can be used to overcome Ca and Mg deficiencies in soils. The fertiliser and the soil conditioning values of the slags depend on the fineness of the materials.

Ingestion of alkaline slag materials by animals upsets the pH of the rumen resulting in 'alkalosis'. Presence of other toxic elements, such as fluorine may also lead to animal toxicity (fluorosis). Where slag poisoning is suspected, treatment should be directed at acidifying the rumen with chloride and sulphate salts of magnesium and ammonium and dilute acetic acid to reinstate fermentation and help restore the cation-anion balance in circulation.

To avoid slag poisoning of animals the material should be ground to fine size (< 2mm) and the slag needs to be incorporated into soil. In most cases slag poisoning has been reported when the animals are allowed to graze soon after slag application. Slag poisoning can be prevented by withholding stock from recently topdressed pastures until at least 25 mm rain has fallen. Intensive grazing results in the ingestion of soils contaminated with the undissolved slag materials. It is important to avoid overgrazing paddocks treated with slags.

MANURE AS A P SOURCE

The application of animal manures either imported on to a farm or recycled from effluents and slurries collected at dairy sheds, animal barns etc. can represent a valuable source of P fertiliser. Manure contains both Pi and Po forms of P, with the Pi mostly in the form of dicalcium phosphate which is readily plant available. Pi is influenced by the total amount of P ingested by the animal and the concentration of P in herbage tends to increase with the amount of P fertiliser being applied, whereas Po concentrations in manure are generally more stable. The Po component in manure requires mineralisation to Pi before it can be taken up by plants.

BROUGHT IN FEED AS A P SOURCE

Feed brought in to farms to supplement animal's diets represents a valuable source of P added to soil. The amount of P present in brought in feed varies depending on the feed type (Table 3.2.3), but can equate to large inputs of P. For example, a farm importing 180 tonnes (dry weight) of palm kernel meal would be importing 1.2 t of P to the farm, with approximately 70% of this ingested P likely to be excreted by the animal and potentially returned to the soil. Across a 100 ha property, this equates to potential P inputs of 8 kg P/ha.

Table 3.2.3 P contents of common animal feeds.

Supplement	P % (dry weight basis)
Maize silage	0.23
Pasture silage	0.30
Pasture hay	0.40
Palm Kernel Meal	0.65
Molasses	0.09
Maize grain	0.31
Barley grain	0.44

Data from DairyNZ Farmfact (2008) and Kolver (2000).

References

DairyNZ FarmFact (2008). 1-71 Palm Kernel Extract (PKE) http://www.dairynz.co.nz/file/fileid/36249

Haynes, RJ (1984). Lime and phosphate in the soil-plant system. Advances in Agronomy, 37, 249-315.

Kolver, ES (2000). Nutritional guidelines for the high producing dairy cow. Proceedings of the Ruakura Farmers' Conference 51, 78-87, 2000.

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Walker, TW and Syers, JK (1976). The fate of phosphorus during pedogenesis. Geoderma, 15, 1–19.

Watkinson, JH (1995) Modelling RPR dissolution in soil. In: Fertilizer requirements of grazed pasture and field crops: Macro- and micro-nutrients. (Eds L D Currie and P Loganathan). Occasional report No. 8. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand.

Revision on Phosphorus

The purpose of the following section is to check your understanding of the P cycle and of the P sources and their reactions in soil.

Sources:

- Soil mineral weathering (apatite)
- Secondary soil minerals (P adsorbed on the surface of hydrous oxides of Fe and Al)
- Soil organic matter
- Fertiliser (superphosphate, reactive phosphate rocks, manure, feed etc)

Plant available form:

$H_2PO_4^-$, HPO_4^{2-} (orthophosphate ion)

Role in plant:

Transfer of chemical energy, synthesis of DNA, RNA and membrane components (e.g. phospholipids).

Deficiency threshold concentrations:

- Ryegrass <0.3% P
- Clover <0.3% P

Table 3.2.4 Nutrient distribution in soil-plant systems

Position or form	Plant Availability or form	Approx. amount* (kg P/ ha, 15 cm depth)
Soil organic matter	Unavailable in the short term (non-labile)	45 - 1560 (YBE Podzol – YBL)[1]
Inorganic minerals (primary and secondary)	Unavailable in the short term (non-labile)	150 - 1920 (YBE Podzol – YBL)[1]
Surface adsorbed inorganic	Sparingly available (labile)	15 - 150
Soil water/solution	Available	0.15
Pasture plants (standing crop, 2000 kg DM)	Inorganic plus organic forms. Organic P requires mineralisation before plant uptake	6

[1] YBE Podzol =Yellow-brown earth, podzolized, Northland

[1] YBL =Yellow-brown loam, Taranaki

*Approximate P content in the top 15 cm of a one ha slice of topsoil

Table 3.2.5 Phosphorus cycle (consult Figure 3.2.2)

Important Transformations	Implications
Adsorption of added fertiliser P by Fe and Al oxides and alumino-silicates	Decreases plant availability of applied P and increases fertiliser requirements. Soil solution P concentrations are low. Most P moves from soil to root by diffusion Provides a large reserve of P in the soil which buffers short-term P removal
Immobilisation of inorganic P into organic P	Slowly reduced P availability until rate of mineralisation equals rate of immobilisation after approximately 20 years of pasture development
Mineralisation of organic P into inorganic P	Mineralisation/immobilisation provides a large reserve of P which buffers short-term P removal
Partitioning of 100% of excreted P into dung by the grazing animal	Nutrient transfer loss mechanism enhances organic P formation

Table 3.2.6 Assessment of Soil P Status:

Form of P	Test	P extracted
Index of plant available P	Olsen P ($NaHCO_3$ pH 8.5)	Weakly adsorbed organic and inorganic P. Inorganic and organic P released from micro-organisms and fine roots damaged upon air drying soil.

Test Your Knowledge

1. Draw a P cycle for a ryegrass/clover pasture.

2. Explain why the acidity produced directly by the dissolution of superphosphate fertiliser is relatively less when compared to the acidity produced indirectly through increased nitrogen fixation in a legume-based pasture.

3. Explain why Allophanic soils require more P fertiliser to increase their Olsen P concentration, compared to Pallic soils?

4. Read also Section 3.7. Then list 4 common P fertilisers used in New Zealand and quote their grades and solubilites in water and 2% citric acid.

Recommended Reading

Fundamentals of Soil Science, 7th Edition. H.D. Foth. pp 196, 305-310. Introductory, basic principles covered.

Fertilisers and Soils in New Zealand Farming. C. During. pp 29-46. Information from New Zealand pastoral experiences.

Soil Science. R. M^{c}Laren and K. Cameron. Oxford University Press. (Read sections 15.1 - 15.4.1, p208-213).

3.3 Potassium in Soils

Key Learning Objectives

After studying this section you should be able to describe:

1. The amounts and forms of potassium (K) present in the soil/plant/animal system.
2. The form of K that is available to plants.
3. The source, process and rate of replenishment for the plant available form of K.
4. Processes that lead to K gains to plant/animal systems or losses from soils.
5. The forms and solubilities of K in the common K fertilisers used in New Zealand.
6. The reactions and fate of different K fertilisers added to soil with respect to:
   - K availability to plants

Introduction

Potassium (K) is a common element in the earth's crust (seventh most abundant element). Refer to Table 3.3.1 for the common potassium-bearing minerals and consult Table 3.3.7 for the relative abundance of K in some New Zealand soils.

Potassium is always found in nature as the K^+ ion - unlike phosphorus, nitrogen and sulphur it does not form covalently bonded organic compounds with C, H and O. Therefore, it is not involved in the structural components of organisms. Virtually all common salts of potassium are soluble. K will form soluble salts with many organic acids (e.g. KCH_3COO, potassium acetate). Thus, the main role played by K in organisms is that of a charge balancing cation that can be used to maintain the electrical neutrality of solutions transporting anionic (negatively charged) organic intermediates around the organism (i.e. photosynthates from shoots to roots) and nutrient anions, NO_3^- and SO_4^{2-} up the xylem vessels.

Table 3.3.1 Common potassium-bearing minerals in New Zealand

Cation	Soils with adequate supplies	Major mineral source
K^+	YGE YBP YBE Recent	Feldspars, micas - weathering to illite, vermiculite, chlorite
Ca^{++}	Rendzina Calcareous Alluvial soils	Calcite, dolomite, apatite Calcium - alumino silicates Feldspars, amphiboles
Mg^{++}	Rich supply in soils formed on mudstone YGE Recent	Biotite, serpentine, hornblende and olivine. Dolomite Moderate supplies from soils containing illite, vermiculite, chlorite

Mica	$KAl_2 (AlSiO_{10}) (OH)_2$
Feldspar	$KAlSiO_3O_8(Na, Ca)$
Biotite	$K (Mg, Fe)_3 (AlSi_3O_{10}) (OH)_3$

Potassium in Soils

Soils rich in feldspars and intermediate weathering products of micas (e.g. illite) are generally rich in K. More strongly weathered products such as vermiculite have lost most of their K in the weathering process. Soil K is characterised by its ease of extraction or plant uptake from soils (Read the following Sections in conjunction with Figure 3.3.1).

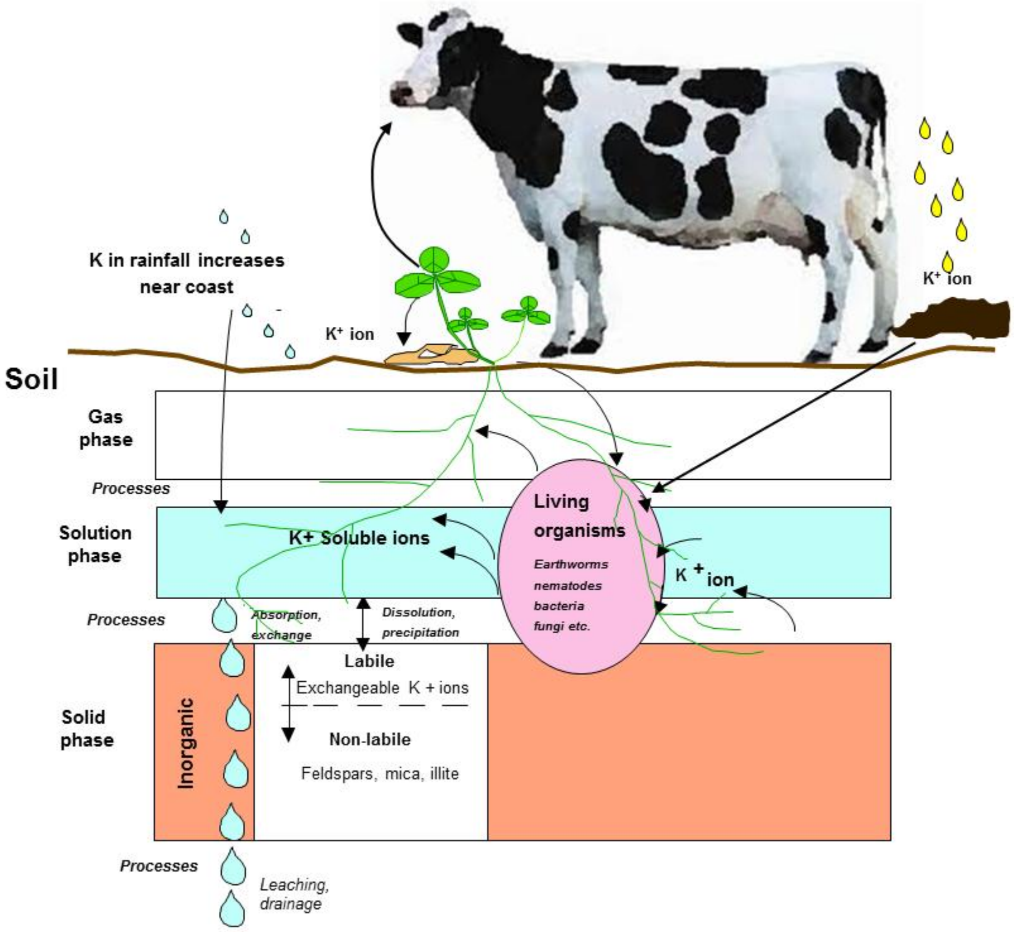


Figure 3.3.1 The Potassium Cycle (Note: K forms no 'organic' compounds)

SOIL SOLUTION POTASSIUM

Soil solution K is easily $^{\text{available}}$ for uptake by plant roots (0.1-0.2% of soil K). This is K^+ ions in the soil water (see Figure 3.3.1) which are in dynamic equilibrium with the following forms of K:

EXCHANGEABLE K

Exchangeable K constitutes 1-2% of soil K as ions held on negatively charged cation exchange sites on soil clay minerals and organic matter surfaces. Exchangeable K must exchange with solution cations before it can be taken up by plant roots (Figure 3.3.2).

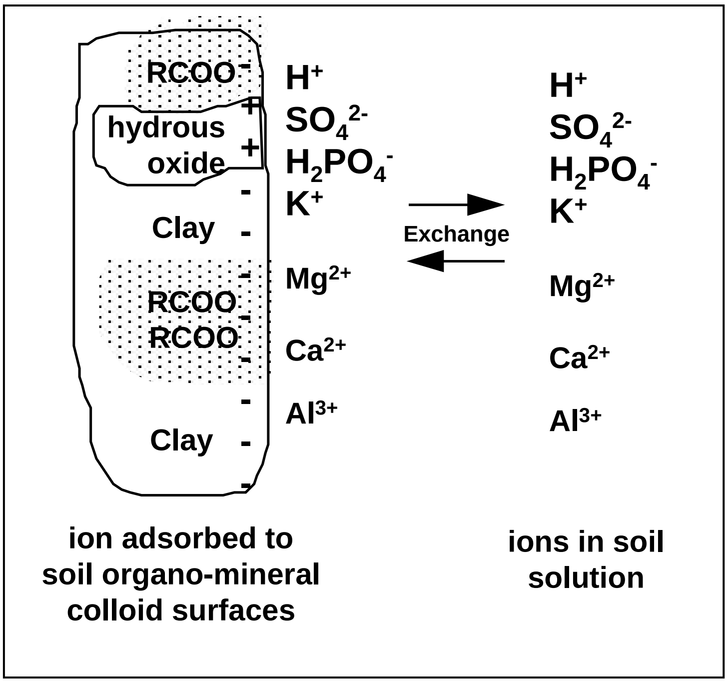


Figure 3.3.2 Exchangeable and solution cations and anions.

FIXED K

Fixed K (1-10% of soil K) is K^+ ions held in the interlayer spaces of the 2:1 layer clay minerals, which are mica weathering products (e.g. hydrous micas -illite – vermiculite; see Figure 3.3.3). The clay lattice must expand with larger hydrated cations (H^+, Ca^{2+}) occupying the interlayer space before fixed K can slowly exchange with solution and exchangeable K and become plant available.

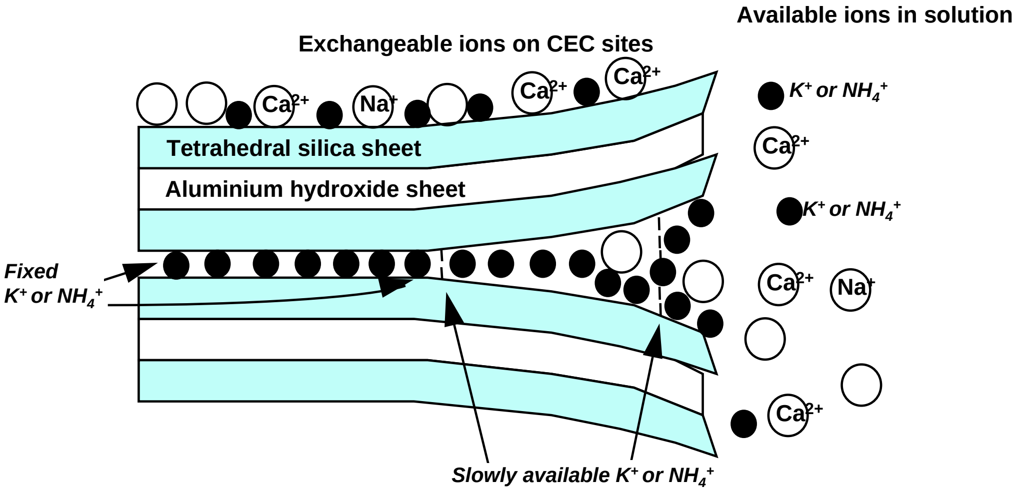


Figure 3.3.3 Potassium (and ammonium) fixation and exchange with 2:1 layer clay minerals (illite and vermiculite) weathered from mica (redrawn from McLaren and Cameron, 1990).

UNWEATHERED MINERAL K

This constitutes 90-98% of soil K still present in soil parent minerals such as feldspars and micas. The slow release of K from ongoing weathering of these minerals will replenish the supplies of exchangeable and solution K, provided that losses of K from the soil solution pool, by plant uptake and leaching, are not faster than the rate of weathering.

Plant Requirements

General K requirements of some high yielding crops are given in Table 3.3.2

Table 3.3.2 K requirements of high yielding crops.

Crop	kg K/ha/year
Grass	200 - 300
Potatoes (8-16 tonnes of tubers)	300 - 600
Cereals (5-10 tonnes grain)	70 - 140

Table 3.3.3 Guidelines for interpreting mixed pasture K (% of DM) herbage analyses.

Deficient	Low	High	Optimum
<2.0	2.0-2.4	>3.0	2.5-3.0

Source: New Zealand Fertiliser Manufacturers' Research Association (2009)

Plant uptake of K is influenced by: (refer to Figure 3.3.1)

(a) The rate at which a crop takes up K is dependent on the concentration of K^+ ions in the soil water film that bathes the root.

(b) The concentration at the root surface is limited by the rate at which K^+ ions will diffuse towards the zone of low K^+ concentration at the root surface or in the rhizosphere soil. Diffusion can be shown to be the dominant transport process. For example:

- Crop transpiration flow = 3 mm/day
- Soil Solution K conc. = 5 x 10^{-4}M
- Water flow x conc. = 0.6 kg K/day/ha

90 days growth allows for 54 kg K to be transported in transpiration flow. This is only 0.1-0.2 of crop requirements. Therefore the rest of the crop demand of 200-300 kg K/ha must move to the root by diffusion.

