Understanding soil analysis data

M A. Hamza

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Understanding soil analysis data
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MA Hamza

July 2008

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Acknowledgments

The cost of the first edition of this publication has been wholly met from the South Coast Soil Health Initiative project managed by Tim Overheu (core funding also provided by the Western Australian and Australian Governments through the National Action Plan for Salinity and Water Quality, hosted by South Coast Natural Resource Management Inc.). I would also like to thank Tim for his helpful comments, contributions, valuable suggestions and coordination support to finalise this publication.

Additional thanks go to Wal Anderson, Ross Brennan, Mike Bolland, Chris Gazey and Ruhi Ferdowsian from the Department of Agriculture and Food, Western Australia, and to Dave Allen from the Chemistry Centre, Western Australia for their technical comments and suggestions on draft versions.

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Front cover

The front cover shows an aerial view of the North Stirling basin with a Department of Agriculture and Food trial site in the foreground.
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Introduction

The aim of this report is to help people who are interested in soil science, but are not specialists in this area, to better understand soil analysis reports in particular, and soil data in general.

An important starting point is acknowledging that agricultural laboratories express analytical results differently. Some are easier to understand than others, but many recipients see only a long list of incomprehensible figures. This publication contains information to assist with the understanding of results from common agricultural analyses. It is not intended to make recommendations for application of fertilisers, or to suggest that one form of analytical data is more useful than any other. It is important however, that any interpretations are cross checked with advice from a local agronomist. It is also important to acknowledge that specialist analyses may not be covered in this document.

When it comes to selecting the right set of tests, your local Department of Agriculture and Food soil resource extension officer or agronomist can help determine the best analytical tests for your farm. When choosing a laboratory to submit your soil samples, you need to make sure it has quality accreditation. This publication has been written for Western Australia. However, the principles apply in all areas. Check with your local agronomist to determine any differences in preferred levels for your region.

Soil analysis reports are generally tailored to provide the required information for both physical and chemical fertilities of the soil. Some soil reports may also include biological analysis. Soil physical fertility represents the ability of the soil to store and conduct water, nutrients and gases. Whereas soil chemical fertility indicates whether there are enough available nutrients for plant growth, or whether fertilisers are needed to correct deficiencies. Soil physical fertility information should include soil texture while the chemical fertility information should cover cation exchange capacity (CEC), the percentage of exchangeable cations, pH, electrical conductivity (EC), organic carbon (matter) and the concentrations of essential macro and micronutrients in the soil, as well as some other elements such as aluminium. Lime, gypsum or dolomite requirements are also included. Organic matter in the soil is important for both chemical and physical fertility and should be an important part of any soil report.

The chemical tests should address accurately both nutritional and toxicity considerations. Ideally, the soil test should not only identify whether a nutrient deficiency exists, but also the degree of deficiency in terms of expected yield loss. It is important that the quantity of nutrient required to correct the deficiency is then determined by field calibration trials. An ideal soil test is one that is reproducible and rapid, as well as being reliably correlated with local responses in plant yield or nutrient uptake.

Calibrating soil test in the field

Two calibration approaches are common in soil fertility:

- Comparing fertilised and unfertilised plots: to quantify plant yield response, the relative yield in the presence (Yf) and absence (Ynf) of the applied nutrient(s) are examined.
  
  \[ \text{Relative yield} \ (\%) = 100 \left( \frac{Y_{uf}}{Y_{f}} \right) \]
  
  \[ \text{Relative yield response} \ (\%) = 100 \left[ \frac{(Y_f - Y_{nf})}{Y_f} \right] \]

- The examined nutrient(s) are applied as treatments to selected soils of varying soil nutrient status. Yields are then compared statistically for significant increase.
These two approaches show if there are adequate or deficient levels of a particular nutrient(s) in the soil and do not take into account the effect of other soil or environmental constraints which might affect yield.

Most of the soil samples must be dried and ground before analysis. To determine the soil fertility level, nutrients must be removed from the soil exchange sites (clay minerals and organic matter) to the soil solution where they can then be extracted and measured.

