

PLANT NUTRITION AND SOILS

(CHEMISTRY IN THE GARDEN)

Plants need water, carbon dioxide and a range of trace minerals known as 'nutrients' to grow. They obtain these nutrients, and most of their water, from the soil.

Soil composition

Soil is made up of three main things: clay, humus and sand. There are also many small organisms that live in the soil, and most of these are useful to the plants.

Clay Clay is made from the breakdown and recombination of silicate rocks. It is made up of alternating layers of silicon oxides then aluminium oxides, with various cations such as Ca^{2+} loosely bound in between the layers. Anions adsorb onto the oxide surfaces, with doubly and triply charged cations sticking better than singly charged ones. Clays are the main source of nutrients in the soil.

Humus This is any organic matter in the soil - i.e. the products of the decay of plants and animals. It is mostly made up of aromatic compounds. Over time it breaks down to carbon dioxide and water so it needs to be continually replaced. Humus is important in regulating the amount of water in the soil.

Sand This is solid particles of ground up rock. A small amount of sand is necessary to ensure the correct water content in the soil.

Sources of plant nutrients

The nutrients available in a given soil ultimately depends on the rock from which the soil was made. If the plants grown from this soil die and decay where they have grown then their nutrients are recycled. However, if the plants have been grown for agriculture then they are removed from the area in which they have grown and their nutrients cannot be recycled. So in soils that are used for cropping, essential nutrients continually have to be replaced.

Replacement of plant nutrients

This can be done either using manure or compost (which are relatively poor sources of nutrients) or a synthetic fertilizer. Synthetic fertilizers are usually used to replace nitrogen (in the form of urea, ammonium sulfate, ammonium nitrate or diammonium hydrogen phosphate), phosphorous, sulfur and potassium. The nitrogen is obtained from the air, the phosphorous is mined as $\text{Ca}_3(\text{PO}_4)_2$, the sulfur is mined in elemental form and reacted with oxygen to form sulfate, and the potassium is obtained from seawater. Other minor nutrients are also sometimes replaced using specialised artificial fertilizers.

Soil analysis

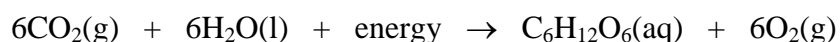
If soil has an inappropriate composition for a given plant species then that plant will not thrive (or maybe will not grow at all) in that soil. To prevent this being a problem, samples of soil are often analysed so that nutrients can be added before seeds are planted. Soil is commonly analysed for potassium, magnesium, calcium, nitrogen and phosphorous (the exact choice of elements to monitor depends on which plants are to be grown) and also for pH. Some of these tests are so simple they can be carried out at home (some examples are given at the end of the article) and others require specialised equipment.

INTRODUCTION

Plants grow in the thin upper layer of the Earth's crust known as soil. Soil is formed over very long times from igneous or sedimentary rock, volcanic ash, sand or peat. With the exception of peat, these are all silicate minerals, so soil is largely made up of silicates and organic material known as humus. Plants use this soil for anchorage and as a source of nutrients and water.

Why plants need soil

Green plants are very effective photochemical factories: they use the energy of light to combine carbon dioxide from the air with water from the soil to make carbohydrates:



This reaction occurs in the chloroplasts of all green plants, using the green pigment chlorophyll to trap the energy from sunlight. The basic building blocks of glucose are then used to build up more complex carbohydrates such as cellulose.

However, plants need more than just carbon dioxide, water and sunlight to keep alive. **Table 1** gives the elemental composition of a 'typical' plant. It can be seen that the composition of plants is not much different from that of animals, and includes significant amounts of nitrogen and phosphorous, as well as trace amounts of many other elements. Although there is enormous variation between the abundance of the most common element, hydrogen, and the least common, molybdenum, both are very important. For example, plants can only use nitrogen in the form of the ammonium ion. Nitrates are converted to ammonium ions by the enzyme *nitrate reductase*, and as this enzyme cannot function without molybdenum, the presence of molybdenum is essential if the plant is to receive nitrogen in a form that it can use. These trace elements, generally called plant nutrients, normally come from the soil in which the plant is growing (**Figure 1**). The plants absorb their nutrients from the soil solution (the film of water which covers all the particles in moist soil), usually in very simple forms. **Table 2** gives a typical composition of the main constituents of the soil solution from which plants must obtain all their requirements for growth.

It is possible to grow plants without soil, using *hydroponics*. The plant is grown in a solution which contains all the required plant nutrients, in the correct proportions. It is possible to determine just how much of any particular nutrient a plant needs by starting with a balanced nutrient solution, and then varying the amount of each nutrient present, one nutrient at a time. When insufficient of the nutrient is present the plant will not thrive. As the amount of nutrient is increased the growth improves, until all that the plant can utilize is present, when adding more of that nutrient produces no additional growth. If the amount of the nutrient is increased still further, the excess may eventually cause toxic effects, and growth is retarded (**Figure 2**). For some nutrients, e.g. potassium, plants can tolerate a large excess before ill effects occur; for others, e.g. boron, the optimum range is narrow.

THE COMPOSITION OF SOIL

Apart from peat, which is derived from plant material, soil is composed of silicate minerals of various types, composed largely of oxygen and silicon, with smaller amounts of aluminium,