(c) The soil solution K supply is inadequate to sustain plant demands. To sustain a high yielding crop K must be desorbed from the exchangeable K pool on the cation exchange sites or released from soil minerals.

(d) The size of the exchangeable K pool is a better measure of K amounts available to plants than the amounts of soil solution K (Figure 3.3.4). But measures of exchangeable K can be unreliable because K can also be released from fixed K and other soil mineral K. Soils with greater amounts of 2:1 layer silicate clays and organic matter (fine textured soils) have higher CEC and hold more K in the exchangeable form. In such soils, as plant growth or leaching depletes soil K, a greater reserve of exchangeable K can be released to maintain the solution K concentration in a range suitable for plant growth (Figure 3.3.4). Sandy or coarse textured soils with low CEC lack this ability. Vice versa in soils with low CEC, more of the added fertiliser K remains in soil solution and is easily taken up by plants or leached. Contrast the sand with a soil of clay loam texture which has a high CEC (Figure 3.3.4).

Table 3.3.4 Assessment of Soil K Status

Form of K	Test	K extracted
Index of plant available K	MAF Quick test NH_4^+ counter ion	Approximately 70% of exchangeable K soil pool; widely used.
Index of long term soil supply	Kc test	Mineral K sequentially extracted with boiling nitric acid. Not routine test.
	NaTPB (sodium tetraphenylboron)	Precipitation of available K as KTPB allowing soil minerals to dissolve at a faster rate than normal. Not widely used. Some use on recent soils.

Measurement of Plant Available K

The common index of plant available K used in New Zealand is the quantity of K^+ ions that can be displaced by leaching columns of soil samples with 1M ammonium acetate solution at pH 7. The NH_4^+ ions displace ***exchangeable K^+*** ions from the CEC sites only. Its relationship to the MAF quick test K assay (a 2 minute shaken extraction of soil with 1M ammonium acetate solution at pH 7) is discussed in specific courses on soil and plant testing (Table 3.3.4).

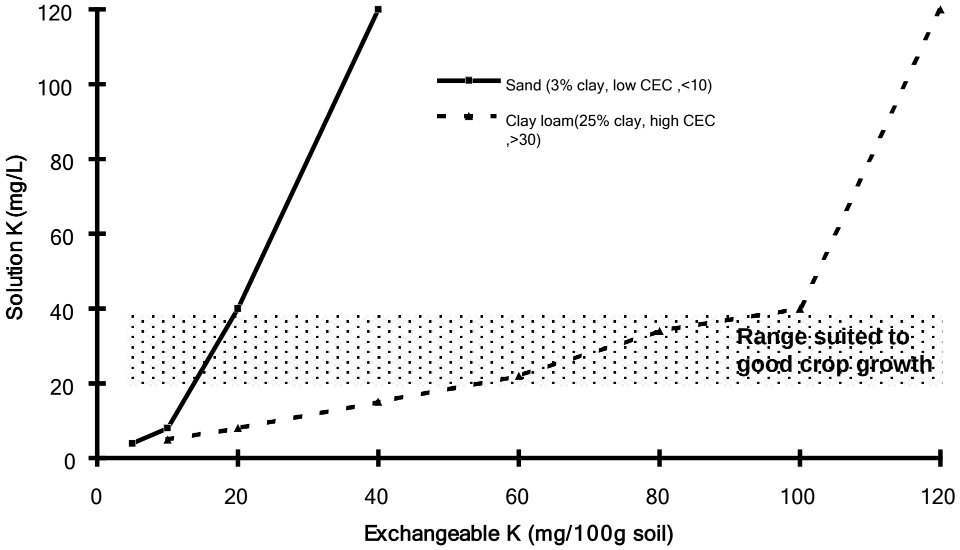


Figure 3.3.4 ***The influence of soil texture (CEC) and increasing exchangeable K on soil solution K concentration.***

The amounts of slowly released mineral K (***reserve K***) can be estimated from measuring the amount of K that is released from soil to sequential extractions of boiling 1M nitric acid This test has been called the ***K_c*** test. The sodium tetraphenylboron test (NaTPB) was developed to give a measure of both ***exchangeable K*** and that fixed K which is slowly released (***reserve K***).

Gains and Losses of Potassium

Relative to the amounts required for annual plant growth, inputs of K in rainfall are low (1-10 kg K/ha). K^+ ions are attracted to cation exchange sites with less bonding strength than the other common soil cations Ca^{2+} and Mg^{2+}, and with less strength than anionic $H_2PO_4^-$. Amounts of K lost by leaching in winter drainage water are significant and will need replacing over time with fertiliser K. Frequent applications of Ca^{2+} in fertiliser (superphosphate) and lime materials will displace K^+ from CEC sites and accelerate leaching losses. Whereas plants require large amounts of K, animals do not and excrete the unwanted K in dung or urine. Large deposits of K in cow urine patches can create hot-spots of K leaching. For a quantitative discussion of K losses, read Section 7.1 on Nutrient Budgets.

K sources and their reactions

COMMON POTASSIUM FERTILISERS

(See also Section 3.7 on Fertiliser and Manure Reference Resource).
The two most commonly used K fertilisers are potassium chloride (50% K) also known as muriate of potash and potassium sulphate (42 % K) (Table 3.3.6). Both these two fertilisers are readily soluble in water, making K immediately available for plant uptake and leaching. Certain plants such as potato are very sensitive to chloride and hence KCl is not recommended for these crops. For pastures, K is often applied as KCl mixed with single superphosphate (Potassic Super, Table 3.3.6).

Reactions in soils

When soluble K fertilisers (KCI and K_2SO_4) are added to soils they dissolve in the soil solution forming potassium ions (K^+). These ions take part in the normal K cycle reactions already discussed:

- exchange reactions
- fixation
- plant uptake
- leaching

MANURE AS A K SOURCE

Animal effluent can be a rich source of K and the application of animal effluent to soils needs to be closely monitored to ensure soil test K target concentrations are not exceeded. For example, if all the effluent generated from a 100 ha pasture based dairy farm milking 300 cows and importing 250 tonnes (dry matter) of maize silage, was spread over an 8ha block, this would equate to a K loading rate of 320 kg K/ha/year.

BROUGHT IN FEED AS A K SOURCE

Supplements such as hay, silage and molasses are high in K (Table 3.3.5) and dairy farms in particular, can import large quantities of K on to farm through purchased supplement. It is important to consider the K being brought in by calculating a nutrient budget and adjusting K fertiliser requirements as required. For example, if a 100 ha dairy farm imported 250 tonnes (dry matter) of pasture silage, they would be importing 58 kg K/ha/year. Approximately 90% of this K will be excreted, potentially returning 52 kg K/ha/year to the soil.

Table 3.3.5 K contents of common animal feeds.

Supplement	K %(dry weight basis)
Maize silage	1.20
Pasture silage	2.30
Pasture hay	2.32
Palm Kernel Meal	0.80
Molasses	3.30
Maize grain	0.40
Barley grain	0.57

Data from DairyNZ Farmfact (2008) and Kolver (2000).

Animal health issues

It is not advisable to apply K to pastures which are to be grazed by cows ready to calve or in early lactation. This is because K can be taken up by the pasture in preference to Ca and Mg. Milk fever or hypomagnesaemia (grass stagger) may result. High soil K concentrations resulting from excessive fertiliser or effluent application or large amounts of brought in feed, can also exacerbate K related animal health issues. To overcome this, an adequate supply of Ca and Mg needs to be maintained either through soil application or animal supplementation, or susceptible animals need to be moved to another area of the farm which has a lower soil K concentration.

K deficient pastures show the greatest yield increases to K when K is applied six weeks prior to the fastest growth rates. In most areas of New Zealand, this is late spring. Autumn application of K may lead to larger leaching losses of K over the winter drainage period. Plants take up K rapidly and in luxury amounts, therefore it is advisable to avoid applying K fertiliser to hay or silage crops which are near harvest, as this will result in elevated fodder K concentrations which are often fed to cows ready to calve or in early lactation.

Table 3.3.6 Common Potassium Fertilisers currently being used in New Zealand.

Product Name (N-P-K-S)	**Fertiliser component**	**K components**		**Other nutrients and important incidental components**			
		Soluble	***Sparingly soluble***				
Muriate of Potash (Potassium Chloride) (0-0-50-0)	KCl	(KCl)			Cl		
Sulphate of Potash (Potassium Sulphate) (0-0-42-18)	SP	SP (K_2SO_4)		SO_4-S			
20% Potash Super (0-7.2-10-9.2)	KCl, SSP	KCl		MCP, $CaSO_4$	Cl	F	Cd
20% Potash Sulphur Super (0-7.2-10.0-8.4)	KCl, SSP, elemental S	KCl		MCP, $CaSO_4$ elemental S	Cl	F	Cd
20% Potash Gold Super (0-7.2-8.4-12.8)	K_2SO_4, SSP	K_2SO_4		MCP, $CaSO_4$ K_2SO_4		F	Cd
Cropmaster 15 (15.2-10-10-7.7)	KCl, DAP, SA	KCl		$(NH_4)_2SO_4$ $(NH_4)_2HPO_4$	Cl	F	Cd

References

DairyNZ FarmFact (2008). 1-71 Palm Kernel Extract (PKE) http://www.dairynz.co.nz/file/fileid/36249

Kolver, ES (2000) Nutritional guidelines for the high producing dairy cow. Proceedings of the Ruakura Farmers' Conference 51, 78-87, 2000.

M^{c}Laren R and Cameron K (1990) Soil Science. Oxford University Press.

New Zealand Fertiliser Manufacturers' Research Association (2009) Fertiliser Use on New Zealand Dairy Farms. Auckland, New Zealand. http://www.fertiliser.org.nz/Site/resource_center/Booklets.aspx

Revision on Potassium

The purpose of the following section is to check your understanding of the K cycle and of the K sources and their reactions in soil. Key phrases or words are given for you to construct paragraphs around.

Sources:

- Soil mineral weathering (micas, feldspars, illite clay)
- Fertiliser (KCl, K_2SO_4)
- Brought in feed
- Effluent

Plant Available form:

K^+ (hydrated potassium ion)

Role in plant:

Important charge balancing cation in transport and cell membrane functions (e.g. stomatal opening), stimulates reproductive growth by countering effects of added nitrogen in promoting vegetable growth.

Deficiency threshold concentrations:

•	Ryegrass	< 2.0% K
•	Clover	< 2.0% K

Table 3.3.7 Nutrient distribution in soil-plant systems

Position or form	**Plant Availability on form**	**Approx. amount (kg K/ha; 15 cm depth)**	
Within soil minerals	unavailable in short term (non-labile), slow release by weathering	50 Peat	30,000 WLBGE SR
Surfaces of soil minerals and organic matter	readily exchangeable plant available (labile)	26-117 Peat Podzol	1200 YBE WWBGC[1]
Soil water	directly available to plant roots	6-20	
Pasture plants (standing crop, 2000 kg DM)	all soluble K	34	

[1] WWBGC = weakly weathered Brown granular clay - parent material basalt, Northland.
YBE = Yellow-brown earth, podzolized, Northland,
WLBGE = weakly leached Brown grey earth, Otago.
SR = Southern recent soil

Table 3.3.8 Potassium Cycle

Important transformations	**Implications**
Nature of soil mineral and rate of weathering (e.g. illite releases K, vermiculite absorbs K)	increased soil supply leads to decreased short term fertiliser requirement
Exchange of K^+ ions on the soil surface; quantity of exchange sites on the soil surface; interactions with soil acidity and lime	changes in amounts of short term plant available K
Partitioning of ~90% of K^+ ions into urine by grazing animal	important K loss mechanisms plus increases susceptibility to leaching by rainfall. Transfer of urine to unproductive areas.

Test Your Knowledge

1. Incorporate the following key words into sentences that make scientific sense in a short paragraph (< 20 lines) on potassium: K^+ ions, exchangeable, illite, vermiculite, feldspar, soil solution, 5 x 10^{-4} M, potassium, texture, leaching.

2. When potassium chloride is added to soils it dissolves in soil solution and releases the potassium ions in to soil solution. Explain the reactions of potassium ions with soil components.

3. Discuss the effect of excessive potassium application on other exchangeable cations in soils.

4. Describe how soils are tested for K availability.

5. Discuss the significance of dairy cow urine patches in losses of K from grazed pastures.

Recommended Reading

Fertilisers and Soils in New Zealand Farming. (1984) C During. Government Printer *Information from New Zealand pastoral experiences.*

Soil Science. R. M^{c}Laren and K. Cameron. Oxford University Press. (Read sections 17.1 to 17.1.3 on p 229-233).

3.4 Nitrogen in Soils

Key Learning Objectives

After studying this section you should be able to explain:

1. The amounts and forms of nitrogen (N) present in the soil/plant/animal system.
2. The forms of N that are available to plants.
3. The source, process and rate of replenishment for the plant available form of N.
4. The processes that lead to N gains or losses.
5. The forms and solubilities of N in the common N fertilisers used in New Zealand.
6. The reactions and fate of different N fertilisers added to soil with respect to:
   - N availability to plants
   - The acidifying effects of N fertilisers

Introduction

Nitrogen (N), more than any other plant nutrient, limits primary production in terrestrial systems. N contained in amino acids, proteins or nucleic acids, makes up 2-4% of plant dry weight, which is a greater percent by weight than any other nutrient element. Therefore, large quantities of N (up to 200-800 kg N/ha) must be taken up by crops during the growing season.

Let us first examine the forms of N in the soil, the sources of this N and the soil processes that control the flow of N through the soil-plant-animal system.

Nitrogen in Soils

The chemical analysis of most topsoils shows us that virtually all (~98%) of total soil N is present in water-insoluble, organic complexes (Figure 3.4.1). Very little N (relative to the total soil N content) is present in ionic forms in the soil solution, or in mineral forms, or ionic forms adsorbed on soil colloid surfaces.

SOIL SOLUTION N

Non-leguminous plants absorb their N from the soil water in the form of nitrate (NO_3^-) and ammonium (NH_4^+) ions. Normally, only 2-3% of the N in soil is present as NO_3^- and NH_4^+ ions in the soil solution. Unlike phosphate ions, the plant available forms of N, $NH4^+$ and especially NO_3^-, are mobile ions in the soil. NO_3^- ions are not sorbed to any extent by soil surfaces; hence the solution phase is quickly depleted by plant uptake and leaching.

EXCHANGEABLE N

The NH$_4^+$ cation is attracted to negatively charged cation exchange sites on soil clay and organic matter surfaces (Refer to Section 3.3 – Potassium in Soils - for further discussion on this process). However, in warm, moist, and aerobic soils with neutral pH very little exchangeable NH$_4^+$ accumulates because nitrification (biological conversion of NH$_4^+$ to NO$_3^-$) continually removes NH$_4^+$ from the soil solution (Figures 3.4.1 and 3.4.2).

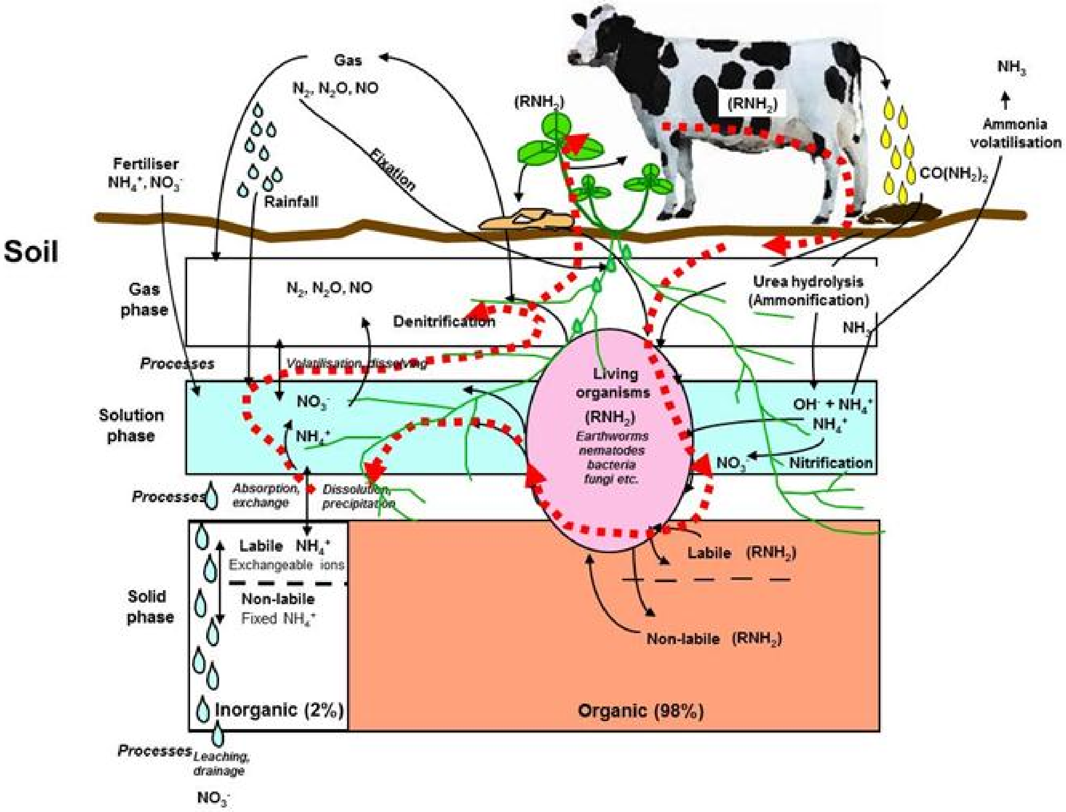


Figure 3.4.1 The Nitrogen Cycle (R represents a complex organic molecule)

FIXED NH$_4^+$

Ammonium ions have a similar ionic radius to K ions (0.143 nm vs 0.133 nm, nm = nanometre = m x 10^{-9}) and can be held in the interlayer spaces of illitic clay minerals such as vermiculite and chlorite (Figure 3.3.3). In topsoils, fixed NH$_4^+$ normally accounts for less than 5% of the total N. In subsoils, which are usually low in organic matter, `fixed NH$_4^+$' may make up 50% of the N present. (Attempts to produce slow release N fertilisers from ammoniated vermiculite were successful, but the product is costly because of its low N content.)