**Principle of soil extraction**

Most of the soil chemical tests are based on extracting elements from the soil solid phase to a soil-free liquid phase (extractant) and then measuring the concentration of these elements in the soil-free liquid phase. The extraction can be done by one or more of the following processes:

- **Ion exchange/desorption:** Where the elements are replaced from the soil solid phase by an element that is more strongly adsorbed to the soil exchange sites. Plant available phosphorus (P) and sulphur (S) in Australian soils are commonly extracted by this method. This method also forms the basis for some of the new techniques to extract nutrients from soil by applying cation/anion exchange resin strip or capsules, and filter paper strips saturated with iron oxide.

- **Dissolution:** Dissolving the elements by water or a more vigorous extracting solution such as an acid or ligand (a molecule, atom or ion bonded to the central metal atom or ion in a coordination compound). In Australia, water is used to extract soluble salts from soil and for measurement of electrical conductivity, gypsum and chloride (Rayment & Higginson 1992b). Acids such as hydrochloric and sulphuric are commonly used to dissolve sparingly soluble calcium phosphate in soil.

- **Complexation:** The availability to plants of micronutrients such as zinc (Zn), iron (Fe), copper (Cu), manganese (Mn) and P is limited by the rate of diffusion through soil, particularly in neutral and alkaline soils. Complexation of these ions in the rhizosphere then becomes an important step in accessing them by plant roots (Lindsay 1974). Accordingly, complexing agents have been used widely in testing for micronutrients in soil. The complexation is achieved when an element in the soil is complexed or paired with a complexing ion or compound, changing the effective charge on the element and retaining it in solution in a complexed form for subsequent analysis.

- **Oxidation/reduction:** Some elements undergo a distinct change in chemical behaviour as a result of either reduction or oxidation. These changes cause the element to be released from the solid phase into either solution or gaseous phase for analysis. An example of this method is the determination of soil organic carbon.

**Soil depth**

Plant roots are commonly more extensive in the subsoil. Accordingly the subsoil environment is more relevant to root growth than the topsoil. However, most fertilisers and soil amendments are applied to the topsoil rather than into the subsoil for practical reasons, which can be problematic. For example, if lime or immobile nutrients were applied to the topsoil, they would not move down in an appreciable amount to meet crop demands in time.

Topsoil is important in other aspects. In rain-fed areas, it separates the subsoil from the atmosphere where the main source of moisture is. It also contains the main accumulation of organic matter and applied fertilisers. Organic matter represents the main residual source of nitrogen (N) in the soil and N content of organic matter must be known before estimating how much N fertiliser needs to be applied. Topsoil is usually high in P because only part of P fertiliser is recovered every year and most P fertilisers are relatively insoluble.
Plant nutrient movement within the soil profile is a complex issue because it is affected by many soil parameters such as pH. It is hard to establish a clear cut line defining borders between different nutrient concentrations at different soil depths. In general, for a satisfactory soil test, both topsoil (0-10 cm) and subsoil (10-40 cm) should be sampled.

Some agricultural laboratories provide soil sample kits which can be helpful in soil sampling. The kits can instruct how to collect a number of soil samples (usually topsoil) which are mixed together in a bag. This means that the analytical report will be an average of the combined samples. However, averages can hide problems if there is a big range in the soil sampled. Areas where vegetation changes or where plant vigour is different are likely to have different soil conditions and these areas should be tested separately.

1. Forms of nutrients in soils

In soil, most plant nutrients are present as minerals, organic matter, exchangeable ions or in solution. The bulk of these nutrients are not readily available for the plant. They only become available through chemical, physical and biological processes which are mostly not fast enough to meet plant demands. In general, the short term supply of cations to plants is governed by the established equilibrium between exchangeable cations and their concentrations in the soil solution. Table 1 shows the average of how many nutrients are contained per tonne of grain of different crops.