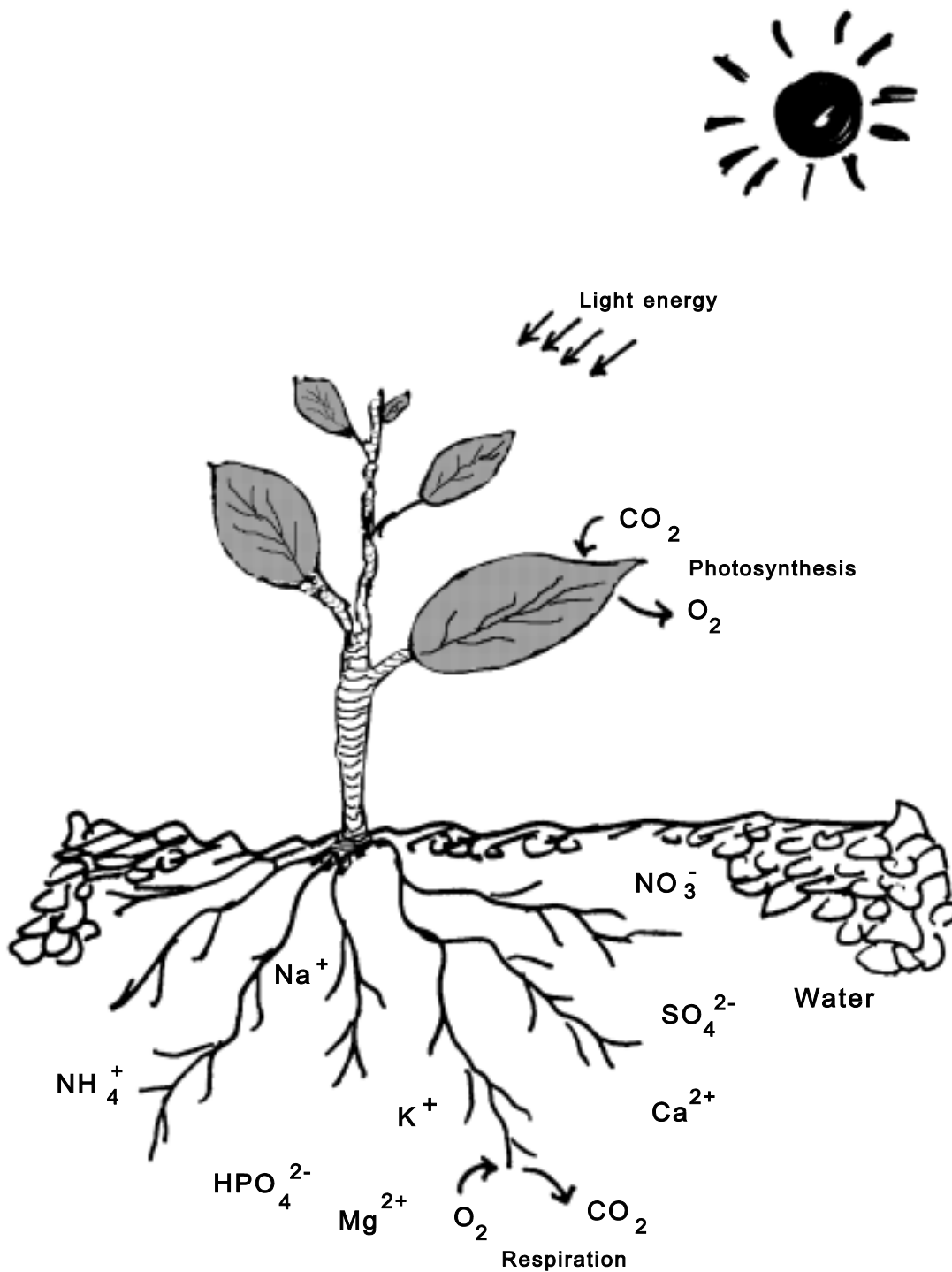


Figure 1 - The plant environment

Table 1 - Typical Plant Dry-matter Composition

Element	Amount by mass		Relative number of atoms
	%	ppm	
Hydrogen	6		60 000 000
Carbon	45		40 000 000
Oxygen	45		30 000 000
Nitrogen	1.5		1 000 000
Potassium	1.0		250 000
Calcium	0.5		125 000
Magnesium	0.2		80 000
Phosphorous	0.2		60 000
Sulfur	0.1		30 000
Chlorine	0.01	100	3 000
Iron		100	2 000
Boron		20	2 000
Manganese		50	1 000
Zinc		20	300
Copper		6	100
Molybdenum		0.1	1

Table 2 - Typical composition of soil solution

cation	conc. / mmol L ⁻¹	anion	conc. / mmol L ⁻¹
Ca ²⁺	10	NO ₃ ⁻	5
Mg ²⁺	3	SO ₄ ²⁻	4
K ⁺	1	Cl ⁻	2
Na ⁺	1	HCO ₃ ⁻	2
NH ₄ ⁺	0.5	HPO ₄ ²⁻ , H ₂ PO ₄ ⁻	0.01

iron, sodium, potassium, calcium and magnesium, and variable and much smaller amounts of all the other elements. As rainwater saturated with carbon dioxide percolates through silicate minerals it dissolves out the simple soluble cations, such as Na⁺, K⁺ and Ca²⁺, and anions such as Cl⁻, in the process of *weathering*. The residue consists largely of oxides of silicon, aluminium and iron. Over hundreds to thousands of years this recrystallises as *clay minerals*. These are *aluminosilicate* compounds, composed largely of silicon, aluminium and oxygen, which have *layer structures* built up like stacks of sandwiches. Silicon atoms, each surrounded by a tetrahedron of oxygen atoms, are linked into sheets by sharing oxygen atoms. Aluminium atoms, each surrounded by an octahedron of oxygen atoms (since aluminium is larger than silicon), similarly form sheets. These sheets combine to form layers by sharing oxygen atoms. In the *kaolin* type of clay minerals one silicon-oxygen sheet is combined with one aluminium-oxygen sheet to form each layer. These layers are then loosely stacked together like stacks of bread-and butter (---bread-butter---bread-butter---). In another type (*smectite* type) a central silicon-oxygen sheet has an aluminium-oxygen sheet on each

side; these are then loosely stacked like a bread and butter sandwich (---bread-butter-bread--- bread-butter-bread---). The crystals of the clay minerals are very small, typically less than 4 μm in size (such a particle would contain about 5,000 layers), and so have large total surface areas. The attractive forces between the layers are weak, and for some clay minerals water can diffuse between the layers, making the effective surface area even larger.