ORGANIC N (RNH$_2$)

The solution phase is quickly depleted by plant uptake and leaching, therefore, the dominant form of N remaining in soils is organic N (RNH$_2$; R = complex organic molecules such as amino acids; e.g. $HOOC-CH_2-CONH_2$), which is not soluble in the soil water. Many of these organic N compounds have functional groups with positive charges in low pH soils and are therefore attached to cation exchange sites. (e.g. ionised amino-acids $HOOCCH_2CONH_3^+$). In soil organic matter, N is usually found in combination with carbon at ratios of C:N of 10-14 : 1. Most of this N is present in high molecular weight polymers, 30-40% of which yield amino-acids upon hydrolysis. The majority of soil organic N appears to be in a stable fraction which is resistant to decay (age from 400-2000 years in radiocarbon dated topsoils).

Origins of N in Soils

MINERAL N

Unlike many other nutrients, N is not abundant in the primary minerals from which most soils are formed. Exceptions would be evaporite deposits containing NO_3^- salts. Nitrate salts are formed as inland seas evaporate, or from mountain runoff into dry valleys (e.g. Chilean nitrate deposits).

Normally <15 μg N/g soil of N as NH_4^+ is present within the structure of silicate minerals. Secondary minerals such as Taranakite may form from weathering allophane in the presence of mildly acid phosphate fertilisers (DAP or Potassic super). Normally only trace amounts are present in soils.

BIOLOGICALLY/CHEMICALLY FIXED N_2

Virtually all nitrogen present in soils is derived from either biological or chemical fixation of N_2 from the atmosphere (79% wt. N_2).

The rhizobium bacteria in the root nodules of a legume crop (e.g. white clover) may be capable of fixing 200-600 kg N/ha/year. More commonly, annual fixation ranges between 10 and 200 kg N/ha/year for low fertility status hill and high fertility status lowland pastures respectively. In undisturbed, clover based pasture soils (uncultivated) this may lead to soil N increases ranging from 0 - 100 kg N/ha/year. As organic N levels in the soil increase, the rate of biological N fixation decreases (the population of legumes-decreases in natural succession to non-legumes) until a steady state equilibrium is reached.

Globally, biologically fixed N is estimated to be 200 million tonnes/year. Chemical fixation of N is now a major industrial activity (~ 50 million tonnes/year) and the major product of this process is urea.

DRY DEPOSITION/RAINFALL

In non-industrial areas of the world inputs in this form are likely to be < 5 kg N/ha/year. In industrialised areas, fossil fuels provide the heat for N_2 and O_2 to combine to produce nitrogen oxides - rates of input may be up to 20 kg N/ha/year. The same process may occur naturally during lightening storms.

Processes Involved in the Cycling of N

It must be evident from the discussion so far that virtually all N must enter the terrestrial N cycle as biologically fixed (Figures 3.4.1 and 3.4.2) or industrially fixed N. Therefore, most N enters the soil either as fertiliser N or after the plant growing cycle has finished with it (i.e. decomposition products of plant and animal proteins).

PLANT UPTAKE OF N

Non-leguminous plants roots absorb their N from the soil water in the form of NO_3^- and NH_4^+ ions (Figure 3.4.2). In well fertilised, warm and aerobic soils, where nitrification is favoured, the NO_3^- supply to plant roots is mostly satisfied by the transpiration flow of soil water containing NO_3^- at ~ 10^{-2} M. In wet, cold soils or acidic soils, where nitrification is not favoured, ammonification still occurs (Figure 3.4.2) and NH_4^+ is the dominant N form in soil solution. Supply to the plant root is probably mostly by diffusion of NH_4^+ from sites of organic matter decomposition. The guidelines for interpreting optimum pasture N concentrations are presented in Table 3.4.1.

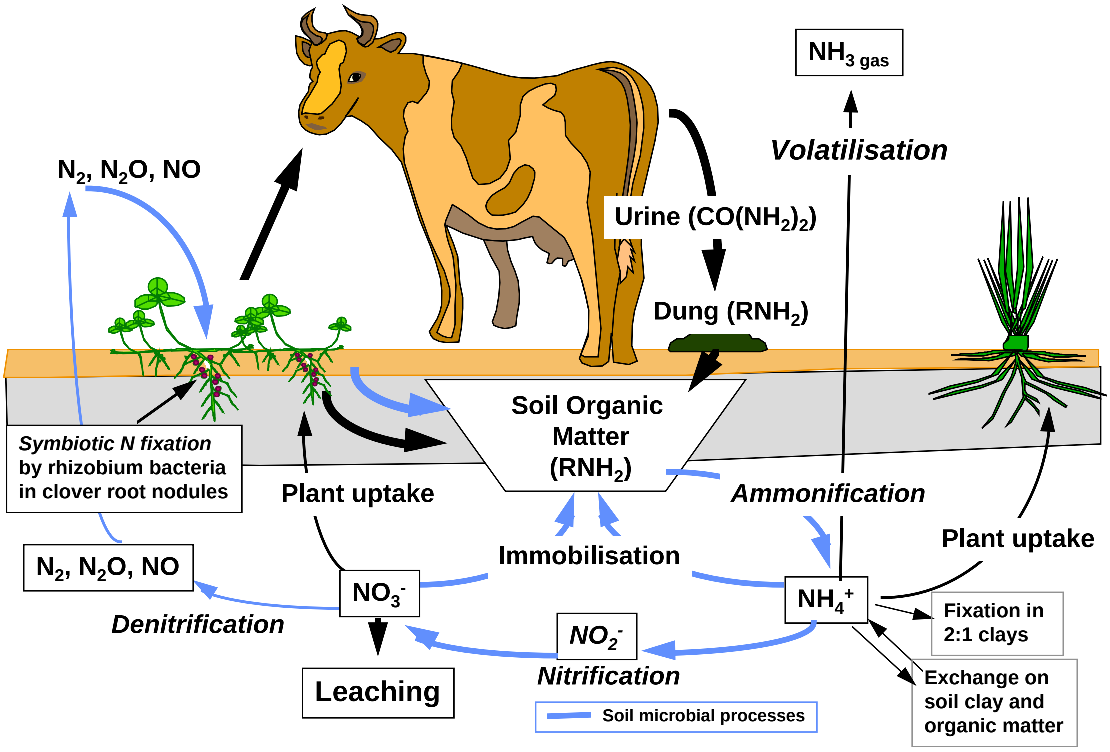


Figure 3.4.2 Transformations of Nitrogen in grazed legume based pasture (R represents a complex organic molecule).

Table 3.4.1 Guidelines for interpreting mixed pasture N (% of DM) herbage analyses.

Deficient	Low	High	Optimum
<4.0	4.0-4.7	>5.5	4.7-5.5

Source: New Zealand Fertiliser Manufacturers' Research Association (2009)

CONVERSION OF SOIL N INTO PLANT AVAILABLE FORMS

Normally only 2-3% of the N in soil is present as NO_3^- and NH_4^+ ions in the soil solution. Thus soil organic N must be continuously decomposed and converted to NO_3^- and NH_4^+

ions in order to supply growing plants with N. These decomposition and transformation reactions are carried out by soil bacteria and fungi. Bacteria and fungi produce extracellular enzymes that digest the complex soil organic N into amino acids and NH_4^+ ions that can enter the microbial cells. This process has been termed ***mineralisation***.

Conditions which stimulate organism growth commonly stimulate decomposition and the release of mineral N forms that are available to plants. The first products of organic N breakdown are NH_4^+ ions (***ammonification***). NH_4^+ ions are subsequently nitrified in the presence of a good oxygen supply to NO_3^- ions. Ammonification ($R\text{-}NH_2 \rightarrow NH_4^+$) is carried out by a variety of soil microorganisms and is, therefore, relatively insensitive to oxygen supply, source of carbon or moderate changes in soil acidity.

Nitrification is carried out by fewer soil micro-organisms, a range of heterotrophic soil bacteria and fungi and not (as was once thought) just species of *nitrosomonas* and *nitro-bacter* autotrophic bacteria, which derive energy from this chemical transformation. As far as is known, all nitrifying organisms are obligate aerobes, which means they require oxygen to nitrify (Table 3.4.2). NO_3^- concentrations in aerobic, warm, and moist cultivated soils are normally higher than NH_4^+ concentrations. In such soils the main source of N taken up by plants is NO_3^-. This is because in warm aerobic soil the rate of nitrification (oxidation of NH_4^+ to NO_3^-) is rapid. In acidic soils nitrification is slow and NH_4^+ is probably the main plant N source. In cold wet soils nitrification is also slow. Wetness restricts the air filled pore space in the soil and oxygen diffusion rates to the site of nitrification become limiting.

Table 3.4.2 The influence of oxygen supply on nitrification rate

% oxygen in soil air	% NH_4^+ nitrified
20	46
11	43
4.5	38
2.1	28
1.0	21
Critical level	
0.4	2

In undisturbed pasture soils the decomposition of soil organic N is slow and it is difficult to measure the low levels of mineral N present. Nutrition of grasses in these soils is considered to be through considerable uptake of NH_4^+ ions rather than NO_3^-. However in cultivated soils, the physical destruction of soil aggregates and mixing accelerate microbial decomposition of soil organic matter, nitrification is rapid, and large quantities of nitrate can be produced.

LOSSES OF N FROM THE SOIL

Leaching (physical)

Nitrate is not adsorbed by positively charged soil surfaces; therefore, large losses of nitrate occur in drainage waters. This is dealt with in subsequent sections. Important factors determining the extent of nitrate leaching are: the use of N fertilisers, the accumulation of nitrate in the soil, the temperature and frequency and intensity of rainfall.

Accumulated soil nitrate is mostly derived from mineralisation of soil organic N and from additions of nitrate fertilisers, hydrolysis and nitrification of urea and ammonium fertilisers and urine spots in grazed pastures.

Denitrification (biological) (N_2O) N_2

Denitrification is the microbial reduction of nitrate to nitrous oxide and nitrogen gas. This process requires soil micro-organisms, a source of NO_3^-, respirable carbon (i.e. decomposable organic matter) and anaerobic conditions, which might be a waterlogged soil or in the centre of soil aggregates (Figure 3.4.3). Under these conditions O_2 required for respiration is in short supply and NO_3^- becomes the terminal electron acceptor for soil organism respiration. Denitrification can also occur through 'incomplete nitrification' as warm moist soils become short of oxygen. The rates of denitrification vary with soil conditions. In heavy clay soils 0.6 kg N/day has been observed in autumn/spring.

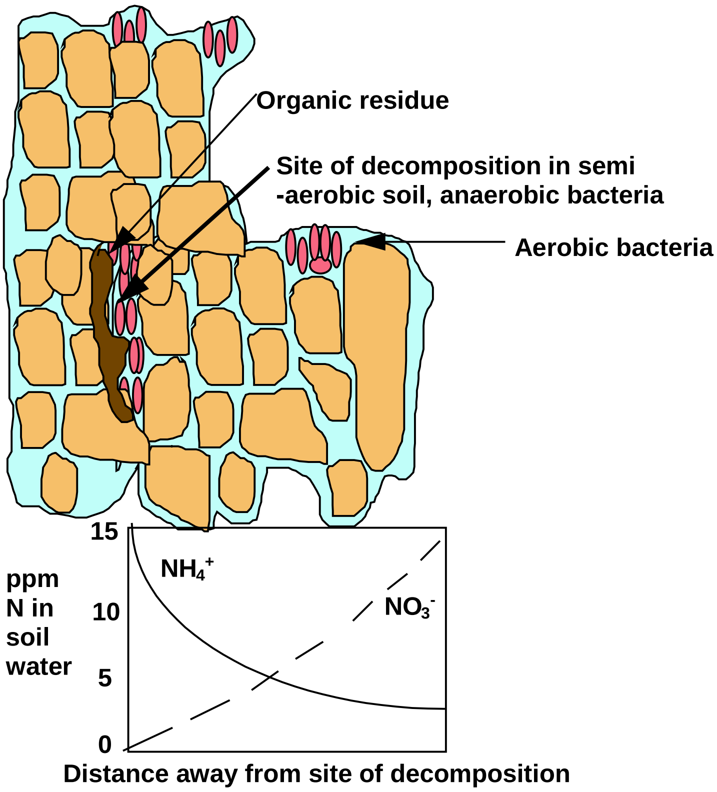


Figure 3.4.3

A microsite of denitrification in an aerobic soil

Volatilisation (chemical)

$NH_4^+ \rightarrow H^+ + NH_3 \uparrow$

Volatilisation occurs only when there is the combination of soil pH above 7 and free NH_4^+ ions. This commonly occurs in urine spots and after urea application. High CEC and low soil pH will reduce the N loss; as will high soil moisture contents, which will allow rapid dispersion of the high concentrations of urea added in urine spots and urea granules. Grazed swards may lose 1 kg N/ha/day from urine spots when stock are present.

$NH_4^+ \rightarrow H^+ + NH_3$ (solid phase)

NH_3 (solid phase) → NH_3 (gas phase) $\uparrow$

At pH 7; 1% of NH_3/NH_4^+ solution is present as NH_3 (solid phase).

Temporary Losses of Plant Available N in the Soil

(Immobilisation/mineralisation of organic N)

Earlier in the discussion it was mentioned that extra-cellular enzymes from soil micro-organisms are required to decompose soil organic N and release plant available N. However, release of plant available N relies on soil micro-organisms not utilising all the N released for the growth.

Most soil micro-organisms are heterotrophic, which means they need an available carbon substrate to respire to produce energy to grow. Mineral N will be released if that substrate is rich in N. If the substrate is poor in N, growth may be stimulated but in order to satisfy their N requirements soil micro-organisms will immobilise all the available mineral N (NO_3^- and NH_4^+) in the soil solution. When this occurs the mineralisation rate is less than the immobilisation rate and ***net-immobilisation*** occurs. If ***net-immobilisation*** occurs, crops growing in the same soil will become N deficient. Whether ***net-mineralisation*** or ***net-immobilisation*** occurs depends mostly on the carbon to nitrogen ratio in the organic substrate added to the soil.

General rules of thumb for:

Immobilisation: NH_4^+ or $NO_3^- \rightarrow R\text{-}NH_2$

Plant materials or crop residues with wide C:N ratios (e.g. cereal straw) will temporarily ***immobilise*** available NH_4^+ and NO_3^- as they decompose in soil. Organic residues that have ratios of C:N that exceed 40:1 (i.e. < about 1% N) may temporarily ***net- immobilise*** N.

Mineralisation: $R\text{-}NH_2 \rightarrow NH_4^+$ or NO_3^-

Ratios of C:N that are less than 20:1 (i.e. > about 2% N) may result in ***net-mineralisation*** of N.

Mineralisation will occur eventually with any residue. Each succession of organism growing on the residues of the previous soil organism narrows the C:N ratio as CO_2 is evolved through respiration.

N UPTAKE AND RHIZOSPHERE SOIL CHEMISTRY

With such large quantities of N being required by plants, the form of N taken up by plants is an important factor determining the uptake of other ions by roots. This is because there must be a charge balance across the root/soil interface when plants take up nutrients. If taking up an excess of positive (+) charge (i.e. all plant N taken up as NH_4^+) a balancing cation must be exuded from roots. This cation is normally H^+ which acidifies the soil outside the root (the rhizosphere).

If taking up an excess of negative (-) charge (i.e. all plant N taken up as NO_3^-) a balancing anion must be exuded from roots. This anion is normally OH^- (or HCO_3^-) which makes the soil outside the root alkaline.

You should consider how pH changes in rhizosphere soil will influence the availability of other nutrient elements. How will the form of N fertiliser affect Al^{3+} ion concentrations in rhizosphere soil? Which components of the soil solid phase will be acid soluble and which ions are displaced from the soil solid phase surface by OH^- ions? (Read Section 3.6 on Other Factors Affecting Nutrient Availability and Loss).

Measuring plant available N in soils

Unlike P, K and S, it is difficult to reliably determine the concentration of N available for plant uptake, as the transformations of N in soils are dynamic and concentrations change hourly/daily and by the time samples are collected and analysed in a laboratory, results are meaningless. Alternatively, measurement of a soils capacity to mineralise organic N for plant uptake can be measured using an anaerobically mineralisable N test. However the actual amount of N which can be mineralised from the organic pool is dependent on soil temperature and moisture in the field and the laboratory test is unable to replicate these conditions. This test is widely used for arable production, but is not commonly used for pasture production. The most accurate method of assessing plant availability of N is to measure the N concentration in the plant tissue itself, however rapid changes in soil N availability can readily influence plant N concentrations.

N Sources and Their Reactions

FERTILISER N FORMS

The most common nitrogenous (N) fertilisers used in New Zealand are urea (46 % N), ammonium sulphate (21 % N), diammonium phosphate (DAP; 18 % N), calcium ammonium nitrate (27 % N), and 'Blood and Bone' (8 % N). While the first four are inorganic soluble fertilisers, the last one is an organic insoluble fertiliser. Identify the forms of N in these fertilisers in Table 3.4.3 and consult Figure 3.4.4 to identify where these fertiliser forms enter the nitrogen cycle. The form of N fertiliser used depends not only on the cost per unit N but also on the overall efficiency of the fertiliser N. The efficiency of fertiliser N varies between the fertiliser forms which is attributed to the difference in the effects of fertilisers on the rate of uptake and assimilation of N, the losses of N through ammonia volatilisation, denitrification and leaching, the N induced cation/anion balance in the plants and the acidifying effects of N. The effects of fertilisers on the above processes should be considered before any decision can be made on the choice of the N fertilisers for dairy pastures.