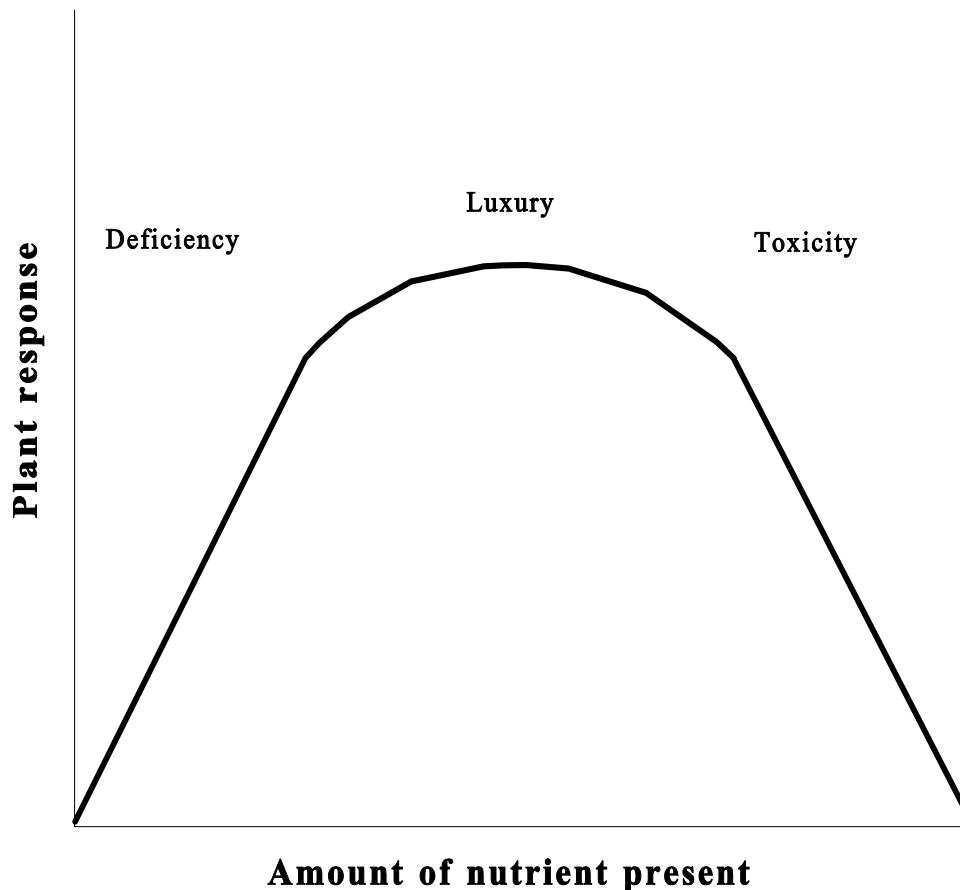


Figure 2 - Response of plant to amount of one nutrient

The clay structures are generally not perfect, and "wrong" atoms are frequently incorporated into the layers. Such mistakes can upset the charge balance in the layers, and lead to unbalanced negative charges appearing in the oxygen sheets. These charges are balanced either by incorporating a hydrogen ion (converting an O^- to -O-H), or by having a cation, such as Ca^{2+} , somewhere nearby between the layers. The edges of the layers also have excess negative charges, which have to be similarly balanced. **Figure 3** represents a typical clay mineral, with loosely bound cations between the layers and at the surface of the particles. The places where hydrogen or cations are present are called *exchangeable cation sites*. The cations bound by the clay particle can interchange with cations in solution. Clay minerals thus have an ability to loosely bind cations and *exchange* them with other cations in the soil solution. This *cation exchange capacity* of clays is an important property of soils. **Figure 4** shows the way in which the cations loosely held in soils can be exchanged for others from the soil solution.

The clay minerals, and also tiny particles of the oxides of iron and aluminium present in soil, have another important property; they adsorb anions on their surfaces. The strength of this anion binding increases with charge, so that singly charged anions, such as Cl^- or NO_3^-

are poorly retained by soil, doubly charged SO_4^{2-} is more strongly bound, and triply charged PO_4^{3-} is very strongly bound.

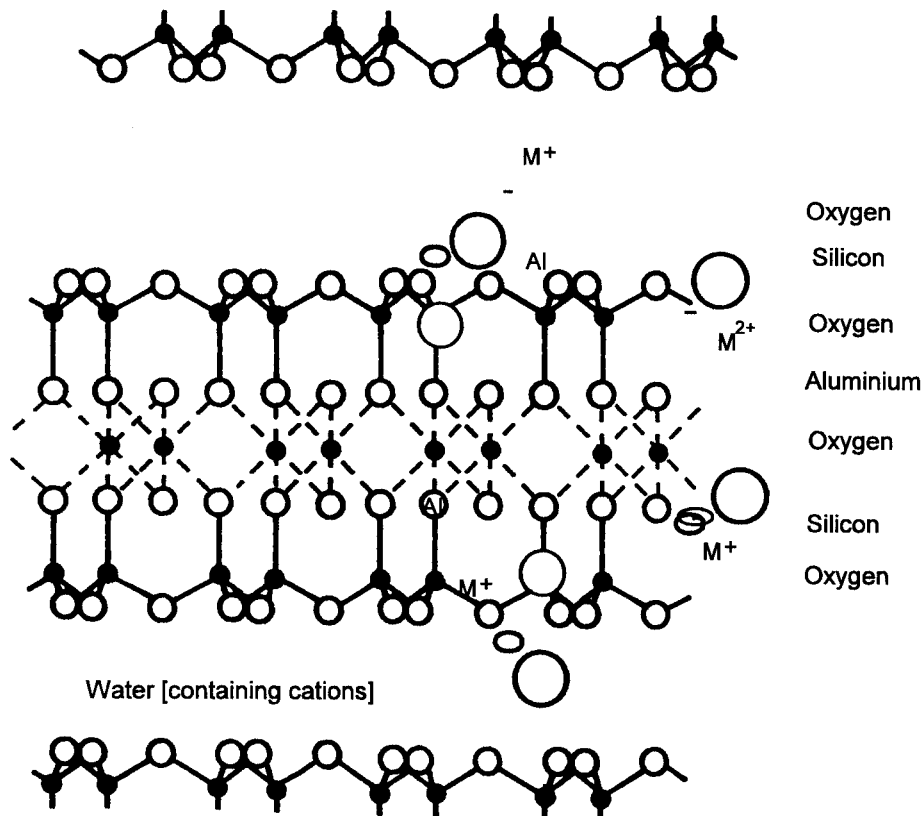


Figure 3 - The structure of a clay mineral, showing cation exchangeable sites

Some New Zealand soils formed from volcanic ash contain a clay mineral called *allophane*. This has a very imperfect aluminosilicate structure in which the layers are thought to curl around to form tiny porous balls about 5 nm in diameter, rather like plastic practice golf balls. These form soils with a very large total surface area -- about a rugby-field of surface for every 10 grams of allophane. These soils have the ability to bind phosphate so strongly that it becomes unavailable to plants, and is said to be "fixed".

Soils also contain organic matter, called *humus*. This is the ultimate product of the decay of plant and animal material, and is intimately mixed in with the clay by the actions of the soil's population of organisms. Humus is largely derived from the most resistant of plant material, the lignin from the cell walls. This contains much aromatic material (six-carbon benzene rings) with attached hydroxy (-OH) and carboxylic acid (-COOH) groups. These can also ionize to form $-\text{O}^-$ and $-\text{COO}^-$ groups, and these charges have to be balanced by a cation in the vicinity, so humus also contributes to the ion exchange capacity of the soil. The humus is slowly, continuously, being broken down to simpler compounds, and ultimately to CO_2 and H_2O and must continuously be replenished with new plant residues to maintain the soil's "condition".

Without the ability of soils to bind both cations and anions the essential plant nutrients would be rapidly washed out of the soil, and plant life would probably not have developed in the forms we know.

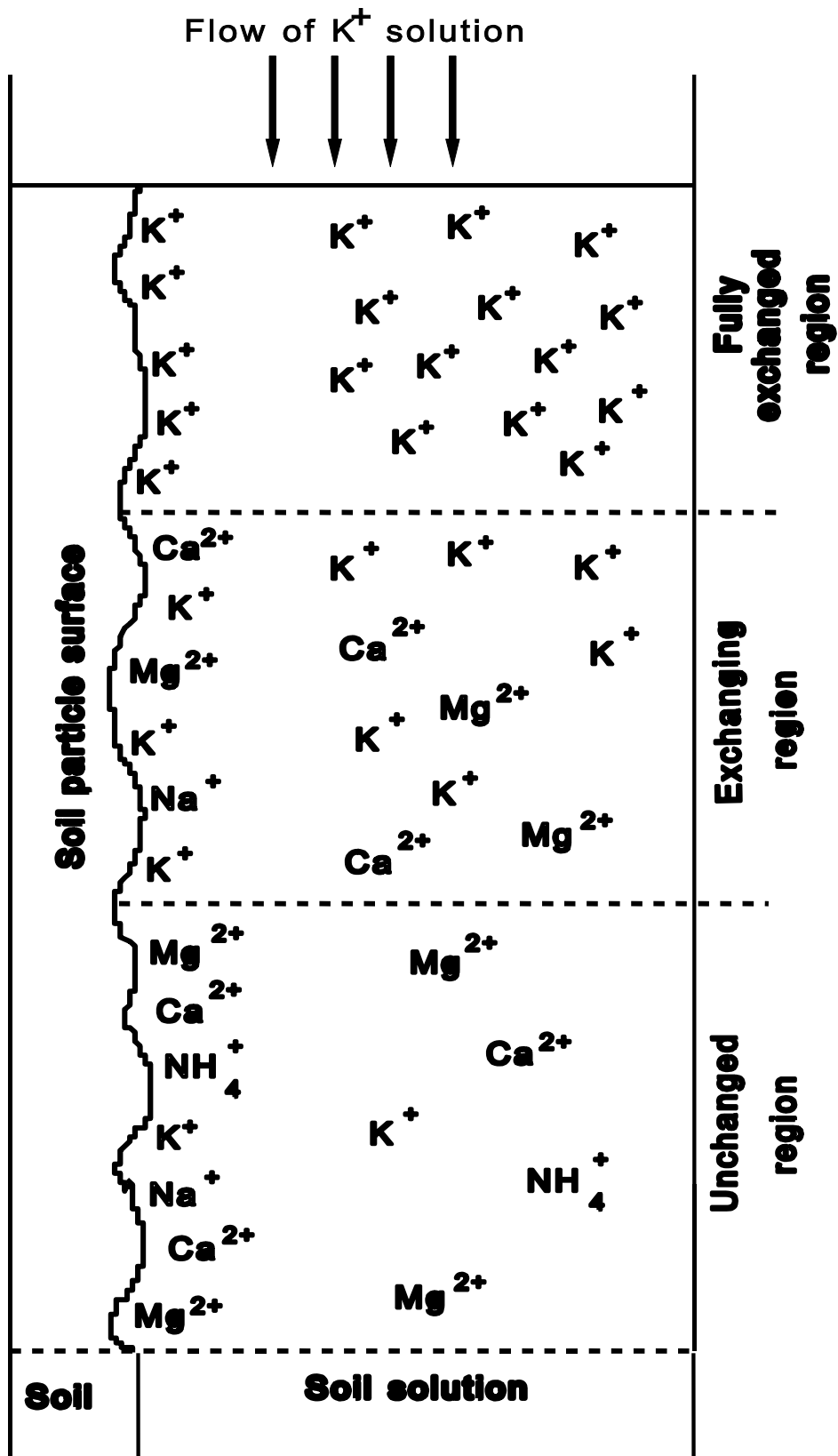


Figure 4 - Exchange of soil-bound cations by solution containing potassium ions. The anions necessary for charge neutralization are omitted for clarity.

The physical properties of a soil are very important in determining its usefulness for

gardening or agriculture. A fertile soil will generally have a balance of clay minerals and organic material, and probably also coarser particles of "sand" as silica or other resistant minerals of the original rock. The humus present improves the physical properties of the soil, and gives it the ability to drain excess water yet retain sufficient moisture for plant growth. The balance of these constituents determines the soil's properties; how well it holds water, and drains, whether it is "sticky" or friable, how well it stands up to repeated cultivation, etc, and so determine its usefulness for agriculture.

Soils have a thriving living population, ranging in size from earthworms to single celled organisms, living on plant and animal residues, which are partly responsible for the creation of fertile soil from weathering rock. Most soil organisms are beneficial, though some eat plant roots or cause or transmit plant diseases.

SOURCES OF PLANT NUTRIENTS

Plant nutrients in soil come originally from the parent material from which the soil was formed. Soils derived from rocks which are rich in nutrients (such as those around basaltic or andesitic volcanoes in New Zealand) are rich in nutrients and so are fertile, while soils derived from sand, or rocks which are poor in nutrients (such as from the greywacke sedimentary rock of most New Zealand mountains), are relatively infertile.

Under natural conditions most nutrients are recycled from plant to soil to plant. Losses by leaching by rainwater depend on how strongly the nutrient is bound to the soil constituents. Weakly bound nutrients, such as NO_3^- , are rapidly leached, while strongly bound nutrients, such as PO_4^{3-} , suffer little loss. The losses by leaching must be replenished to maintain the fertility of the soil. If any nutrient is repeatedly taken from the area by cropping, then the soil will ultimately become depleted in that nutrient, and the fertility of the soil will decrease.

Phosphorus

Figure 5 schematically illustrates these effects for the essential nutrient phosphorus.

The phosphorus originally comes from the *weathering* of the parent material, which releases phosphate ions into the soil solution. This phosphate is *adsorbed* onto soil constituents, forming "reservoirs" of various types and capacities, some of which release phosphate ions into the soil solution easily, while others strongly bind phosphate. Plants absorb phosphate from the soil solution, and incorporate it into their tissues as they grow. When the plants die, decay processes slowly convert the complex phosphorus compounds in the plant tissues back to simple phosphate ions (*mineralization*) and the cycle repeats. Under "natural" conditions the losses by leaching are to some extent made up by weathering of more parent minerals to release fresh phosphate.

If a crop is removed from the area then the soil will contain less phosphate, the phosphate reservoirs will gradually become depleted and the soil will become less fertile. The phosphate content of the soil can be increased by addition of phosphorus as "inorganic" phosphate which goes straight into the soil solution (if soluble), or dissolves slowly (if sparingly soluble). Alternatively, phosphorus can be added as complex organic phosphorus compounds, such as are present in plant or animal materials, which release their phosphorus slowly as they decay.

Phosphorus is bound so firmly to soil that leaching losses into waterways are generally small,

though erosion which carries phosphorus-rich soil particles into the waterways can encourage the growth of algae and weed in rivers and lakes (*eutrophication*).