ACIDIFYING EFFECTS OF N FERTILISERS

One of the main effects of N fertiliser is acidification of soils (Figure 3.4.4). Application of N fertilisers, such as urea and ammonium sulphate and DAP to soils produces acid by three processes. Firstly, the natural process of oxidation of ammonium ions to nitrate ions (nitrification) releases acid. Secondly, plant uptake of the positively charged cation NH_4^+ causes plant roots to release H^+ to balance the charge. Thirdly, in the high pH environment in fresh urine patches or around a urea granule caused by urea hydrolysis NH_4^+ is converted to NH_3 gas and may be volatilised leaving a H^+ ion in the soil. On the other hand hydrolysis of urea (or any organic N) to NH_4^+ generates OH^- (alkali) as does plant uptake of NO_3^- and denitrification of NO_3^- to N_2O or N_2 gases.

The extent of acidification caused by N fertilisers and N fixation ultimately depends on the fate of the N in the N cycles. For example if amounts of NH_4^+, urea, or biologically fixed N are lost from the cycle as NO_3^- in drainage waters then the net acidity generated by nitrification cannot be neutralised by alkalinity generated by NO_3^- uptake or denitification. A general rule of thumb to assess where acidification occurs is if the form of a nutrient leached, lost, or stored, is more negative than the form of N in inputs. If such is the case, then acid is generally left in the system. Examples are NH_4^+ fertiliser and nitrate leaching, N_2 fixation and NO_3^- leaching, NH_4^+ fertiliser and animal product removal (RNH_2), or soil organic matter (RNH_2) increase. N fertilisers containing nitrates such as calcium nitrate and potassium nitrate are unlikely to cause soil acidification. The addition of NO_3^- and subsequent NO_3^- leaching does not generate acidity in the soil.

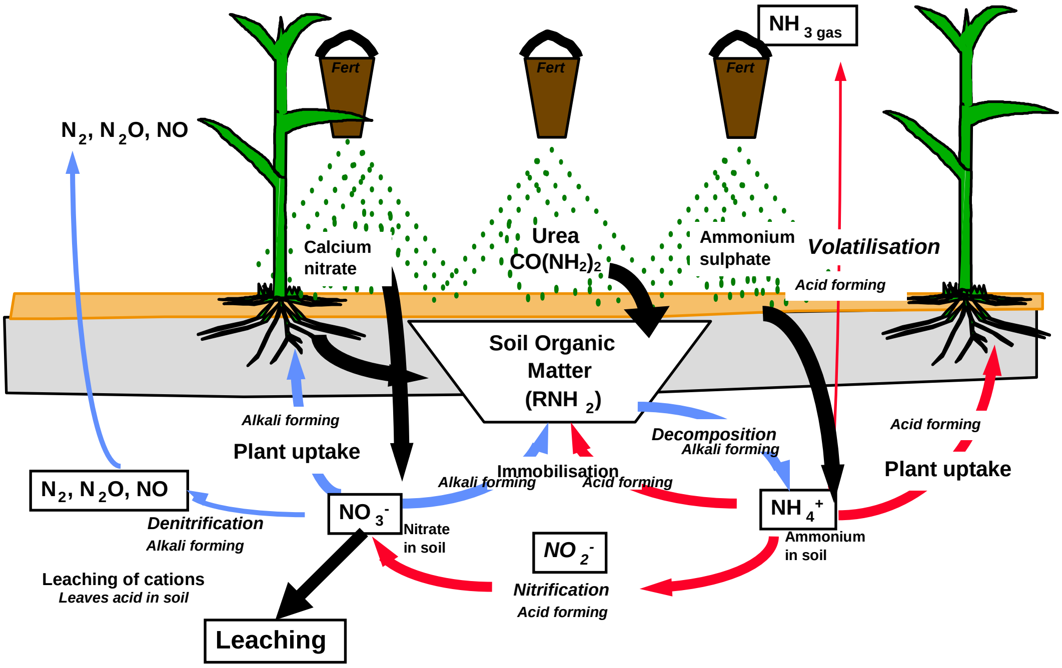


Figure 3.4.4 The role of nitrogen fertilisers and the nitrogen cycle in soil acidification (See also Section 3.6).

It is estimated that approximately 1.72, 4.11 and 5.24 kg lime (calcium carbonate; $CaCO_3$) is required to overcome the acidity produced by the application of 1 kg N as urea, DAP and ammonium sulphate, respectively. Fixation of atmospheric N and the subsequent leaching of nitrate formed from the mineralisation of the fixed N result in the acidification of the soils. It has been shown that in high producing pastures approximately 400 - 550 kg $CaCO_3$/ha is required annually to neutralise the acidity produced by these processe

APPLICATION

Irrespective of the crop, N fertilisers should be applied when plant growth is active and not when halted by low temperature, wetness, or drought (See the Overseer® website for the *Code of Practice for Nutrient Management* for guidelines on N fertiliser use.). The rate of N fertiliser applied in a single application is important as research has shown that above or below certain rates, N fertiliser application becomes inefficient. The optimum N application rate is 25-50 kg N/ha for pastures and 50-75 kg N/ha for silage and hay crop.

REACTIONS OF N FERTILISERS IN SOILS

When N fertilisers are added to soils, depending on the form of N present in the fertilisers, they undergo different chemical and biological reactions. The N transformation reactions in soils, which have been discussed earlier in this section, include:

- Mineralisation
- Immobilisation
- Nitrification
- Denitrification
- Ammonification
- Ammonia volatilisation
- Ammonium fixation
- Nitrate leaching

While the first five reactions involve soil micro-organisms (with the exception of the ammonification of urea), the last three reactions involve only the chemical/physical processes. It is important to understand these transformation processes in order to understand the reactions of nitrogen fertilisers in soils. The reactions of particular interest that influence fertiliser N utilisation and losses are: ammonification, ammonia volatilisation, nitrification and nitrate leaching. These four processes are discussed in more detail below.

Ammonification

For example when urea – or urine - ($CO(NH_2)_2$) is added to soils first it undergoes ammonification reaction (Eq. 1.1, Figure 3.4.4). This process is also known as "urea hydrolysis" and is carried out in the presence of urease enzyme in the soils. In this process ammonium (NH_4^+) ions are produced. This process also releases alkali hydroxyl ions (OH^-) and hence the pH around the urea granules in soil increases to a maximum of 8.

$$CO\,(NH_2)_2 \quad => \quad 2NH_4^+ \; + 2OH^- + CO_2 \qquad \text{(Equation 1)}$$

Table 3.4.3 Common Nitrogen fertilisers currently being used in New Zealand

Product Name (N-P-K-S)	**Fertiliser component**	**N components**		**Other nutrients and important incidental components**			
		Soluble	***Sparingly soluble***				
Urea (46-0-0-0)	urea	urea					
Sulphate of ammonia (SA) (21-0-0-23)	SA	$(NH_4)_2SO_4$		SO_4 - S			
Calcium ammonium nitrate (CAN) (27-0-0-0, 8%Ca)	CAN	CAN			Ca		
Diammonium phosphate (DAP) (18-20-0-0)	DAP	$(NH_4)_2HPO_4$		HPO_4-P		F	Cd
Ammoniated super (6.5-6.7-0-15)	SA, SSP	$(NH_4)_2SO_4$		$CaSO_4$	MCP		
Nitrogen super (6.2-6.3-0-15.3)	SSP			$CaSO_4$	MCP	F	Cd
Cropzeal 20N (19.5-10.1-0-12)	SA, DAP	$(NH_4)_2HPO_4$, $(NH_4)_2SO_4$		SO_4 - S		F	Cd
Hydro green (14-5-15-1)	KCl, K_2SO_4	NH_4, NO_3		K, SO_4-S, Cl		F	Cd
Nitrophoska (12-10-10)	-	2:1 NH_4:NO_3 ratio		K	Cl	F	Cd
N-rich ammo (13.7-0-0-14)	SA, urea	$(NH_4)_2SO_4$ urea		SO_4-S			
Cropmaster 15 (15.2-10-10-7.7)	SA, DAP, KCl	$(NH_4)_2HPO_4$, $(NH_4)_2SO_4$		HPO_4-P, SO_4-S, K	Cl	F	Cd

The ammonium ions (NH_4^+) formed through ammonification or added through ammonium fertilisers (ammonium sulphate and DAP) is subjected to several fates in the soil which include:

- retention onto soil particles (ammonium fixation)
- loss through ammonia volatilisation.
- uptake by plants
- conversion to nitrite and nitrate (nitrification)
- utilisation by microorganisms (immobilisation)

Ammonia Volatilisation

Ammonium ions in an alkaline medium dissociate into gaseous ammonia which is subjected to volatilisation losses (Eq. 1.2). Ammonia volatilisation occurs when the soil pH is high (>7.5). In the case of urea, the initial increase in soil pH through ammonification process is likely to result in ammonia volatilisation.

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O \text{ (pKa 7.6)} \qquad \text{(Equation 2)}$$

In New Zealand, although most of the ammonia volatilisation in dairy pasture occurs from urine patches, a Lincoln University study has shown that approximately 12%, 5% and 1% of N is lost through ammonia volatilisation when N is added as urea, DAP and ammonium sulphate to the surface of pasture or bare cropped soil, respectively.

Nitrification

The biological conversion of ammonium to nitrate is known as nitrification (Eq. 1.3). The ammonium ions are released indirectly from the ammonification reactions of organic matter, urea and organic form of nitrogen fertilisers or directly from the solubilisation of ammonium fertilisers. Nitrification reaction is a two step process in which the ammonium is first converted (oxidised) into nitrite and then to nitrate. Since the rate of conversion of nitrite to nitrate is faster than the conversion of ammonium to nitrite, it is unlikely that nitrite which is toxic to plants accumulates in soils. The nitrification process produces acidic hydrogen ions and thereby decreases the pH. Since per unit N, more acidic ions are produced during nitrification than alkali ions during ammonification, urea fertiliser ultimately acidifies the soils (Equation 4). Ammonium fertilisers (ammonium sulphate and DAP) undergo only the nitrification process releasing acidic ions. This is one of the reasons why these fertilisers are more acidifying than urea fertiliser.

$$2NH_4^+ + 4O_2 \rightarrow 2NO_3^- + 4H^+ + 2H_2O \qquad \text{(Equation 3)}$$

Net effect $CO(NH_2)_2 \rightarrow 2NO_3^- + 2H^+$ (Equation 4)

Nitrate formed through nitrification of ammonium or added through nitrate fertilisers, (calcium nitrate) is subjected to various processes which include:

- Plant uptake
- Leaching losses
- Immobilisation
- Denitrification

Nitrate leaching

Ammonium ions have to be converted to nitrate ions (nitrification process) before any significant leaching loss can occur. In many areas of New Zealand, nitrate leaching occurs during late autumn, winter and early spring due to high rainfall and low evapo-transpiration. However, even during summer, rainfall with high intensity could cause nitrate leaching due to rapid water infiltration through cracks, root channels and earthworm holes. Leaching losses from pasture soils will occur from both fertiliser N and urine N. A recent study by AgResearch has indicated that fertiliser application to dairy pasture accelerates leaching loss. Eight percent and 19% of the total N added as urea at the rates of 200 and 400 kg N/ha, respectively was lost through leaching (See also Section 5.1 on Nutrient Cycles and Nutrient Budgeting on Dairy Farms).

Nitrate accumulation in pasture

Recently there has been some concern about nitrate accumulation in pasture and forage crops and the subsequent nitrate poisoning of animals. The rate of nitrate accumulation is dependent on plant species, supply of N, and the rate of plant growth (nitrate reduction to amino acids).

SPECIES

In legume-based pastures, nitrate accumulation is unlikely to occur in legume plants which are actively fixing N in their root nodules. In grasses, however, high concentration of nitrate is found in the year of sowing and it decreases with the age of the crop. High N mineralisation rates in the recently tilled seed-bed can produce high soil NO_3^- concentrations during the first season. While in some plant species (e.g. ryegrass), accumulation of nitrate is mainly caused by a high nitrate uptake, in others (e.g. winter forage oats) accumulation is mainly caused by a slow rate of nitrate reduction. In young plants, most of the N is assimilated into protein resulting in high organic N, whereas in old and dead leaves only a small amount of N is assimilated into organic N resulting in high nitrate accumulation. Differences in nitrate accumulation have been found between species and varieties. Nitrate accumulating species include oats, maize, rye, wheat and barley and non-accumulators include the grasses timothy, brown top, and cocksfoot. In general, forage crops which produce considerable amounts of leafy materials, such as ryegrass converts nitrate N to organic N, whereas grain crops such as oat converts less nitrate to organic N resulting in nitrate accumulation.

N FERTILISERS

In legume-based pastures, application of N fertilisers is likely to increase nitrate concentration in the herbage. A number of reasons have been attributed to fertiliser-induced nitrate accumulation in pasture. Firstly, the application of N fertilisers decreases the rate of biological N fixation and hence the legume plants become dependent on soil mineral N, mostly nitrate. An increase in the uptake of mineral nitrate increases nitrate accumulation in plants. Secondly, the application of N fertilisers influences both the uptake of N and the dry matter production. Under favourable growing conditions with sufficient N supply, the production of dry matter increases resulting in the assimilation of most of the absorbed N into organic N; whereas under poor growing conditions the N uptake increases more than the dry matter yield resulting in nitrate accumulation. Low dry matter yields with high nitrate contents are often found in plants grown under low light intensity (under cloudy and shade conditions) and deficiency of mineral nutrients.

SEASON

It has often been observed that nitrate concentration in herbage is likely to be high after a short spell of drought period. In New Zealand the accumulation of nitrate in pasture has been noticed under cool and cloudy weather conditions, especially after a period of dry spell. Two reasons can be attributed for this. Firstly, during the late summer drought period, the nitrate concentration builds up in the soil and upon re-wetting; soil organic matter mineralisation can be rapid, generating even higher soil nitrate concentrations. Secondly, the moisture stress during the drought period causes dry matter yield depression resulting in less reduction of nitrate to organic N. It has been observed that drought during the heading and ripening period increases the nitrate concentration in oats. Crops grown in summer fallow are found to contain more nitrate than crops grown on stubble land. In Europe, high nitrate in plants also occurs more frequently in late summer and autumn. The quantity of light at that period is small and so the possibility for synthesis of organic compounds would be limited. The uptake of N, however is generally maintained at high level because of relatively high soil temperature and good supply of water.

NITRATE POISONING IN GRAZING CATTLE

Cattle appear to be more susceptible than sheep and horses. Pasture and forage poisoning ascribed to a high nitrate content has been reported in dairy cattle in New Zealand and overseas. Losses of weight and milk production and non-infectious abortion have been noted as sub lethal effects in dairy cattle. The trouble appears to be of sporadic occurrence, and other factors besides nitrate content may be involved. Nitrate poisoning in cattle can be minimised by proper grazing management. Research suggests that following N fertiliser application, ryegrass pasture must have grown at least 2 live leaves per tiller before plant N concentrations are at a safe level for grazing. When ryegrass has between 2-3 live leaves per tiller, pasture quality and pasture persistence is also optimised, therefore ryegrass leaf stage is a simple, but useful approach to pasture management. Hungry cattle should not be allowed to graze new pasture in cloudy weather conditions, especially after a dry period. Under this condition the pasture samples should be tested for nitrate levels and animal should be given pasture as only part of the ration. Under the acute toxicity conditions it is important to consult a vet and methylene blue acts as antidote and prevents the occurrence of nitrate poisoning.

Other N sources

Effluent as a N source

Farm nitrate leaching losses are often exacerbated on areas where animal effluent is spread on to soil due to high concentrations of N in the urine component of the effluent. The N content in the urine produced by dairy cattle can range from 30-120 kg N/cow/year, compared to sheep which have much lower urine N return ranging from 5-25 kg N/sheep/year. Similarly, the amount of N excreted by dairy cows via faeces ranges from 20-70 kg N/cow/year, whereas for sheep this figure is only 2-9 kg N/sheep/year. It is important to account for these sources of N, especially if effluent is only spread over a small area of the farm. For example, if all the effluent generated in the farm dairy (i.e. ~10% of dung and urine collected)from an 100 ha pasture based dairy farm milking 300 cows and importing 250 tonnes (dry matter) of maize silage, was spread over an 8 ha block, this would equate to a N loading rate of 360 kg N/ha/year.

BROUGHT IN FEED AS A N SOURCE

Supplements such pasture silage and palm kernel are high in N (Table 3.4.4) and dairy farms in particular, can import large quantities of N on to farm through purchased supplement. It is important to consider N sources from supplements when calculating a nutrient budget and adjusting N fertiliser requirements as required. For example, if a 100ha dairy farm imported 250 tonnes (dry matter) of pasture silage, they would be importing 68 kg N/ha/year. Approximately 75-80% of N eaten by dairy cows is excreted, so 54 kg N/ha/year can potentially be deposited back to soil in urine and manure.

Table 3.4.4 N contents of common animal feeds.

Supplement	N %
Maize silage	1.28
Pasture silage	2.72
Pasture hay	2.72
Palm Kernel Meal	2.24
Molasses	0.64
Maize grain	1.28
Barley grain	1.76

Data from DairyNZ Farmfact (2008) and Kolver (2000).

References

DairyNZ FarmFact (2008). 1-71 Palm Kernel Extract (PKE) http://www.dairynz.co.nz/file/fileid/36249

Kolver, ES (2000) Nutritional guidelines for the high producing dairy cow. Proceedings of the Ruakura Farmers' Conference 51, 78-87, 2000.

New Zealand Fertiliser Manufacturers' Research Association (2009) Fertiliser Use on New Zealand Dairy Farms. Auckland, New Zealand. http://www.fertiliser.org.nz/Site/resource_center/Booklets.aspx

Revision on Nitrogen

The purpose of the following section is to check your understanding of the N cycle and of the N sources and their reactions in soil.

Sources:

- Nitrogen gas via biological and industrial fixation
- Mined evaporite deposits (e.g. $NaNO_3$ and KNO_3)
- Dry deposition/rainfall
- Manufactured N fertiliser
- Animal urine and faeces
- Brought in feed supplements

Plant Available form:

- NH_4^+ (ammonium ion)
- NO_3^- (nitrate ion)

Role in plant:

Amino acid synthesis and chlorophyll synthesis; providing the basic components for protein synthesis and carbon fixation.

Table 3.4.5 Nutrient distribution in soil-plant systems

Position or form	Plant availability or form	Approx. amount (kg N/ha, 15 cm depth)
Soil organic matter	slowly available	850-1590-9000 Peat-1BGE, Podzols-YBL
Fixed in clay	unavailable, NH_4^+ in clay minerals (e.g. vermiculite)	30-100 Vc
Soil water	readily available to plant	60-120
Pasture plant (standing crop, 2000 kg DM)	NO_3^- & amino acids and protein (R.NH2)	80

[1]BGE = Brown-grey earth. Otago
YBL = Yellow-brown loam. Taranaki
Vc = in soils with clay fraction dominated by vermiculite

Table 3.4.6 Nitrogen cycle

Important Transformations	Implications

Biological fixation of nitrogen	Legume vigour causes N inputs to vary 20 kg N/ha/year in hill country to 300 kg N/ha/year in fertile lowland pastures
Immobilisation of mineral N (NO_3^- and NH_4^+)	Short term loss of available nitrogen leading to large reserves of soil nitrogen as pasture soils are developed
Mineralisation of soil organic matter $R\text{-}NH_2 \rightarrow NH_4^+ \rightarrow NO_3^-$)	A secondary and large source of plant available N in developed pasture soils responsible for large losses of N from cultivated soils
Nitrification ($NH_4^+ \rightarrow NO_3^- + H^+$)	Important acidification process in soils
Partitioning of 60-80% of N into urine	Ammonia volatilisation from urine spots- accelerated leaching loss of N

Test Your Knowledge

1. Examine the phosphorus and nitrogen cycles and draw up a list of the major differences in the cycling processes and chemical forms of each element.
2. Explain why urea fertiliser causes less acidification of soil than does ammonium fertiliser (Consult Figure 3.4.4).
3. Explain the role of urine patch size in the relatively greater loss of N from dairy pastures compared to sheep-grazed pasture.
4. Discuss the ways by which you can reduce the leaching losses of nitrogen in soils.
5. Discuss why the nitrogen cycle is an important process in the acidification of soils under legume based pasture.

Recommended Reading

Soil Science. R. M^{c}Laren and K. Cameron. Oxford University Press. (Read sections 14.1 - 14.4.7 , p 192 – 200).

3.5 Sulphur in Soils

Key Learning Objectives

After studying this section you should be able to explain:

1. The amounts and forms of S present in the soil/plant/animal system.
2. The form of S that is available to plants.
3. The source, process and rate of replenishment for the plant available form of S.
4. Processes that lead to S gains or losses in the system.
5. The forms and solubilities of S in the common phosphate fertilisers used in New Zealand.
6. The reactions and fate of different S fertilisers added to soil with respect to:
    - S availability to plants
    - The acidifying effects of S fertilisers

Introduction

Sulphur (S) is essential in forming plant protein because the amino acids cysteine and methionine contain sulphur. Sulpho-lipids are essential for membrane integrity. Sulphur- containing amino acids are in high concentrations in animal fibres. Adequate sulphur nutrition of pastures (~ 0.3% S) is essential for good wool production. The chemistry of S in soils involves similar processes to the P and N cycles. The reactivity of the inorganic anion sulphate for anion exchange sites on soil surfaces is midway between the strong adsorption of the orthophosphate ion and the weak almost non-existent attraction of nitrate. Like N, the main store of S in the soil is in soil organic matter and, also like N; S undergoes several chemical transformations (oxidation and reduction) in the soil, which the orthophosphate ion does not.

Sulphur in Soils

Some soil parent rocks (i.e. primary minerals) will contain sulphur mainly in the form of sulphides (S^{2-}; e.g. iron sulphide FeS). Concentrations in basic igneous rocks average 600 µg S/g. During weathering sulphides in surface soils are oxidised rapidly to sulphate (SO_4^{2-}) (Refer to Figure 3.5.1 for detail of the S cycle in soils). Over time, SO_4^{2-} is leached from soils in 'aquic' environments where rainfall exceeds evapotranspiration. Soils in such environments, when used continuously for agricultural production, develop S deficiency in crops and pastures.

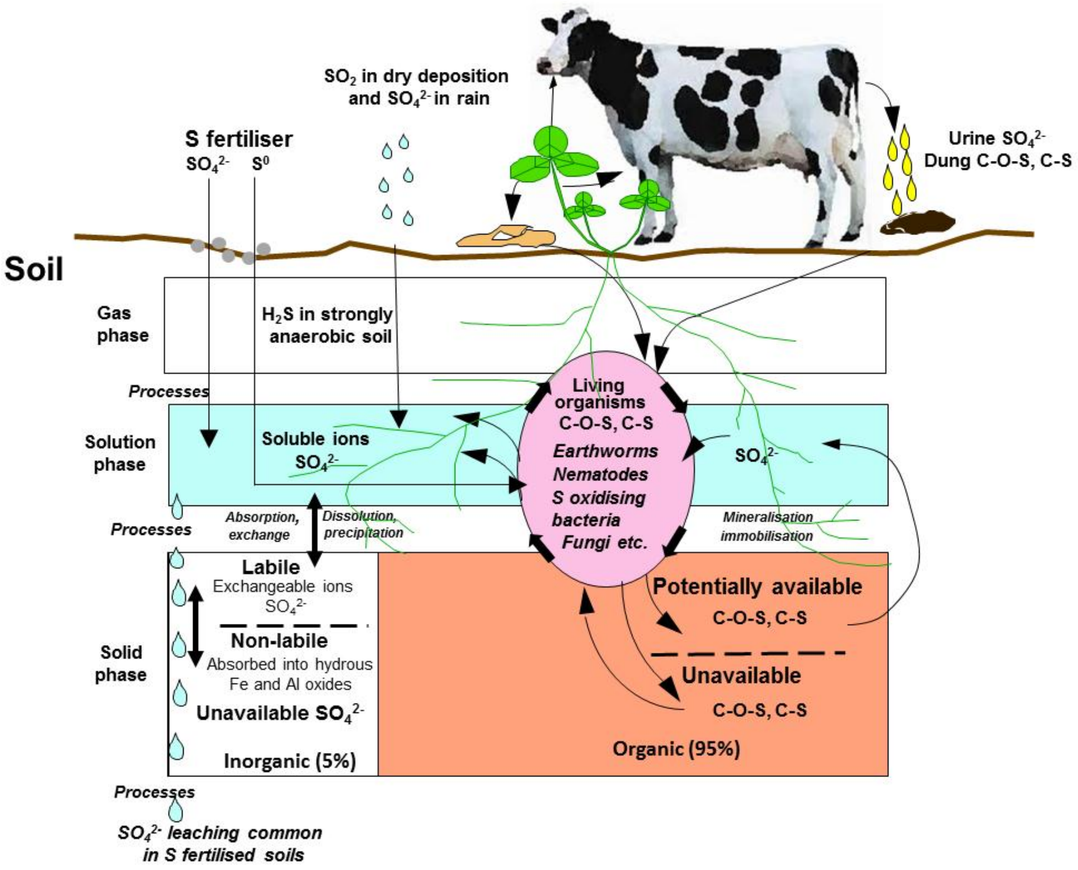


Figure 3.5.1 Sulphur cycling in the soil-plant-animal system

The other main input of S into soil/plant systems is through inputs of dry deposition and rainfall. Ledgard and Upsdell (1991) have published rainfall distribution relationships from the analysis of rainfall collected at various stations throughout New Zealand (Figure 3.5.2). Such a regular distribution may not apply to industrialised countries where the refining of oil and burning of fossil fuels produce large quantities of sulphur dioxide (SO_2) gas. Until SO_2 was scrubbed from the exhaust gases of Europe's power stations, Norway and Sweden suffered from acid rain (Sulphurous acid - SO_2 dissolved in rain) and much European farmland had adequate S inputs as SO_2 in dry deposition or acid rain. Compliance with recent 'clean air' acts and removing the SO_2 from exhaust gases is renewing the S fertiliser requirement in European agriculture.

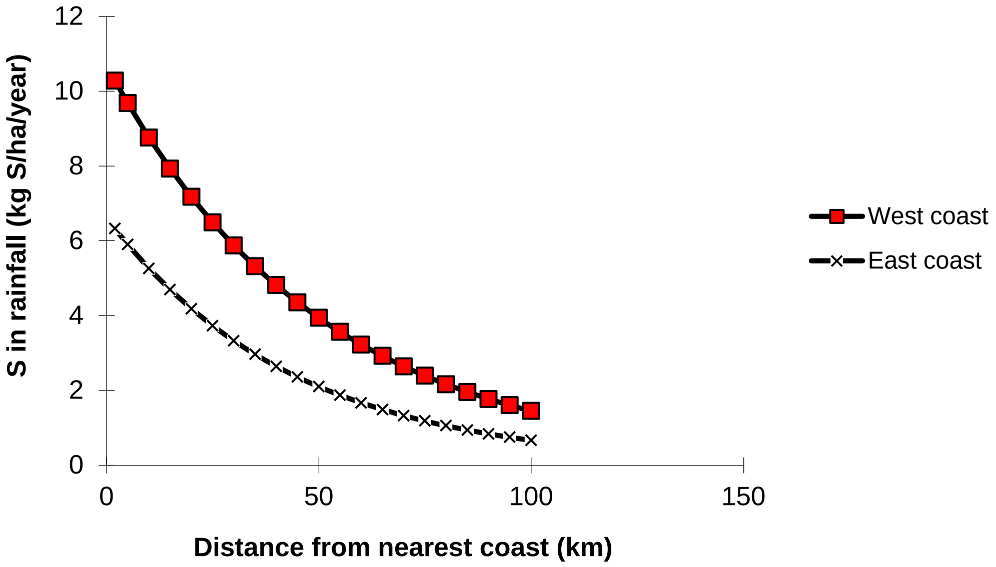


Figure 3.5.2 The influence of distance from coast on amounts of sulphur in rainfall in New Zealand.

A unique feature of the S cycle in New Zealand is that intermittent eruptions from Ruapehu may add elemental S in ashfall. In the 1995/96 eruptions, ash layers of 1 mm contributed up to 400 kg S/ha. The source of the elemental S is the geothermal steam that heats the crater lake. Once eruptions have discharged all the crater lake contents, the S content of subsequent showers decreases.

Sulphate is a common anion in fertiliser materials. For example, superphosphate is a mixture of calcium sulphate (gypsum form) and calcium phosphate. Ammonium sulphate, potassium sulphate and many trace elements are supplied in the sulphur form.

Amounts and Forms of S in Soils

In well-aerated soils S is mainly present in two forms:

- Organic S, R-SH or C-O-S (Figure 3.5.1), and
- SO_4^{2-} in soil solution and adsorbed onto clay minerals

It is common for organic S to be around 95% of total soil sulphur in most New Zealand soils, which may contain ~ 500 kg S/ha in a 10 cm depth.

Table 3.5.1 Nutrient distribution of S in soil-plant systems

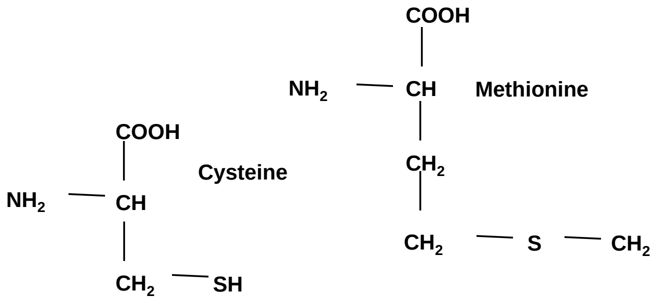
Position or form	Plant availability or form	Approximate amount (kg S/ha, 15 cm depth)
Soil organic matter	slowly available (non-labile)	200-2000
Soil water	readily available	[1]BGE-YBL10-30
Pasture plant (2000 kg DM)	inorganic + organic forms	[1]BGE-YBL 5

[1]BGE=Brown-grey earth, Central Otago; YBL=Yellow-brown loam, Taranaki

ORGANIC S

Organic S can be divided into two chemically identifiable fractions:

Carbon bonded S: including amino acids cysteine and methionine, as shown below:



Non-carbon bonded S including phenolic and choline sulphates as well as sulpholipids:

$(CH_3)_3N^+CH_2CH_2OSO_3^-$ Choline sulphate

The C:N:S ratio of soil organic matter is 125:10:1.2. Much of the S in soil organic matter is structureless polyanions in which the form of S has not been determined. These are decomposition products of plant and animal debris mixed with microbial residues. Unlike soil organic phosphate which can mostly be extracted in alkali, 30 – 40 % of organic sulphur in soils remains non-alkali soluble.

MINERAL S

It is uncommon to find significant quantities of sulphides in aerobic topsoils. Sulphides may appear temporarily after water-logging has made a topsoil, containing considerable organic matter, strongly anaerobic. Under these anaerobic conditions the decomposition of organic S may yield sulphides (e.g. tidal muds, subsoils) and H_2S gas (hydrogen sulphide – rotten egg smell).

Secondary sulphate minerals may be found in soils, particularly subsoils and in topsoils in arid regions or coastal sands. In New Zealand, these forms are only important in glasshouse soils where high rates of fertiliser and evaporation have caused sulphate minerals to form in the surface soil. Periods of flood irrigation are used to leach and reduce the concentration of these salts.

PLANT AVAILABLE FORM

SO_4^{2-} is the common ionic form of S in soil solution that is available for plant uptake. Plants require between 15 to 50 kg S/ha/year. Soil testing to measure plant available S utilises a weak solution of monocalcium phosphate, which displaces both weakly adsorbed sulphate and equal amounts of organic S. It is considered that this weakly adsorbed organic S will be rapidly mineralised to SO_4^{2-} and is considered to be part of the plant 'available' S measurement.

Processes Influencing the Plant Available Pool

Immediate source:

The immediate source of S is SO_4^{2-} present in the soil solution (Figure 3.5.1). In superphosphate fertilised pastures, SO_4^{2-} may be the dominant anion in the soil solution and drainage waters. As solution sulphate is taken up by plant roots, the concentration is replenished by:

Desorption of SO_4^{2-} from the soil clays

This combined labile pool (solution plus sorbed SO_4^{2-}) can be measured in soil tests by extracting soil samples with K_2HPO_4 or $Ca(H_2PO_4)_2$ solutions. The $H_2PO_4^-$ ions displace SO_4^{2-} ions from soil surface sorption sites where SO_4^{2-} may be sorbed by ligand exchange reactions or held less strongly by non-specific sorption to positively charged soil surfaces (the same hydrous oxide surfaces that are involved in P sorption). Pool size may vary from 2-400 mg S/kg soil. In soils with high anion sorption capacity (ASC or % P retention), pool size commonly increases with soil depth. This occurs particularly in allophonic soils (i.e. Yellow-brown loams) that have a good history of lime and phosphate fertiliser use. This is because phosphate ions compete for anion sorption sites, whereas, liming reduces soil surface positive charge. Both processes (competing anion and reduced soil surface positive charge) will desorb/exchange SO_4^{2-} ions from soil surface sorption sites.

Mineralisation/Immobilisation

Mineralisation of organic sulphur releases SO_4^{2-} to be plant available. These transformations to and from organic soil S parallel those of the mineralisation and immobilisation processes of the N cycle.

$$\text{Organic S} \xrightarrow[\textit{bacteria, fungi}]{\textit{mineralisation}} SO_4^{2-}$$

$$SO_4^{2-} \xrightarrow[\textit{plants, bacteria, fungi}]{\textit{immobilisation}} \text{protein S, lipid S, etc.}$$

Net mineralisation is likely to occur when the C:S ratio of the substrate, being decomposed by soil bacteria and fungi, is below 200:1 (e.g. healthy clover). Soil SO_4^{2-} will be released into solution but unlike NO_3^-, which mainly accumulates in soil solution, most SO_4^{2-} will accumulate in the sorbed form. Given this fact, do you think SO_4^{2-} will be leached from the topsoil as easily as NO_3^-?

Decomposition of straw or litter with less than 0.15% S (C:S > 200:1) may temporarily immobilise SO_4^{2-} from soil solution.

Oxidation of elemental S^o

Natural populations of sulphur-oxidising bacteria occur in New Zealand soils. This allows elemental S (S^o) fertilisers to be used. The slow oxidation of fertiliser S^o by the autotrophic bacteria, thiobacillus, and some heterotrophic organisms, will yield plant available SO_4^{2-}. The sulphur oxidising organisms that are common in New Zealand soils, will oxidise either S^{2-} (sulphides), or S^o to sulphate. See a fuller discussion under elemental S fertilisers.

$$S^{2-}, S^{o} \xrightarrow{\textit{oxidation,} \quad \textit{thiobacillus-sp.}} SO_4^{2-}$$

Leaching of sulphate

Sulphate is not strongly adsorbed by most New Zealand topsoils unless they have very high anion retention characteristics, such as Allophanic soils, Yellow-brown loams (YBL) or red and brown loams. Even in these soils of high anion retention, if P fertiliser has been applied, or if they have high organic matter contents (i.e. a high surface negative charge in the topsoil), sulphate will not be retained in the topsoil but will be leached to the more positively charged subsoil. It is common in YBLs for sulphate to accumulate in the subsoil to concentrations of 200 – 400 ppm S. In many cases, this S (below the main pasture root-zone) is believed to have limited availability to common pasture plants. In Pallic soils and Yellow-grey earths (YGEs) the sulphate will be leached further down the profile. The S lost in leaching will be dependent on the amount of S fertiliser added to each soil, the timing and frequency of rainfall after fertiliser application, and the rates of sorption and immobilisation in topsoil (See Sections 5.1 and 5.2). Sulphate leaching is also accelerated because approximately 60% of the S excreted by the grazing animal is returned in the urine patch as $SO_4^{=}$. This saturates anion sorption capacity in the soil and $SO_4^{=}$ leaves in drainage water. A similar fate to NO_3^-.