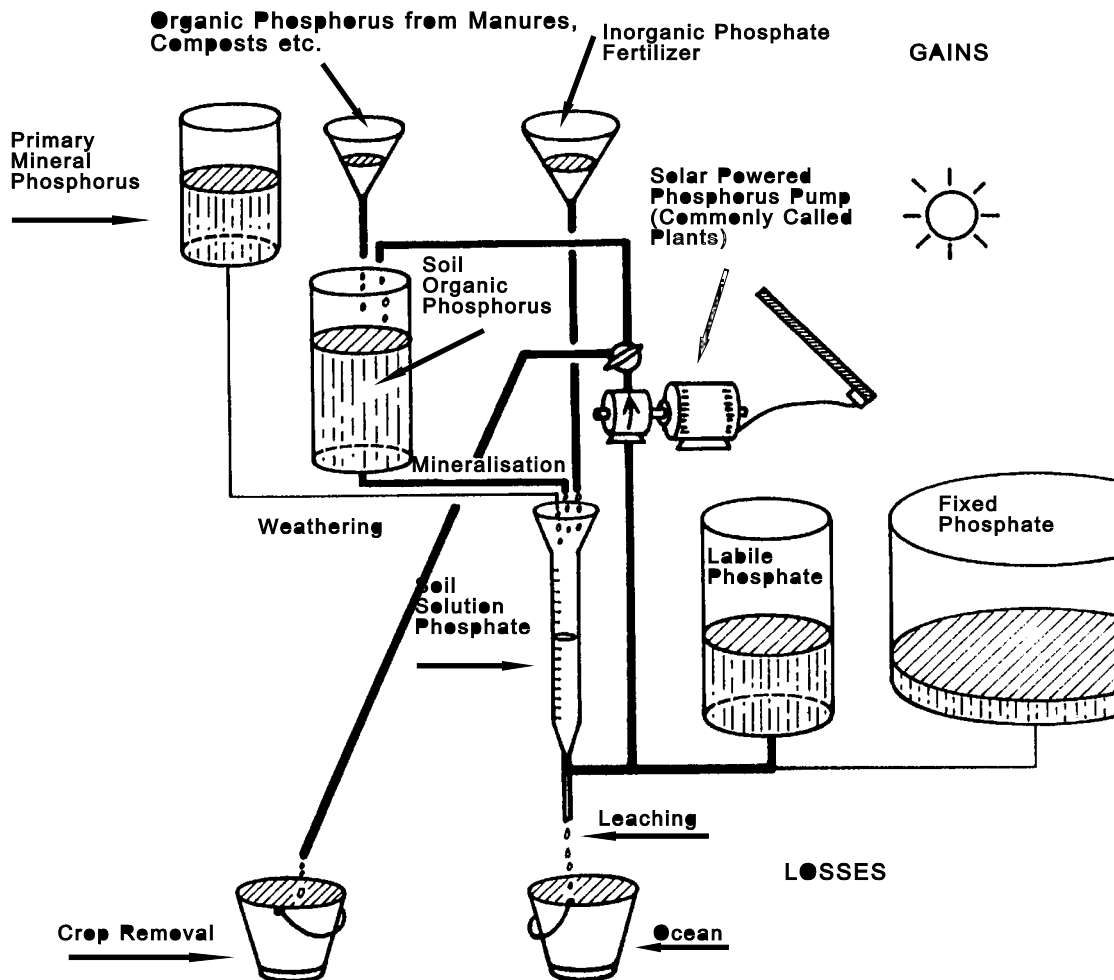


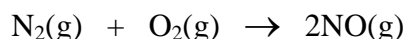
Figure 5 - Schematic diagram of the phosphate cycle

Nitrogen

Nitrogen is one essential nutrient which behaves quite differently. There is virtually no nitrogen in rocks; most of the world's nitrogen is in the air, which is 80% dinitrogen, N_2 . However, most plants are unable to make use of dinitrogen, and can only absorb nitrogen from the soil solution in the form of nitrate or ammonium ions.

The dinitrogen of the air must be converted into nitrate or ammonia by the process of *nitrogen fixation* before it becomes available to plants. This nitrogen fixation can occur by either a physical process, or a biological process.

The physical process occurs whenever air is heated to a high temperature. The dinitrogen and dioxygen of the air combine to form nitric oxide



This reaction occurs naturally in lightning strikes and forest fires. Human activity causes many more high temperature processes, such as in internal combustion and jet engines, thermal power plants, steel and cement works, etc, and has greatly increased the amount of nitrogen fixation. The nitric oxide formed undergoes further reactions in the atmosphere, and is finally converted into nitric acid, which is washed out by rain and enters the soil as nitrate ions. Too much of this type of nitrogen fixation can cause atmospheric smog and acid rain. Biological processes in the soil reduce the nitrate to ammonium ions.

Biological fixation occurs in certain micro-organisms which have the ability to convert dinitrogen into ammonia, using the enzyme *nitrogenase*, for which the element molybdenum is required. Some of these micro-organisms live freely in the soil (*e.g.* the bacterium *azotobacter*). These bacteria fix the nitrogen for their own needs, but when they die and decay the nitrogen in their cells becomes available for plants. Other bacteria form an alliance (*symbiosis*) with certain plants (*e.g.* *rhizobia* with legumes). The plant provides a safe place for the bacteria to live (in nodules on its roots), and a food supply (carbohydrate obtained from photosynthesis). In return the bacteria provide the plant with fixed nitrogen as ammonium ions.

Much of New Zealand agriculture is dependent on this relationship. Clover in the pasture has bacteria in root nodules which fix nitrogen, so the clover plant is rich in nitrogen. This is eaten by herbivores, and the excess nitrogen is excreted onto the soil in the animal's urine, when it becomes available to the grasses which form the bulk of the pasture. Farmers would have to use much more nitrogen fertilizer to achieve the same amount of pasture growth without the assistance of the nitrogen fixing bacteria in nodules on clover roots.

The life of fixed nitrogen in the soil is short. Both nitrate and ammonium ions are bound weakly by ion-exchange processes, so they are both leached out by rainwater, and finish up in ground water in wells and in rivers. Nitrate and ammonium ions encourage the growth of weed and algae in rivers and lakes, and when these are used for water supplies the toxicity of nitrate ions can cause health problem if the concentrations become too high. Nitrogen is also lost from the soil by the activities of *denitrifying bacteria*. These convert the nitrate and ammonium ions back to dinitrogen, or more usually, to nitrous oxide (N_2O). This is a *greenhouse gas* and so increasing the amount of fixed nitrogen in the soil indirectly increases the amount of nitrous oxide in the atmosphere and potentially contributes to the raising of the temperature of the earth. Farming practices which lead to high levels of nitrogen in the soil can therefore contribute to environmental problems.

Other Nutrients

Cycles similar to that described for phosphorus can be drawn for other major nutrients such as potassium, calcium or magnesium, and for trace nutrients, such as cobalt, molybdenum or selenium, which are derived from the soil parent material.

THE REPLACEMENT OF PLANT NUTRIENTS

Removing crops, or animals, from an area steadily drains nutrients from the soil, and these must be replaced if the soil is to remain fertile. The types of plants which are grown in modern agriculture usually require higher levels of nutrients for optimum growth than are

usually present in New Zealand soils. To increase soil fertility to the level required by the "high growth" plants used in modern agriculture, and to maintain this level with continual crop removal, essential plant nutrients have to be regularly added to the soil. The main nutrients required are nitrogen, phosphorus, potassium, sulfur, calcium and magnesium. In particular areas certain trace elements, such as magnesium, sulfur, copper, zinc, boron and molybdenum may also be lacking, and may have to be added to produce optimum growth.

It should always be kept in mind that additional plant nutrients can produce improved plant growth only if the growth is being limited from the potential determined by the plant genetics and climate by a deficiency of some nutrient, or nutrients, and if the fertilizer makes up the deficiency.

There are two main options for adding these nutrients; the *organic way*, using only "natural" materials, and the use of *fertilizers*, which generally contain relatively simple inorganic compounds. The term "inorganic fertilizer" is commonly used to mean "manufactured", or "not natural", though the chemical meaning is simply "not carbon-based". In chemical terminology "organic" means carbon based, whether originating naturally or by manufacture. The organic (carbon-based) compounds of plants are made in the plant from the carbohydrates formed from carbon dioxide by photosynthesis, and plants can not use the organic components of composts or manures. Plants absorb their inorganic nutrients as simple anions and cations, so complex organic materials have to be broken down by the process of *mineralization*, releasing the nutrients as simple ions, before they become available to plants.