S Fertilisers and Their Reactions in Soils

Sulphur added to soils through fertilisers needs to be converted to the SO_4^{2-} form for it to become available for plant uptake. In New Zealand, most S is added as SO_4^{2-} through superphosphate and limited use of S-containing fertilisers such as ammonium sulphate, potassium sulphate, and magnesium sulphate (Epsom salts or kieserite) and as $S^0+SO_4^{2-}$ through sulphurised superphosphates. In all but extreme S-leaching environments, the traditional use of superphosphate to remove P limitations has provided sufficient S for pasture growth. In recent years, the increasing use of S-free N (e.g. urea) and P fertilisers (e.g. triple superphosphate, RPR and DAP) has increased the awareness that S deficiencies in crops and pastures could resurface.

COMMON S FERTILISERS

Sulphur fertilisers are available in different forms that include fast release (water-soluble), slow release (water-insoluble) and mixed fast and slow release (Table 3.5.2). The important fast release fertilisers which contain S in the SO_4^{2-} form include potassium sulphate (18%

S), ammonium sulphate (24% S), ammonium sulphate nitrate (14% S), single superphosphate (12% S) and gypsum (19% S).

In single superphosphate, S is present as gypsum ($CaSO_4.2H_2O$). Elemental S is the major source of slow release S fertiliser, which is available in the form of both powder (flowers of S) and prills with a range of particle sizes. When elemental S is mixed with soluble S fertilisers (e.g. sulphurised superphosphate) the products supply both fast release and the slow release S forms. In these products, elemental S is dry blended or incorporated in the form of molten S. The most common product is sulphurised superphosphate in which the elemental S is added as a molten mixture during acidulation of the rock phosphate with sulphuric acid. The total S content of these products depends on the amount of elemental S added and a range of sulphurised superphosphate grades is currently available in the market.

REACTIONS OF SULPHATE SULPHUR FERTILISERS

Fertilisers containing sulphate S include single super phosphate, gypsum, potassium sulphate, ammonium sulphate, and magnesium sulphate. The last three are readily soluble in water. In single superphosphate, sulphur is present as gypsum ($CaSO_4.2H_2O$). Although gypsum is considered to be soluble, it dissolves slowly in the soil solution. It takes up to a month for a moist soil surface to supply sufficient water (from the soil or via rain) for the gypsum component of a 2 mm superphosphate granule to fully dissolve. This is the reason why gypsum shells of superphosphate remain on the soil surface, long after the more soluble calcium monophosphate has moved into the soil. The sulphate ions released from fertilisers undergo adsorption and immobilisation reactions similar to resident soil sulphate discussed earlier (Figure 3.5.1).

Table 3.5.2 Common sulphur fertilisers currently being used in New Zealand

Product Name (N-P-K-S)	**Fertiliser component**	**S components**		**Other nutrients and important incidental components**			
		Soluble	**Sparingly soluble**				
Elemental sulphur (S^0) (0-0-0-100)	S^0		S^0				
Maxi Sulphur Super 50 S (0-5.1-0-50)	S^0, SSP	$CaSO_4$ SO_4-S 6.4%	S^0	MCP-P	Ca	F	Cd
Sulphur Super extra (0-7.2-0-29)	S^0 ,SSP	$CaSO_4$ SO_4-S 9.2%	S^0	MCP-P	Ca	F	Cd
Superphosphate (0-9.0-11.5)	SSP	$CaSO_4$		MCP-P	Ca	F	Cd
Ammonium sulphate (AS) (20.5-0-0-24.0)	AS	$(NH_4)_2SO_4$		NH_4-N			
Gypsum (0-0-0-19)	Gypsum	$CaSO_4$			Ca		
Sulphate of potash (SP) (0-0-42-17)	SP	K_2SO_4		K			
Pasturezeal (3-9.6-0-10)	SSP, urea	$CaSO_4$		MCP-P	Urea-N	F	Cd
Cropmaster 20 (19.5-10-0-12.5)	DAP, AS	$(NH_4)_2SO_4$		HPO_4-P		F	Cd
Kieserite (0-0-0-16) 16% Mg	Kieserite	$MgSO_4$		Mg			

In most New Zealand soils, SO_4^{2-}-carrying fertilisers provide adequate S nutrition, particularly in soils derived from volcanic ash (Allophanic soils, Brown-granular clays, Red and brown loams). In some of the other soils, such as Pallic soils, Yellow-brown sands, and pumice soils, SO_4^{2-} adsorption is low and, hence, S is liable for leaching when added in SO_4^- form. In these soils elemental S containing fertilisers are considered to be more suitable.

In general, fertilisers containing sulphate S are recommended for pasture establishment, whereas, fertilisers containing elemental S are more suitable as a maintenance source.

ELEMENTAL SULPHUR

Elemental sulphur is incorporated into fertilisers to:

- provide a slow release form of S in soils prone to leaching conditions,
- to produce high analysis S or PKS fertilisers that have low transport costs.

For the S in elemental S to become plant available it needs to be converted to SO_4^{2-}. This conversion process is known as S oxidation and is brought about by certain soil micro-organisms.

Oxidation of S^0

Oxidation of elemental sulphur to sulphate S is achieved by two processes which include chemical (abiotic) and microbial (biotic). At ambient temperatures and pressures, the microbial oxidation is the predominant process in soils and is carried out by *chemoautotrophic* bacteria (genus Thiobacillus) and *heterotrophic* (Fungi and actinomycetes) soil organisms.

$$S^0 + 2O_2 \rightarrow SO_4^{2-} + 2H^+ \qquad \text{(Equation 1)}$$

Factors affecting S° oxidation rates:

Oxidation of S° requires:

i) an exposed *surface* of S^0 particles
ii) a thin film of *water* on the surface of S^0 particles in which the microbes can live
iii) the presence of S^0 oxidising *microbial organisms*
iv) diffusion of O_2 from the soil atmosphere through the water film
v) diffusion of CO_2 to supply a C source for the growth of the microbes
vi) diffusion of H^+ and SO_4^{2-} ions through the water film into the surrounding soil for removal of *reaction products*
vii) diffusion of the *nutrients* to the reaction site to sustain the microbial growth

The rate of S^0 oxidation is affected by elemental S, soil and climatic factors. The three most influential factors are:

i) *Particle size:* The surface area of elemental S particles in contact with soil micro-organisms is important for oxidation, and hence the finer the particle size, the faster the rate of oxidation of elemental S. In New Zealand's climate, the S^0 particle size must be less than 150 µm for oxidation to supply the fertiliser S within one year.

ii) *Soil Moisture:* The rate of S^0 oxidation is optimum at 'field capacity' of the soil and decreases both at the high and low moisture contents. High moisture content results in low aeration and thereby reduces the supply of O_2 for S^0 oxidation. At the low moisture content the diffusion of nutrients ions to microbes is limited thereby decreasing the rate of oxidation.

iii) *Soil temperature:* S^0 oxidation is slow < 4°C. In short term experiments it increases exponentially up to 40°C and at long-term experiments it increases linearly with temperature.

$$K = ab^t$$

$$K = a + bt$$

where K is the rate of S oxidation, t is temperature and a and b are constants.

Use of S^0 fertilisers in New Zealand:

Based on the soil temperature and moisture, New Zealand can be divided into three climatic regions for which different elemental S particle sizes are recommended for application. Ideally the oxidation should take place at a rate that releases sufficient $S0_4^{2-}$ for plant uptake without causing leaching problems. In general, bigger particle sizes are used for warm and moist conditions in which microbial activity is high and smaller particle sizes are used for cool and dry conditions. To maintain the long-term availability of S the products should contain a range of elemental S particle sizes.

There are *two major concerns* regarding the use of elemental S. Firstly, the use of *finely ground elemental S* on its own creates *an explosive fire hazard* and is, therefore, unsuitable for aerial topdressing. Prilled or granulated elemental S products are developed to overcome this problem. In addition to sulphurised superphosphates, another product that is in commercial use is an S bentonite prill. This product is produced by mixing bentonite clay with molten elemental S. The prills are safe to use on their own and disperse easily on wetting to release the fine elemental S particles for oxidation.

The second concern is that *microbial oxidation of elemental S* produces acid resulting in *soil acidification*. Approximately a maximum of 3.2 kg lime is required to neutralise the acidity produced by 1 kg elemental S. At a rate of 40 kg S per hectare approximately 500 kg lime about once every 4-5 years would be required to overcome the acidity problems associated solely with the regular use of elemental S.

S^0 oxidation, RPR dissolution and ammonia conservation:

Granulation of RPR with S^0 not only supplies S and P but also the release of protons during S^0 oxidation which increases the rate of dissolution of the RPR. This effect is known as 'biosuper' effect. Similarly, when elemental sulphur is mixed with poultry manure the protons released during the oxidation of S° can be utilised to reduce the loss of ammonia from poultry and animal manures.

Other S sources

EFFLUENT AS A S SOURCE

Approximately 60% of excreted S is excreted in animal urine and this highly concentrated S source is susceptible to leaching. Animal urine contains both organic and inorganic forms of S and like P, research has shown that the amount of S excreted is related to the amount of S ingested in the animals diet. It is important to consider the amount of S which is being applied to land as effluent using a nutrient budget, as excess S in a farm system can lead to increased S leaching losses.

BROUGHT IN FEED AS A S SOURCE

In contrast to P, K and N, the concentration of S in supplementary feed is generally low (Table 3.5.3). However, it is important to consider these S sources when calculating a nutrient budget as a 100 ha dairy farm importing 250 tonnes (dry matter) of pasture silage, would potentially add 5 kg S/ha/year to soil if 85% of the ingested S was excreted evenly across the farm.

Table 3.5.3 S contents of common animal feeds.

Supplement	**S % (dry weight basis)**
Maize silage	0.13
Pasture silage	0.24
Pasture hay	0.26
Palm Kernel Meal	0.21
Maize grain	0.12
Barley grain	0.17

**Data from Gourley et al. (2010) and Kolver (2000).*

References

DairyNZ FarmFact (2008). 1-71 Palm Kernel Extract (PKE) http://www.dairynz.co.nz/file/fileid/36249

Gourley CJP, Dougherty WJ, Aarons SR, Hannah M (2010) Accounting for Nutrients on Australian Dairy Farms. Department of Primary Industries, Ellinbank, Victoria. pp. 50-52. Final Report.

Kolver, ES (2000) Nutritional guidelines for the high producing dairy cow. Proceedings of the Ruakura Farmers' Conference 51, 78-87, 2000.

Ledgard, SF and Upsdell, MP (1991) Sulphur inputs from rainfall throughout New Zealand. New Zealand Journal of Agricultural Research. 34, 104-111.

Revision on Sulphur

The purpose of the following section is to check your understanding of the S cycle and of the S sources and their reactions in soil.

Source:

- Present in sedimentary rocks as sulphides and sulphite, highest content in shales and slates
- Rainfall increases with proximity to coast
- Soil organic matter
- Fertilisers (superphosphate, elemental S^0)
- Brought in feed supplements

Plant available form:

- SO_4^{2-} (sulphate ion)

Role in plant:
Essential for protein synthesis, particularly important for efficient nitrogen fixation in legumes.

Table 3.5.4 Sulphur cycle

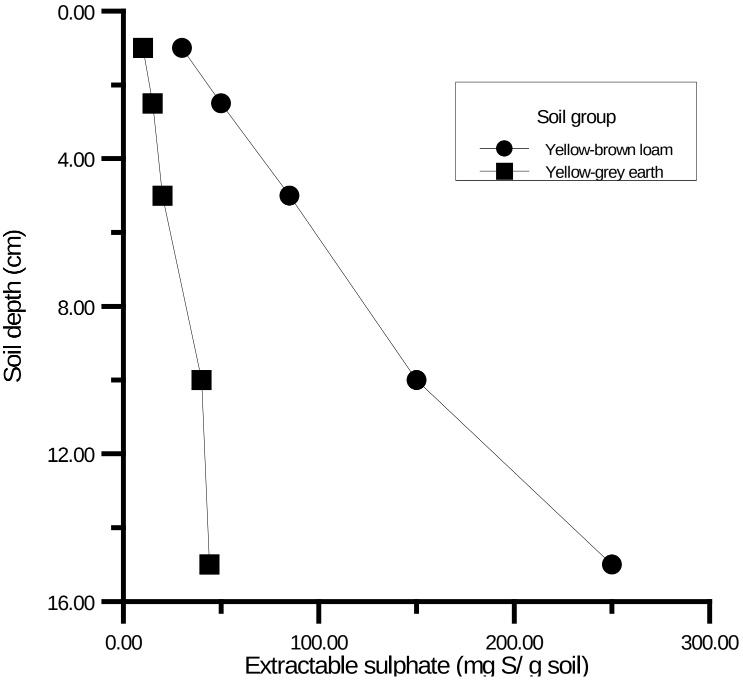
Important transformations	Implications
Sulphate inputs in rainfall	areas closer to coast have lower fertiliser requirements (1-10 kg S/ha/year)
Weak adsorption of sulphate by Fe and Al oxides and alumino silicates	in most soils sulphate is easily leached – sulphate may accumulate in subsoils that contain large amounts of short range order minerals e.g. YBL
Immobilisation of sulphate into soil organic matter	short term loss of available sulphate leading to a large reserve of soil sulphur as pasture soils are developed
Mineralisation of soil organic matter	main source of plant available sulphur in developed pasture soils
Partitioning of 60% of S into animal urine	important loss mechanisms which increases susceptibility of sulphur to leaching loss and loss by animal transfer

Table 3.5.5 Assessment of Soil S Status

Form of S	Test	S extracted
Index of plant available S	Weak solution of monocalcium phosphate	weakly adsorbed sulphate and very small amounts of organic S may be included
		Soil test incorporates organic S in extract as part of 'available' S measurements; inorganic and organic S done by ICP, inorganic S above done by HPLC

Test Your Knowledge

1. Explain the differences between the extractable sulphate concentrations measured for the Allophanic (Yellow-brown loam) and Pallic (Yellow-grey earth) soils in the figure below. Both soils have received 250 kg of superphosphate per year for 40 years. Superphosphate contains 12% S as sulphate.



2. Discuss the climatic and the soil conditions in which elemental sulphur fertiliser is used as a source of sulphur.

Recommended Reading

Fertilisers and Soils in New Zealand Farming. C During pp 79-91. *Information from New Zealand pastoral experiences.*

Soil Science. R. M^{c}Laren and K. Cameron. Oxford University Press. (Read 16.1 to 16.4, p 221-226).

3.6 Other Factors Affecting Nutrient Availability and Loss

Introduction

In earlier sections, we described the main forms of nutrient reserves in soils. In this section we highlight some of the factors controlling the rate of nutrient release and uptake by plants in soils. A soil is a dynamic mixture of minerals, organic residues and living micro- and macro-organisms. Soil properties that influence soil fertility status are not static.

The important factors which influence soil during soil development and through current farming practices are shown in Figure 3.6.1. In this brief discussion we will concentrate on soil acidity.

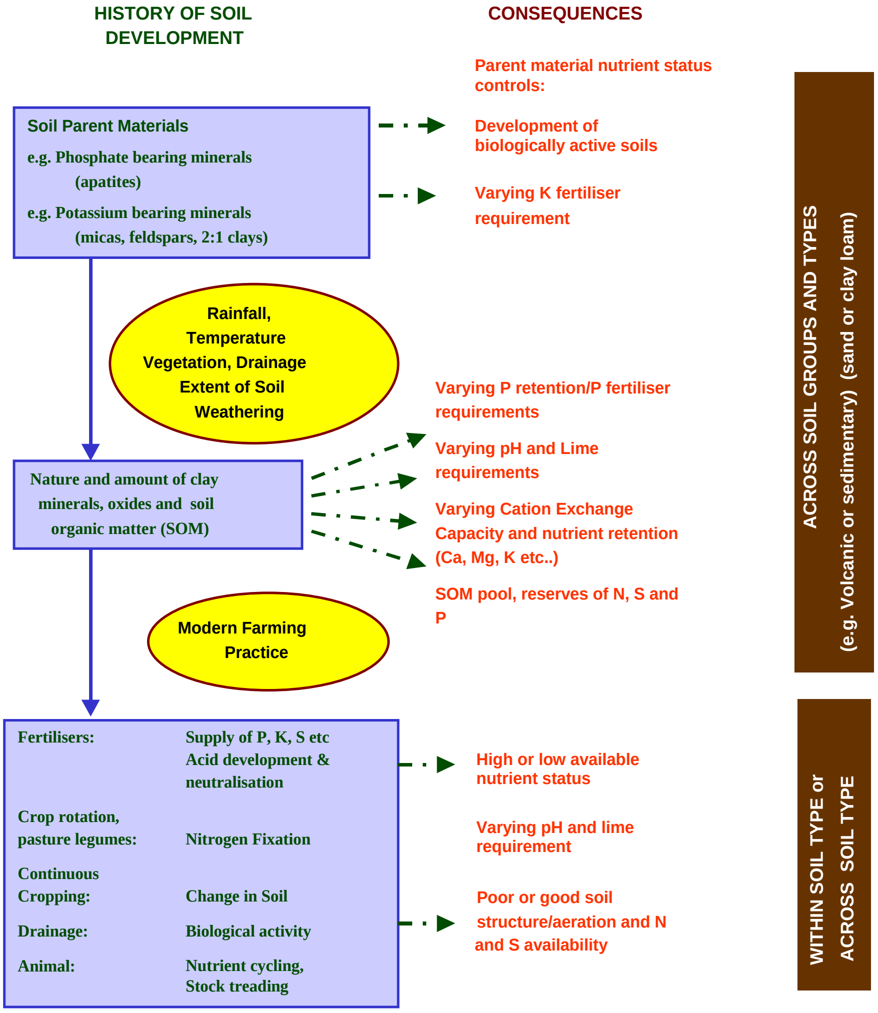


Figure 3.6.1 Main factors affecting nutrient retention and plant availability

The influence of soil acidity on plant nutrition

Many agricultural and garden plants will not grow well in acid soils. Therefore it is important to understand what soil acidity is, how soil acidity is formed and how to reduce the negative effects of soil acidity on plant growth. The reasons for the effects soil acidity has on plant root growth and nutrient availability to plants are summarised in Figure 3.6.2.