Composts and manures

In *organic* agriculture nutrients are replenished using only natural materials, though what is and what is not natural is often debated. The main "organic" nutrient sources are composts and manures.

Composts are formed from plant residues, and have much the same chemical composition as the plants from which they are made (**Table 1**). Composts are *not* a rich source of plant nutrients, and need to be used in large amounts if they are the only source of nutrient replenishment. Their main use is to boost the amount of soil organic matter (humus), and composts should be regarded primarily as *soil conditioners*. There is also a philosophical problem that if compost is made from "imported" plant material, then the area from which the material was obtained has been depleted in nutrients. As example, continual use of lawn mowings to make compost depletes the lawn area of nutrients, which need to be replenished to keep the lawn healthy. Therefore, while all available plant material should be converted into compost to maintain humus levels and to recycle nutrients, this does not really solve the nutrient deficit problem. An additional problem arises if a region is deficient in some particular nutrient. The plants (and animals) grown in the region will also be deficient in this nutrient, and so also will be composts made from plants grown in the area.

Manures are usually the faeces of herbivores. In the digestion process the animal absorbs as much as it can of the nutrient elements for its own needs, so the residue finally excreted consists of plant material depleted in nutrients. The nutrients not incorporated into the animal are excreted in the animal's urine, which is a better source of plant nutrients than the faeces. As with compost, manures are useful mainly as soil conditioners. They are not a rich source of plant nutrients, and need to be used in large amounts if they are the only source of nutrient replenishment. The old gardening advice "to dig in six inches of well rotted stable manure" is

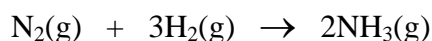
fine in principle, but not very practicable for most modern gardeners, and there remains the problem that the area where the animal was feeding has been depleted of the nutrients.

Animal residues, such as "blood and bone" form another type of "natural" fertilizer. These can contain high levels of nutrients, which are generally released slowly into the soil solution as the complex compounds are broken down, which has advantages. Again these nutrients have been "mined" from the soil where the animals fed.

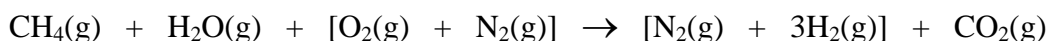
Fertilizers

The only answer to the "nutrient mining" problem is to bring fresh nutrients into the area from some richer source, and fortunately natural processes have concentrated the major nutrients in locations around the world.

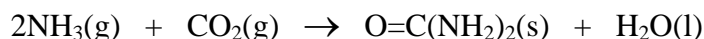
All "synthetic" **nitrogen** fertilizers obtain their nitrogen from the atmosphere. This is "fixed" using the *Haber process*, in which dihydrogen and dinitrogen at high temperature and pressure are combined over a catalyst, which speeds up the reaction forming ammonia:



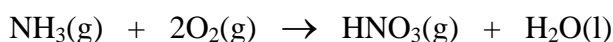
The hydrogen required for the Haber process is normally made using methane separated from natural gas. Methane is reacted with water and air at high temperatures over catalysts to form a mixture of dihydrogen, dinitrogen (from the air) and carbon dioxide. Carbon dioxide and water are removed (the carbon dioxide is used later to make urea), leaving dihydrogen and dinitrogen in the correct proportion to combine to form ammonia (unbalanced equation)



The ammonia obtained from the Haber process is converted into a form more useful as fertilizer. It can be combined with carbon dioxide to form urea, which is chemically identical to the urea excreted in the urine of animals



or combined with sulfuric, nitric or phosphoric acid to form ammonium sulfate, ammonium nitrate or diammonium hydrogen phosphate ($\text{NH}_4)_2(\text{HPO}_4)$. The nitric acid is formed by oxidizing ammonia over a catalyst



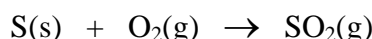
Phosphorus is a relatively abundant element in the earth's crust, and occurs naturally in marine deposits of *phosphate rock*, as calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, or the minerals *apatite*, $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$, or *hydroxy apatite*, $\text{Ca}(\text{OH})_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$ (hydroxy apatite is the mineral that forms bones and teeth). The phosphate rock from the Pacific region is found on coral islands where flocks of sea birds roost. It is thought that the phosphate in their excreta, derived from their fishy diet, combines over time with coral to form the phosphate rock. Some phosphate rock is sufficiently soluble so that the phosphorus from the finely ground rock is available to plants. Other phosphate rock is too insoluble for direct use, and is commonly treated with sulfuric acid to make a mixture of calcium sulfate and the more soluble calcium hydrogen phosphate, called *superphosphate*.



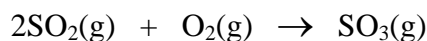
Phosphate rock can also be reacted with excess sulfuric acid to make phosphoric acid, H_3PO_4 , which can be converted into ammonium hydrogen phosphate, $(\text{NH}_4)_2(\text{HPO}_4)$ for use in soluble fertilizers, or into sparingly soluble magnesium ammonium phosphate $\text{Mg}(\text{NH}_4)(\text{PO}_4)$ (magamp) for use as a slow-release fertilizer.

Sulfur is also an essential nutrient, and some areas of New Zealand are sulfate deficient. Use of superphosphate, or ammonium, potassium or calcium sulfate (gypsum) as fertilizer supplies the needed sulfate.

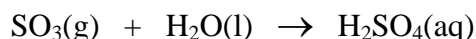
The sulfuric acid needed to make superphosphate is obtained by burning sulfur to form sulfur dioxide



which is oxidised over a catalyst to form sulfur trioxide



which reacts with water to form sulfuric acid



The sulfur is obtained from deposits of elementary sulfur found in volcanic areas of the world, or is extracted from natural gas, which in some places contains hydrogen sulphide.

Sulfur dioxide is released into the atmosphere from volcanoes. This is ultimately converted into sulfuric acid in the atmosphere; this is washed out by rain, so providing a "natural" source of sulphur. The 1995 eruption of Ruapehu "topdressed" much of the central North Island with economically useful amounts of sulphate. Sulfur dioxide is also released into the atmosphere when coal or oil containing sulfur is burned in power stations, and the resulting sulfuric acid in the atmosphere causes "acid rain" in some industrialized areas.

Potassium is the other main nutrient needed, and this is obtained from sea water, directly or indirectly. When sea water evaporates sodium chloride (common salt) crystallises first. If the liquid remaining (bittens) is evaporated potassium chloride crystallises. In some places this occurred over geological times when oceans were isolated by geological processes and then evaporated, leaving large deposits of salt (which crystallised first) and of potassium chloride (which crystallised later). The potassium chloride can be used directly as a fertilizer, and is satisfactory for use at low rates, but this has the disadvantage that chloride is also added, and many plants are not very tolerant of high levels of chloride. It is therefore usual to convert the potassium chloride to potassium sulfate (which also occurs in natural deposits) for use as a fertilizer.