Severe problems are caused when soils are so acid that either most Ca has been lost in drainage from the soil, or, the acidic conditions have increased the solubility of previously insoluble Al and Mn. The most important biological processes that become inhibited are plant root growth (Ca is required for the elongation of new roots, and high concentrations of Al^{3+} ions instead of Ca^{2+} in the soil water stop root growth), infection of clover root nodules by nitrogen fixing bacteria and the activities of bacteria responsible for the turnover and decomposition of plant and animal remains.

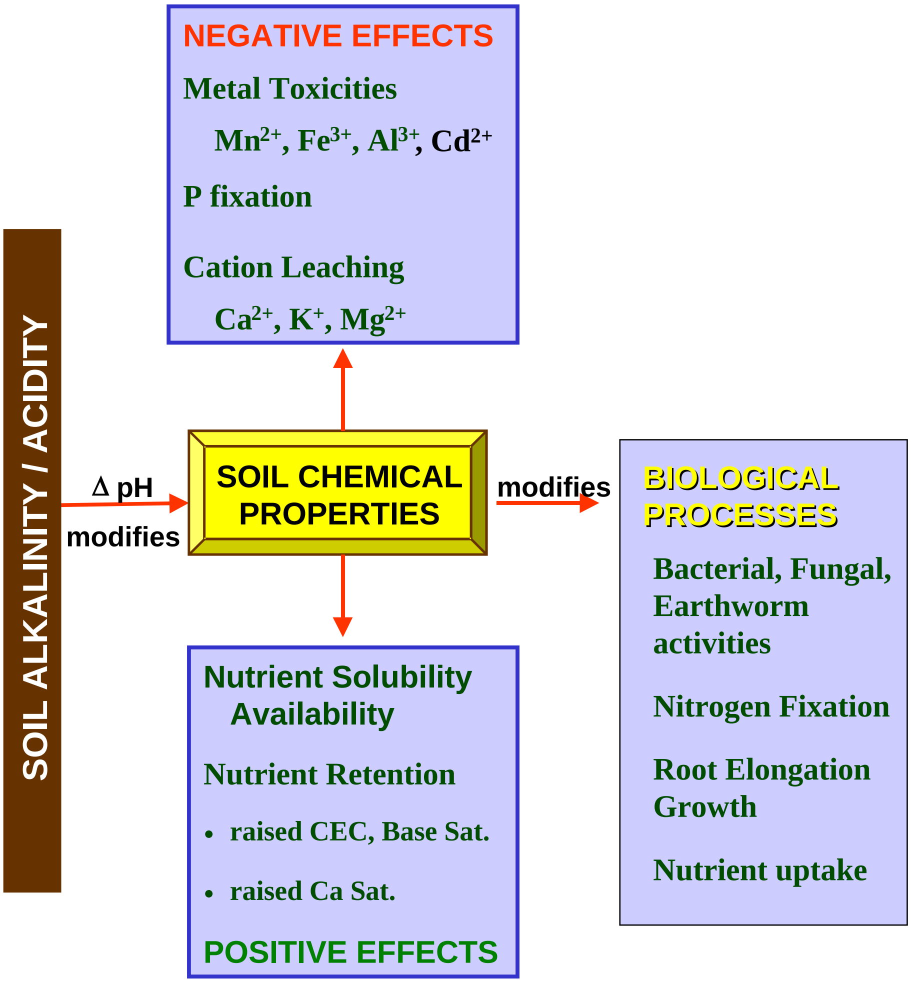


Figure 3.6.2 Negative effects of soil acidity and positive effects of overcoming soil acidity on nutrient availability, metal toxicity and plant growth.

Development of Soil Acidity

The development of soil acidity is a natural process. It is the process that naturally weathers elements from the parent minerals. Most acid is produced by micro-organisms and plants from the transformations of carbon and the nutrient nitrogen. In climates where drainage occurs most soils will become acidic with time.

Increasing the amounts of carbon and nitrogen used by growing plants, as is done in agricultural production systems, usually leads to accelerated soil acidification. This acid accumulates as exchange acidity (Al^{3+} and H^+) on the cation exchange sites on the soil particles.

Review of fertilisers and their role in acidifying soils

Soil acidification can be accelerated directly by the application of acid-forming fertilisers (S^0 – Section 3.5) and ammonium base fertilisers (Figure 3.4.4). Whether plant roots acidify their root zone is mainly controlled by the form of nitrogen they take up. Uptake of NH_4^+ will lead to acidification through H^+ counter-ion extrusion from roots, whereas NO_3^- uptake leads to a pH increase through OH^- counter-ion extrusion. Host soil acid is generated through leaky carbon (C), nitrogen (N), and sulphur (S) cycles. For example, if the form of the element entering the cycle is more positively charged (e.g. NH_4^+ fertiliser) than the form leaving (e.g. NO_3^- leaching), then H^+ ions are left to acidify the system (Figure 3.4.4).

Measurement of Soil Acidity

To maintain the healthy growth of plants and soil organisms, from time to time lime must be added to neutralise the exchange acidity. To know how much lime is required we must have a method of measuring how acid a soil is. This method is called the pH test. Soils behave like weak acids and in the simplest terms, acidic soils are soils that can donate hydrogen ions to the soil water molecules, forming hydronium ions in the soil water.

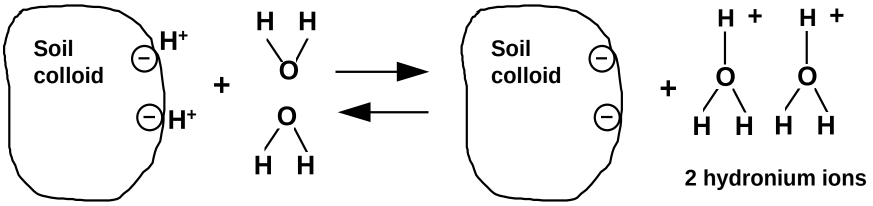


Figure 3.6.3 The formation of hydronium ions in an acidic soil

The more acidic a soil, the higher the concentration of hydronium ions in the soil water. In the most acidic New Zealand soils the concentration of hydronium ions is at least 10,000 times greater than in the least acidic (or most basic) soils. Because of this enormous range in concentration a logarithmic scale is used to describe acidity. This scale is termed the pH scale.

$$pH = -\log[H^+]$$

Where $[H^+]$ is the concentration of hydronium ions in the soil water.

The key point to grasp is that when acidity is expressed in terms of pH, a scale is obtained on which pH=7 is considered the midpoint. If the pH is less than 7 the solution is said to be acidic. If the pH is greater than 7 the solution is said to be basic. pH 7 is therefore the "neutral point".

Concentrated solutions of strong acids, such as sulphuric acid, have pH values < 1 while concentrated solutions of strong bases, such as sodium hydroxide (caustic soda), have pH values approaching 14.

Figure 3.6.4 gives an indication of the degree of acidity, or pH, of a number of common liquids. We observe from this figure that virtually all New Zealand soils have pH values between 4 and 8. In fact, the vast majority have pH values between 5.0 and 6.5, i.e. they are slightly acid.

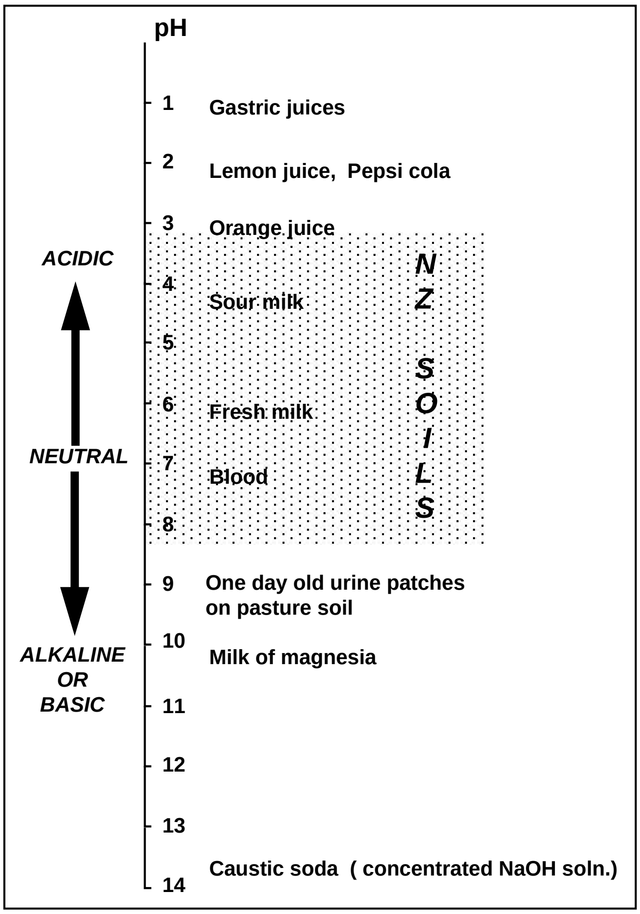


Figure 3.6.4 The pH of a number of common liquids.

When we talk of "Soil pH" we are referring to the pH we obtain when a sample of soil is stirred with a relatively large volume of water. In New Zealand the test is carried out by mixing 10 g of air-dried soil with 25 ml of distilled water and then measuring the pH - usually with a special electrode and meter.

SOIL pH BUFFERING AND RESERVE ACIDITY

Mineral dissolution

To some extent the soil minerals will neutralise the acid produced by plants and micro-organisms. For example, soils developed on limestone are likely to contain some calcium carbonate ($CaCO_3$) which can "mop up" acidity. This is because $CaCO_3$ is a basic salt - it dissolves in water to form a strong base ($Ca(OH)_2$) and weak acid (H_2CO_3), so the net effect is a basic or **alkaline** solution. Whereas acidity is related to the concentration of H^+ ions, alkalinity is related to the concentration of **hydroxyl ions** (OH^-).

The reaction for $CaCO_3$ dissolving in water may be written:

$$CaCO_3 + 2H_2O \Leftrightarrow Ca(OH)_2 + H_2CO_3$$

$$OH^- \text{ ions, from the dissociation of } Ca(OH)_2$$

$$Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2OH^-$$

$$\text{neutralise excess } H^+$$

$$2OH^- + 2H^+ \Leftrightarrow 2H_2O$$

Some soil minerals such as silicates have very little neutralising value; hence soils formed on rocks that have high silica contents tend to be quite acidic. In these soils H^+ ions react and weather the silicate minerals resulting in the production of aluminium hydroxides and aluminium hydroxide polymers and free aluminium ions as the conditions become more acidic. The free aluminium ions (Al^{3+}) are toxic to plant roots.

$$Al^{3+} + H_2O \Leftrightarrow AlOH^{2+} + H^+$$

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

$$Al(OH)_2^+ + H_2O \Leftrightarrow \underbrace{Al(OH)_3}_{\text{insoluble compound}} + H^+$$

Exchange acidity

Hydrogen ions will also exchange with nutrient cations held on the negatively charged surfaces of the clay mineral and organic colloid surfaces (see earlier Figure on cation exchange, and Section 3.3 on Potassium in Soils).

As more acidity is produced, more nutrient cations are displaced into soil solution where they are susceptible to leaching. Very acidic soils therefore have their cation exchange sites mostly full with acidic cations H^+ and Al^{3+}. Such soils are said to have a low *Base saturation (BS) or % Base saturation (% BS)* (Table 3.6.1). At high pH, BS is high and vice versa.

Table 3.6.1 Approximate Percentage base saturations at different levels of soil pH.

Soil pH	% Base Saturation (% BS)
7	~ 100
6	70
5	30
4	20

Optimum soil pH (0-7.5 cm soil depth) for pasture production is 5.8 to 6.1 for mineral soils and 5.0 for organic soils (peat). These pH's represent conditions where little Al^{3+} is on exchange sites and therefore non-toxic to plants.

WHY ARE WE CONCERNED ABOUT SOIL PH?

Textbooks tell us that in excessively acid soils, one or more of the following effects may be observed.

1. Some plants simply do not grow well at low pH (i.e. they are not adapted and partly because low Ca and high Al concentrations prevent root elongation).

2. The activities of many of the following soil organisms are reduced:
   Nitrogen-fixing bacteria
   Bacteria that convert ammonium to nitrate
   Organisms that break down organic matter.

3. Elements such as aluminium and manganese become so soluble they are toxic to plant growth.

4. Cadmium becomes more soluble and is taken up by plants in large quantities. The products derived from these plants (including animal offal products), are a potential source of toxicity (See Section 6 – Issues of Contaminants in Fertilisers and By Products).

5. Phosphorus and molybdenum may become insoluble and unavailable.

6. A low pH may indicate low levels of calcium and magnesium present.

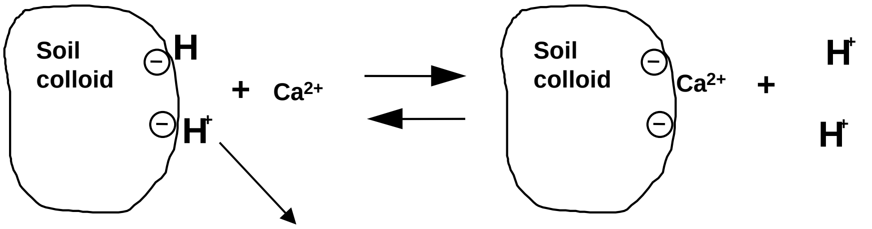
7. Various agricultural chemicals, especially certain herbicides and nematicides, are less effective.

You should note that there is no such thing as a "correct pH" because different plants have different pHs at which they grow best.
It is stated in point 5 above, that at low pH, phosphorus and molybdenum may become insoluble and unavailable. The implication is that if the pH is increased (by liming) then phosphorus and molybdenum will become more available. It should be noted however, that liming will only increase the amount of plant-available molybdenum on soils which have a reserve of molybdenum. There are some soils in New Zealand (e.g. some highly weathered "gumland" soils of Northland and deep acid peats in the Waikato) that have no reserve molybdenum and hence liming has no effect on the amount of plant-available molybdenum. In such cases molybdenum must be applied as a fertiliser.

Similarly, an increase in the availability of phosphorus can only be expected on soils which have accumulated a reserve (in this case organic phosphorus or inorganic "fixed" phosphorus) of this element. This effect is known to occur to some extent on soils in the Manawatu and Wairarapa regions, but its extent on other soils is not known.

Liming to overcome soil acidity

Soil acidity is normally overcome by the addition of lime. The complete reaction for lime (CaCO3) neutralising soil acidity is complex. The first stages of the process were given in the preceding subsection. However, additional reactions that occur are the displacement of exchangeable H^+ ions from the clay colloids by Ca^{++} ions:



$$2OH^- + 2H^+ \Leftrightarrow 2H_2O$$

$$2OH^- + Ca^{2+} \Leftrightarrow Ca(OH)_2$$

$$CaCO_3 + 2H_2O \Leftrightarrow Ca(OH)_2 + H_2CO_3$$

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow HCO_3^- + H^+$$

Since the CO_2 gas can escape from the reaction site, this series of reactions tends to be driven to the left.

It should be clear from the complete set of reactions above that lime neutralises both H^+ ions in solution and H^+ ions on the soil colloids. This means that to become neutral a soil will use up more $CaCO_3$ than can be calculated from the estimated amount of H^+ ions in the soil solution (i.e. the pH measurement).

This added effect that causes the soil pH measurement to resist change when liming materials are added is called **pH buffering**. The capacity of a soil to buffer its pH (i.e. resist change in soil acidity) depends on how much acidity is held on the soil surface. That is to say it depends on its CEC (see Cation Exchange Capacity notes), which in turn depends on its clay and organic matter content.

A soil will be more buffered if it has fine texture (e.g. a clay loam) and/or high organic matter content, and will consequently require more lime to raise the pH by a certain amount. As a general guide, approximately 3 tonnes/ha of lime ($CaCO_3$) will raise the pH from 5.5 to 6.0 on clays and silt loams derived from sedimentary parent materials and with organic carbon contents of between 4 to 8% or organic matter contents of 8 to 16% respectively.

In very acidic soils, generally with pH less than 5, H^+ concentration in soil solution is a product of the hydrolysis of Al^{3+}

$$Al(H_2O)_6^{3+} \rightarrow Al(H_2O)_5OH^{2+} + H^+ \rightarrow Al(H_2O)_4(OH)_2^+ + 2H^+$$

The continued removal of H^+ from the soil solution will ultimately result in the precipitation of Al^{3+} and its replacement from the adsorbed sites with Ca^{2+}.

LIMING MATERIALS

Definition:

Materials which can be added to soil to neutralise the acidity (protons, H^+ ions) in soil solution.

Liming materials:

- Calcium oxide - burnt lime
- Calcium hydroxide - slaked lime
- Calcium carbonate - lime/calcite
- Basic slag - silicates (animal poisoning)
- Fluidised bed boiler ash
- Dolomite - calcium magnesium carbonate

Neutralising value of liming materials:

Is expressed in terms of:

- Calcium carbonate equivalent (CCE):
- Ca and Mg contents
- Ca and Mg oxide contents

Calcium Carbonate Equivalent (CCE)

CCE is defined as the acid neutralising capacity of an agricultural liming materials expressed as a weight percentage of pure calcium carbonate.

$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$

100 g $CaCO_3$ neutralises 72 g of HCl

$MgCO_3 + 2HCl \rightarrow MgCl_2 + H_2O + CO_2$

84 g of $MgCO_3$ neutralises 72 g of HCl

84 g of $MgCO_3$ is equivalent to 100 g $CaCO_3$ in terms of neutralisation

100 g of $MgCO_3$ is equivalent to $(100/84)*100 = 119$ g $CaCO_3$ in terms of neutralisation of acid

Liming value of $MgCO_3 = 119$

Table 3.6.2 CCE of liming materials

Liming materials	Chemical formula	Neutralising value
Burnt lime	CaO	179
Slaked lime	$Ca(OH)_2$	136
Dolomite	$CaMg(CO_3)_2$	109
Lime	$CaCO_3$	100
Slag	$CaSiO_3$	86

Table 3.6.3 Lime conversion factors

From	To	Multiply by
Ca	CaO	1.4
Ca	$CaCO_3$	2.5
Mg	MgO	1.67
Mg	$MgCO_3$	3.5
Mg	Ca	1.67
Mg	$CaCO_3$	4.17
MgO	$CaCO_3$	2.5
$MgCO_3$	$CaCO_3$	1.19

Dissolution of liming materials in soils

Depends on the characteristics of both the liming materials and the soil.

Liming materials

Reactivity and particle size

Soil characteristics

pH and calcium saturation

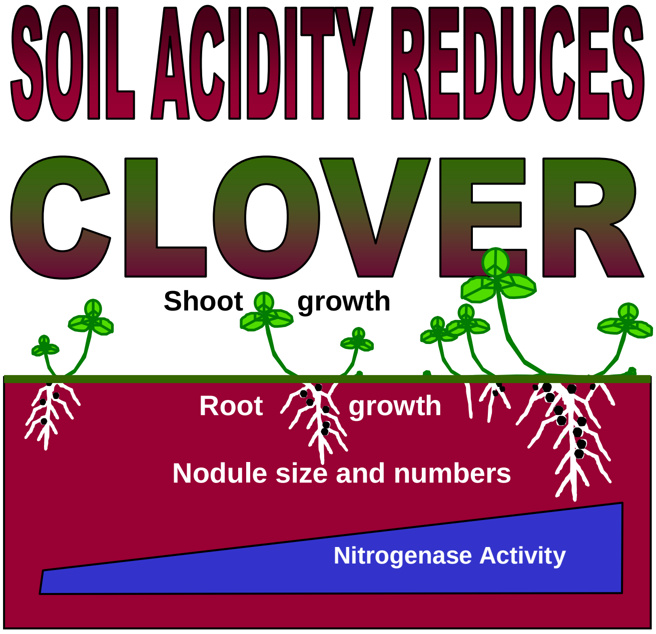
Effects of liming materials

Direct

- Increases the pH and thereby increases the pH - induced surface negative charge
- Reduces soil acidity and thereby decreases the activity of Al and Mn
- Increases the retention of cations and thereby decreases their leaching

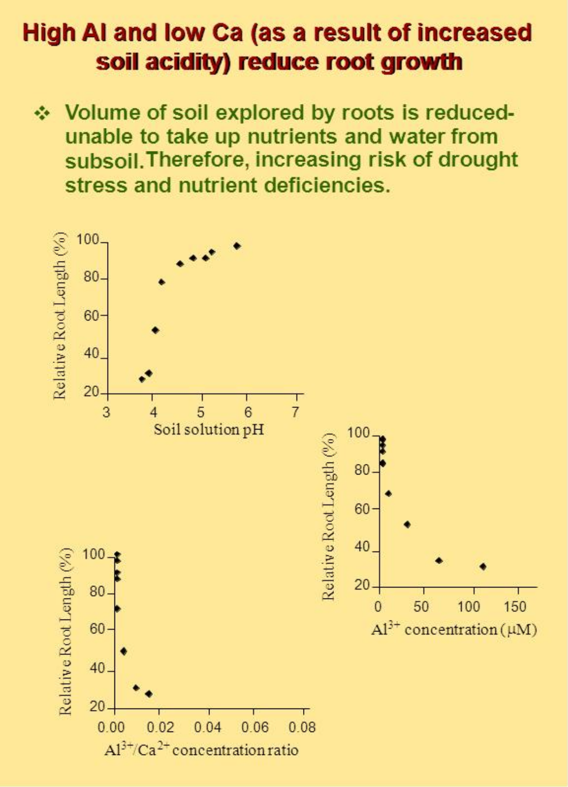
Indirect

- Decreases the solubility of heavy metal cations and their uptake
- Increases the solubility of anions, such as molybdenum and phosphorus and thereby increases their availability
- Increases the leaching of nitrate and sulphate
- Enhances nitrification
- Enhances the mineralisation of organic matter and thereby increases the release of plant nutrients
- Enhances nitrogen fixation
- Improves soil structure



Nitrogenase is an enzyme in rhizobium bacteria which is involved in atmospheric nitrogen (N_2) fixation in root nodules.

Figure 3.6.5 The effect of soil acidity on clover shoot growth.



High Al and low Ca (as a result of increased soil acidity) reduce root growth

- Volume of soil explored by roots is reduced- unable to take up nutrients and water from subsoil.Therefore, increasing risk of drought stress and nutrient deficiencies.

Figure 3.6.6 The effect of Al and Ca concentration on root growth.

P-sparing effect of lime.

Is defined as the lime-induced reduction in the amount of phosphate fertiliser required to achieve a given yield. The reduction of P requirement results directly from an increased solubilisation of soil phosphorus and its subsequent uptake, and/or indirectly from an increase in uptake due to reduced Al and Mn activity.

Liming should not be practiced in the expectation that fertiliser P inputs can be reduced in the long term. The over-use of lime, resulting in soil pHs greater than 7, will cause deficiencies in a number of trace elements including Fe, Mn, Zn, Cu, and Co.

3.7 Fertiliser and Manure Reference Resource

Introduction

Fertilisers are grouped based on:

- Major Nutrient Content (N, P, K, S fertilisers)

- Solubility in Water
  - Soluble fertilisers (fast release)
  - Insoluble fertilisers (slow release)

Forms of N, P, and S Fertilisers

Table 3.7.1 Forms of N, P and S fertilisers used in New Zealand.

Nutrient	**Fertilisers**	
	Fast-release	**Slow-release**
Nitrogen	Urea Ammonium sulphate Potassium nitrate Calcium-ammonium Nitrate	Elemental S coated urea IBDU
Phosphorus	SSP, TSP, DAP, MAP	DCP, RPR, PAPR, SSP-RPR
Sulphur	Ammonium sulphate Potassium sulphate Gypsum (in SSP)	Elemental S

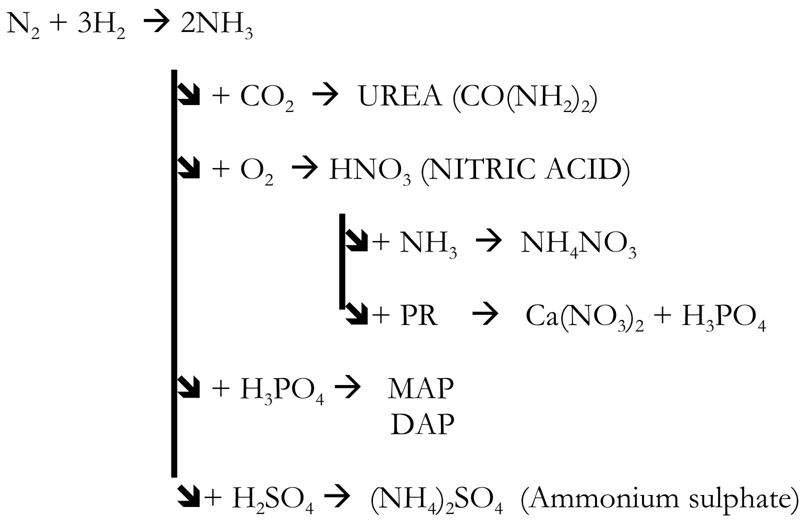
SSP = Single superphosphate
TSP = Triple superphosphate
DAP = Diammonium phosphate
MAP = Monoammonium phosphate
DCP = Dicalcium phosphate
RPR = Reactive phosphate rock
PAPR = Partially acidulated phosphate rocks
IBDC = Isobutylidene diurea

The primary source of N, P, K and S for fertiliser manufacture are:

- N fertilisers = ammonia gas
- P fertilisers = phosphate rock
- K fertilisers = K minerals
- S fertilisers = elemental sulphur

NITROGEN FERTILISERS

Most of the N fertilisers are manufactured using ammonia gas (NH_3)



$N_2 + 3H_2 \rightarrow 2NH_3$

$+ CO_2 \rightarrow$ UREA ($CO(NH_2)_2$)

$+ O_2 \rightarrow HNO_3$ (NITRIC ACID)

$+ NH_3 \rightarrow NH_4NO_3$

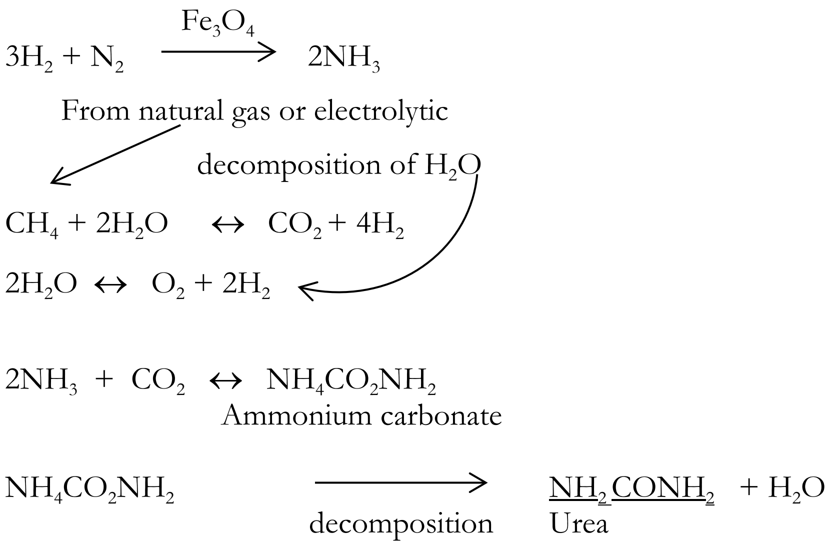
$+$ PR $\rightarrow Ca(NO_3)_2 + H_3PO_4$

$+ H_3PO_4 \rightarrow$ MAP
DAP

$+ H_2SO_4 \rightarrow (NH_4)_2SO_4$ (Ammonium sulphate)

Manufacture of Urea

Ballance Fertiliser (Haber Bosch Process)



$3H_2 + N_2 \xrightarrow{Fe_3O_4} 2NH_3$

From natural gas or electrolytic decomposition of H_2O

$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$

$2H_2O \leftrightarrow O_2 + 2H_2$

$2NH_3 + CO_2 \leftrightarrow NH_4CO_2NH_2$

Ammonium carbonate

$NH_4CO_2NH_2 \xrightarrow[\text{decomposition}]{} \underline{NH_2CONH_2} + H_2O$

Urea

Ammonium Sulphate $(NH_4)_2SO_4$

A by-product of the steel industry. NH_3 liberated in coke production is scrubbed from exhaust gases in sulphuric acid.

$$2NH_3 + H_2SO4 \rightarrow (NH_4)_2SO_4$$

Table 3.7.2 Nitrogen Fertilisers.

Fertiliser Name	Nutrient Content (%)			
	N	P	K	S
Ammonium sulphate	21			24
Ammonium nitrate	33			
Monoammonium phosphate	11	21		2
Diammonium phosphate	18	20		2
Urea	46			
Potassium nitrate	14		39	
Calcium nitrate	16			
Calcium ammonium nitrate	27			
Blood and bone	5-8	5-8		
IBDU	32			

PHOSPHORUS FERTILISERS

Table 3.7.3 Soluble P Fertilisers.

Fertilisers	Total P (%)	Citric P (%)	Water P (%)
Monoammonium phosphate	20-21	19-20	19-20
Diammonium phosphate	19-20	18-20	18-20
Single superphosphate	9-10	7-8	6-7
Triple superphosphate	19-21	16-19	16-19
Lime reverted Superphosphate	5-8	3-4	1-2
Blood and Bone	5-8	4-7	<1

Table 3.7.4 Insoluble P Fertilisers.

Fertilisers	Origin	Total P (%)
PAPR:		
Hyphos (Historic 1985)	New Zealand	16.0
ESPARP	Australia	10.1
Granphos	United Kingdom	16.4
Novaphos	Germany	-
SSP/RPR mixes:		
Longlife	New Zealand	10.8
Coastal super	Australia	9.5
Thermal phosphates:		
Basic slag	Germany	8.1
Fused magnesium phosphate	Japan	10.3
Rhenania phosphate	Germany	12.7
Calciphos	Australia	13.0

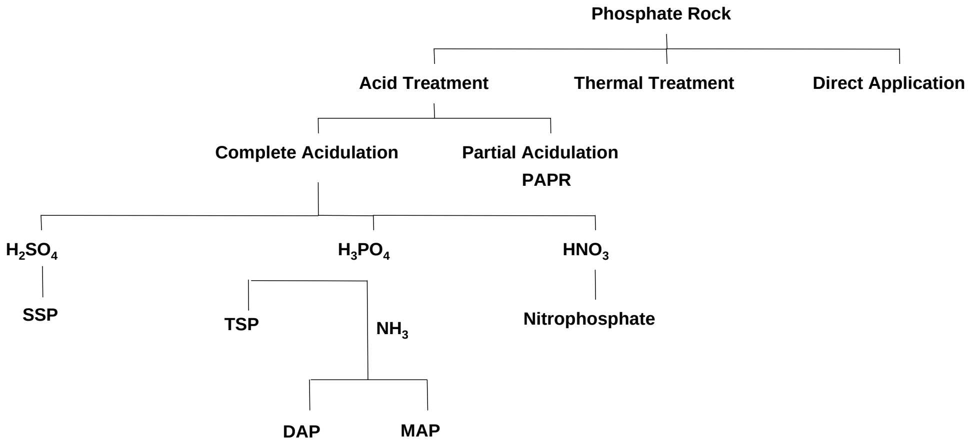
Table 3.7.5 Phosphate Rocks.

Phosphate rock	Total P (%)	Citric P (% total P)
Duches	13.5	6
Nauru	15.6	22
Central Florida	14.6	20
Khouribga	14.4	26
Jordan	15.0	26
Youssafia	13.8	27
Egyptian (RPR)	13.0	33
Arad (RPR)	14.4	30
Moroccan (RPR)	14.0	32
Sechura (RPR)	13.2	43
Gafsa (RPR)	13.0	33

Reactive Phosphate rocks (RPR) = Citric P (>30% total P)

P Fertiliser Manufacture

Phosphate rock (PR) is the primary source of P fertilisers



Thermal Phosphate (Slow Release)
Calcium magnesium phosphate
Rhenania phosphate

Direct application

RPRs : NCPR, Sechura
SSP-RPR mixtures: longlife

Phosphate rock (PR) + Sulphuric acid (H_2SO_4)

SSP = acid to rock ratio is <6
H_3PO_4 = acid to rock ratio is >6

1. Single superphosphate (SSP)

$$\underset{}{Ca_{10}(PO_4)_6F_2} + 7H_2SO_4 \rightarrow 3\,\underset{\text{MCP}}{Ca(H_2PO_4)_2} + \underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O} + 2HF\uparrow$$

SSP is a mixture of MCP + gypsum + residual rock

2. Triple superphosphate (TSP)

$$Ca_{10}(PO_4)_6F_2 + 12H_3PO_4 \rightarrow 9Ca(H_2PO_4)_2 + CaF_2$$

3. Partially Acidulated Phosphate Rock (PAPR)

PR + H_3PO_4 or H_2SO_4 or both
(less than 100% acidulation)
→ MCP + unreacted PR

Table 3.7.6 Potassium Fertilisers.

	Nutrient Content % w/w			
	N	**P**	**K**	**S**
Potassium chloride (muriate of potash)	-	-	48-52	-
Potassium nitrate	14	-	39	-
Potassium sulphate (fertiliser grade)	-	-	40	17

SULPHATE FERTILISERS

Sulphuric acid is used to solubilise phosphate rock hence many phosphatic fertilisers are also sulphur carriers. Elemental S^o is oxidised slowly in soil and finely divided S^o can be added to other fertilisers or prilled with expanding bentonite clays.

Table 3.7.7 Sulphate Fertilisers.

	Nutrient Content %			
	N	**P**	**K**	**S**
Fast Release				
Ammonium sulphate	21	-	-	24
Ammonium sulphate nitrate	26	-	-	14
Potassium sulphate	-	-	40	17
Superphosphate	-	9-10	-	12
Gypsum	-	-	-	18-20
Slow Release				
Sulphur elemental	-	-	-	100
Sulphur phosrock 5%	-	13	-	5
Sulphur phosrock 20%	-	11	-	20
Sulphur coated urea	32	-	-	27
Mixed slow/fast release				
Di-calcic phosphate plus S	-	4	-	23
Sulphur dolophos	-	5	-	17
Sulphur supermag	-	-	-	16
Sulphur superphosphate	-	8	-	20
Sulphur super extra	-	7	-	27
Super/lime 50/50	-	5	-	5

NB: All fertiliser mixtures containing superphosphates, potassium sulphate or ammonium sulphate also contain sulphur. Slow release forms contain elemental S^0.

Table 3.7.8 Elemental sulphur based fertilisers.

Type	S (%)		
	S^0	SO_4^{2-}	Total S
Agriculture S	100	-	100
S^0 prills	100	-	100
S^0/bentonite	75-85	-	75-85
Sulphurised SSP	9	9	18
Sulphurised SSP extra	18	9	27
Sulphurised PAPR (Hyphos-S)	11	-	11
Sulphurised RPR	50	-	50
Sulphur impregnated urea	20	-	20
Thiovet (fine spray)	85	-	85

Organic Nutrient Sources

Table 3.7.9 Nutrient concentration of various wastes (dry weight basis).

Waste	Unit	N	P	K	S	Ca	Mg
Layer manure compost	(g/kg)	32.8	10.8	6.7	8.5	18.5	6.2
Broiler manure compost	(g/kg)	25.7	6.7	10.1	5.2	16.2	3.5
Pig manure compost	(g/kg)	15.2	6.5	8.2	3.4	4.2	3.7
Mushroom compost	(g/kg)	17.5	7.5	9.2	3.5	21.5	5.2
Biosolid compost	(g/kg)	21.8	10.1	5.9	7.0	19.7	4.2
Dairy effluent	(mg/L)	110	25	250	2.1	23.4	14.8
Whey effluent	(mg/L)	1250	350	1200			
Piggery effluent	(mg/L)	125	18	285	100		
Sewage effluent	(mg/L)	21	11	15	15		