The so-called "un-natural" inorganic fertilizers are thus derived from the very natural sources of the air (plus natural gas as a hydrogen source) for nitrogen, coral rock plus sea-bird droppings (plus sulfur from volcanoes or "sour" natural gas to make superphosphate) for phosphorus, and the ocean for potassium.

Minor nutrients

Magnesium levels in soils are usually adequate, though prolonged use of lime can deplete magnesium ions in exchangeable cation sites through competition by calcium ions. Occasional use of dolomite, $\text{CaMg}(\text{CO}_3)_2$, or magnesium sulfate, supplies magnesium.

Calcium levels are also usually adequate, though prolonged use of ammonium sulfate can deplete levels. The use of lime or superphosphate usually supplies adequate calcium. **Iron** and **manganese** are usually abundant in soils, but become very insoluble at higher pH levels. Plants probably absorb iron as a soluble "chelate" formed with a chelating (complex forming) agent excreted by the roots. Manganese levels are in a delicate balance between deficiency and toxicity, and can cause problems in some acid soils.

Other **minor nutrients** are *usually* present in adequate amounts, but can be deficient in particular regions. Local deficiencies can sometimes be identified by the symptoms shown by plants (e.g. yellowing of leaves caused by a deficiency of the magnesium needed to make chlorophyll), or by chemical analysis of the soil or plant material. Once the problem is identified then fertilizers containing the trace element can be applied. If a deficiency problem is suspected it may be simpler to use a fertilizer containing a mixture of the commonly lacking trace nutrients.

Fertilizers are commonly labelled with four numbers, which give the percentages of N, P, K and S; e.g. superphosphate is labelled 0 9 0 12 (9% P and 12% S). A variety of mixed fertilizers with different compositions are available; one available with all the major nutrients has composition 7 5 7 14.

One important factor in choosing fertilizers is how rapidly the nutrients become available to plants. Soluble inorganic compounds, such as urea, ammonium nitrate and potassium phosphate, are immediately available, and are commonly used for hydroponic solutions, and as foliar feeding solutions (plants can absorb soluble nutrients from solutions sprayed on their leaves). It is often better if the nutrients are released into the soil slowly throughout the growing season of the plant, and *slow release* fertilizers are used for this reason.

Sometimes nutrient deficiencies affect animals which eat the plants, rather than the plants themselves. Many of the soils of the central North Island plateau contain little cobalt, which is not required by plants, but is required by animals to make vitamin B₁₂. Cobalt is added as a fertilizer supplement and is taken up by the plants thereby providing the animals' requirements. There is also some evidence that added selenium, which is also present in low concentration in some New Zealand soils, may improve animal health though it is not needed by plants.

SOIL ANALYSIS

The nutrient status of soils can be determined by chemical analysis, in which the amount of a particular element in a known weight of soil is measured. However, not all of the element present in the soil may be available to plants, so forms of analysis which attempt to mimic the ability of plants to extract nutrients from the soil are commonly used. For example, the soil may be extracted with a citric acid solution, and the amount of the nutrient in the solution determined. The best extracting solutions have been found by trials in which the results of analysis using different extracting solutions are compared with plant growth observed in field trials.

The available cationic nutrients are generally determined by extracting a known weight of air-dried soil with an extracting solution, and then determining the amounts of K⁺, Mg²⁺, Ca²⁺, etc, present using atomic absorption or atomic emission spectrophotometers, which measure the amount of light characteristic of a particular element absorbed or emitted when

the solution is sprayed into a flame. One common determination for the amount of available phosphate is described below.

The other important parameter that needs to be monitored is the pH of the soil. Soil becomes progressively more acidic over time as a soil is leached by rainwater saturated with carbon dioxide. The cations are slowly replaced by hydrogen ions in reverse order to the strength of their binding by the soil, and carried away to the oceans by the percolating water. The singly charged ions are lost first, then the doubly and finally the triply charged ions, and the soil progressively becomes more acid in character.

Over geological time, even the aluminium and silica is leached away, and the surface of the land is steadily lowered. This exposes a fresh layer of subsoil to the weathering process, which releases new supplies of nutrients into the newly forming soil in a process of continuous renewal of the topsoil with its nutrients. The physical movement of soil particles, by gravity, wind or water in the process of *erosion* can greatly speed this process, especially on slopes.

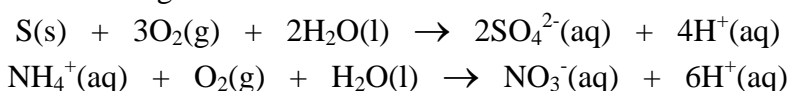
For gardeners and farmers the soil acidity is a useful indicator of availability of nutrients. This property is often referred to as *soil pH*, though more strictly it refers to the pH of the soil solution. The "soil pH" is readily measured (see below), and gives useful information about the state of a soil. In *acid soils* (pH < 6), many of the exchangeable sites in the clay minerals and humus are occupied by hydrogen or aluminium ions. Remaining nutrient cations are readily released by the soil, but there may not be much of these nutrients present. In very acidic soils, cations such as Fe^{3+} and Al^{3+} appear in the soil solution, and these are quite toxic to many plants. At the other end of the pH range, in basic soils (pH > 8), which are generally derived from limestone, the cation nutrients generally become less available.

Plant species have evolved to grow in soils with a particular pH range, and may not thrive in soils with acidities outside this range. For examples; rhododendrons grow best in strongly acid soils, most trees, shrubs and grasses in slightly acid soils, and many common vegetable crops grow best in neutral to slightly basic soils.

The acidity of a soil can be adjusted to suit the type of plants being grown. Most New Zealand native forest plants have developed to grow under the prevailing acid soil conditions, but the soil pH needs to be raised for optimum growth of most crop plants. The use of acid fertilizers, such as superphosphate, makes the soil more acidic. Soil is normally made less acidic by using lime (finely ground limestone, CaCO_3). For faster reaction, "slaked lime" can be used. This is made by heating limestone to form calcium oxide (quicklime, CaO), and then reacting this with water to form calcium hydroxide, $\text{Ca}(\text{OH})_2$. Lime also adds the necessary nutrient calcium, and improves the texture of acid soils (makes them less "sticky") by replacing the H of the -OH groups between the layers of the clay minerals by Ca^{2+} ions.

If the soil is deficient in magnesium, the mineral *dolomite*, $\text{CaMg}(\text{CO}_3)_2$ can be used instead of lime to raise the pH.

On the rare occasions when the soil pH needs to be lowered, e.g. to grow rhododendrons, this can be achieved by applying sulfur or ammonium sulphate. These are oxidized, releasing hydrogen ions and so making the soil more acidic:



General analysis

First look at where the soil is, and where it came from. Was the soil formed in position by weathering of the local substrate? What is the nature of the local substrate (sedimentary or igneous rock, volcanic ash, sand, - -)? Or has it been deposited from elsewhere; by the sea, by a river, by the wind, or by human activity? Or was it formed in peat, which is the largely organic residue of an ancient swamp?

Much can be learned about a soil just by looking at it and touching it. Look at the soil profile of a freshly cut bank, or dig a hole about 40 cm deep, and study the soil profile. Note the colour and feel of the soil, and the way these change with depth. Note the amount of organic material (plant debris) present -- high for peaty soils to low for clay subsoils. Soils with much organic material are generally dark coloured, soils with little organic material but high in iron(III) oxide are yellow and those low in iron are grey. Rub a sample between your fingers; is it fine and smooth or coarse and gritty? Does it stick to your fingers, or rub off cleanly? Shake a sample of the soil up with water and let it settle; sand and coarse unweathered mineral particles will settle rapidly, fine clay particles will stay suspended as "muddy" water for a long time, while coarse organic material may even float. Try to find what can be deduced from these properties for your local soil.

Animal life

Carefully crumble about 100 g of freshly collected soil and look for larger animals, such as earthworms and grass grubs. Spread the soil over a sieve (or piece of mesh curtain). Place the sieve over a piece of paper, cover, and leave in a dark place overnight. Try to identify the livestock which falls onto the paper.

Soil pH

Place about 10 g (a teaspoonful) of soil in about 100 ml of distilled water (or fresh rainwater) in a clean stoppered bottle and shake occasionally for about 5 minutes. Allow the solids to settle then **gently** press a glass electrode into the sediment layer and use a pH meter to determine the pH of the solution. If you do not have access to a pH meter, dip a non-bleeding pH "stick" into the solution and compare the colour developed with the chart; or filter the solution through **fine** filter paper (or centrifuge the solution) to produce a colourless solution then add a few drops of universal indicator, and compare the colour with the chart to determine the pH. What types of plants will grow well in soil with this "soil pH"?

Available Phosphate determination.

Phosphate is usually analysed by using a reaction with molybdic acid in the presence of a reducing agent. An intensely blue coloured compound (phosphomolybdic acid) is formed, and the colour intensity is proportional to the amount of phosphate present. The colour is compared with that developed in solutions containing a known amount of phosphate.

For analysis of an inhomogeneous material such as soil the collection of a *representative sample* is **extremely** important. The phosphate level will vary from place to place, and with

depth. You could choose a sample from some marked place (and the results would apply only to that place) or collect samples from typical places in an area, e.g. from hill-sides, from the level, near trees, etc, etc, and then thoroughly mix them, to get an average value for the area. The usefulness of the result will depend on how representative of the whole area your sample is.

Collect a soil sample (or samples). Allow to air dry for a few days so that reproducible results can be obtained. Roughly grind the soil using a pestle and mortar (thoroughly mix if average samples are being used).

Accurately weigh out about 0.5 g of soil and place in a stoppered flask, Add 100 mL of the extractant solution A, and shake (or stir with a magnetic stirrer) for 30 minutes. Filter through a **fine** filter paper.

Pipette 50 mL of the filtrate into a 100 mL volumetric flask, and add about 30 mL of water. Add 8 mL of reagent C and make up to 100 mL. The blue colour is developed over 10 minutes and is stable for 24 hours.

Pipette 0, 5, 10, 15, 20 and 25 mL of the standard solution E into labelled 100 mL volumetric flasks and fill to about 80 mL with water. Add 8 mL of reagent C and make up to 100 mL.

Compare the intensity of colour of the unknown and standard solutions. If you have a colorimeter, use a blue filter. If you have a spectrophotometer, the maximum absorption is at 880 nm, though a secondary maximum at 660 nm can be used. If you have no instrument, look sideways through the flasks at white paper and try to interpolate the unknown among the standards (or better, pour each solution into a *marked* test tube, filling them all to the same depth, and look down the tubes at white paper.

Estimate the extractable phosphate content of the solution and hence of the soil:

$$\mu\text{g P g}^{-1} \text{ of soil} = 4 \times \mu\text{g P ml}^{-1} \text{ in solution.}$$

Phosphate retention by soil

The ability of soils to bind phosphate gives useful information about the likely effectiveness of addition of phosphate fertilizers. In this test the soil is shaken with a standard phosphate solution, and the amount of phosphate adsorbed is determined by analysing the residual solution. The test is most useful for comparing different soils.

Accurately weigh about 5 g of ground air dried soil and place in a stoppered container. Add 25 mL of reagent F (which contains 1 mg P mL⁻¹) and shake or stir for 24 hours. Filter through **fine** filter paper.

Pipette 5 mL of the filtrate into a 500 mL volumetric flask, and make up to the mark. This solution would contain 10 $\mu\text{g P mL}^{-1}$ if the soil had not adsorbed any phosphate. Prepare calibration solutions by pipetting 10 and 25 mL of solution F into 50 mL volumetric flasks, and make up to the mark. Pipette 5 mL of each of these solutions, and of solution F, into labelled 500 mL volumetric flasks and make up to the mark.

Pipette 5 mL of the analysis solution, and of each of the calibration solutions, into separate labelled 100 mL volumetric flasks, add about 80 mL of water and 8 mL of reagent C to each and make up to the mark. Compare the blue colours after 30 min as for the previous test. The

calibration solutions correspond to 80, 50 and 0% phosphate retention, respectively.

Solutions for phosphate analysis

Reagent A (Truog's reagent). Dissolve 7.5 g of $(\text{NH}_4)_2\text{SO}_4$ plus 5 mL of $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ in 2.5 L of distilled water.

Reagent B. Dissolve 30 g of ammonium molybdate in 1 L of water (warm to dissolve, but do not heat above 60° C). Dissolve 0.667 g of antimony potassium tartrate in 250 mL water. Add these solutions to 1.25 L of $5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ (353 mL conc. H_2SO_4 made up to 1.25 L). Mix and make up to 2.5 L and store in a dark bottle. If antimony potassium tartrate is not available, the test can still be applied, but the colour development is slower. Allow the solutions to stand for at least 30 minutes, or heat in a boiling water bath for 10 minutes before comparing the colours.

Reagent C (Murphy and Riley reagent). Take as much of reagent B as required and dissolve 1 g of ascorbic acid (vitamin C) for every 100 mL. Mix thoroughly. This solution does not keep for more than 24 hours.

Reagent D; Phosphate standard stock solution ($100 \mu\text{g P mL}^{-1}$). Dissolve 0.220 g of potassium dihydrogen phosphate (KH_2PO_4) in water and make up to 500 mL in a volumetric flask. Add 0.5 mL of toluene if the solution is to be kept for any length of time.

Reagent E; Phosphate working solution ($1 \mu\text{g P mL}^{-1}$). Pipette out 5 mL of the stock solution D and make up to 500 mL. Prepare as required.

Reagent F (1 mg P mL^{-1} at pH 4.6). Dissolve 4.4 g of KH_2PO_4 and 16.4 g of anhydrous sodium acetate in water in a 1 L volumetric flask, add 11.5 mL of glacial acetic acid, and make up to the mark.

Written by Prof. Neil Curtis (Victoria University) with assistance from Dr. Cyril Childs.
Edited by Heather Wansbrough.