Table 1. Average nutrients contained in 1 tonne of grain of different crops. Note that amounts can vary by as much as 30 per cent due to differences in soil fertility level, crop varieties and seasons (published and unpublished data)

<table>
<thead>
<tr>
<th>Crop</th>
<th>N</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>S</th>
<th>Cu</th>
<th>Zn</th>
<th>Mn</th>
<th>B</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/t</td>
<td>kg/t</td>
<td>kg/t</td>
<td>kg/t</td>
<td>kg/t</td>
<td>kg/t</td>
<td>g/t</td>
<td>g/t</td>
<td>g/t</td>
<td>g/t</td>
<td>g/t</td>
</tr>
<tr>
<td>Barley</td>
<td>21</td>
<td>3</td>
<td>4</td>
<td>0.4</td>
<td>1.5</td>
<td>2</td>
<td>5</td>
<td>17</td>
<td>15</td>
<td>2</td>
<td>0.3</td>
</tr>
<tr>
<td>Wheat</td>
<td>23</td>
<td>3</td>
<td>4</td>
<td>0.3</td>
<td>1.3</td>
<td>2</td>
<td>4.5</td>
<td>22</td>
<td>35</td>
<td>4.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Chickpea</td>
<td>33</td>
<td>3.2</td>
<td>9</td>
<td>1.6</td>
<td>1.4</td>
<td>2</td>
<td>7</td>
<td>34</td>
<td>34</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Faba beans</td>
<td>41</td>
<td>4</td>
<td>10</td>
<td>1.3</td>
<td>1.2</td>
<td>1.5</td>
<td>10</td>
<td>28</td>
<td>14</td>
<td>13</td>
<td>3</td>
</tr>
<tr>
<td>Field peas</td>
<td>38</td>
<td>3.4</td>
<td>9</td>
<td>1</td>
<td>1.3</td>
<td>1.8</td>
<td>5</td>
<td>35</td>
<td>14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Canola*</td>
<td>35</td>
<td>6</td>
<td>9</td>
<td>4</td>
<td>4</td>
<td>9</td>
<td>6</td>
<td>40</td>
<td>30</td>
<td>16</td>
<td>0.3</td>
</tr>
<tr>
<td>Lupins</td>
<td>55</td>
<td>3.5</td>
<td>10</td>
<td>2.7</td>
<td>2</td>
<td>2.4</td>
<td>5</td>
<td>30</td>
<td>60</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>Oats</td>
<td>20</td>
<td>3</td>
<td>4</td>
<td>0.5</td>
<td>1.5</td>
<td>2</td>
<td>5</td>
<td>25</td>
<td>37</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>Hay</td>
<td>30</td>
<td>3</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

When interpreting a soil report we should consider that grain yield will be determined by the least available essential nutrient, whether this is a macro or micronutrient (Figure 1). This concept is called the ‘Law of the minimum’ and was introduced by the German chemist, Justus von Liebig. It indicates that plant growth is constrained by the essential element that is most limiting. Other limitations could be moisture or any chemical or physical factors. If a factor is not limiting, increasing it will do little or nothing to enhance plant growth. In fact, increasing it may actually reduce plant growth by throwing the system further out of balance.

In general, there are 16 essential elements for plant growth. An essential element for plant growth can be defined as follows:

1. It cannot be substituted by any other element.
2. The plant can not complete its life cycle without it.
3. It is directly involved in the nutrition of the plant as a constituent of an essential metabolite or required for the action of an enzyme system (Mengel & Kirkby 1982).

![Figure 1](image.png)

**Figure 1.** An illustration of the ‘Law of the minimum’ where copper (Cu) is the least available element, resulting in only 60 per cent of the potential yield.

The 16 essential elements or nutrients are:

- Carbon (C)
- Hydrogen (H)
- Oxygen (O)
- Nitrogen (N)
- Phosphorus (P)
- Sulphur (S)
- Potassium (K)
- Calcium (Ca)
- Magnesium (Mg)
- Iron (Fe)
- Manganese (Mn)
- Copper (Cu)
- Zinc (Zn)
- Molybdenum (Mo)
- Boron (B)
- Chlorine (Cl)

Oxygen and carbon are obtained from the air, while hydrogen is obtained from splitting the water inside the plant. All the other 13 elements are absorbed from the soil. Silicon and sodium might be required by some higher plants and cobalt may be essential for some legumes (Chatel et al. 1978). Nutrients interact with each other, resulting in either a decrease (antagonism) or an increase (stimulation) in their availability to the plant.

In general, plant nutrients can be classified into four groups depending on their biological functions (Table 2, Mengel & Kirkby 1982).
Table 2. Classification of plant nutrients

<table>
<thead>
<tr>
<th>Nutrient element</th>
<th>Most common uptake form</th>
<th>Biological function</th>
</tr>
</thead>
<tbody>
<tr>
<td>P, B</td>
<td>H₂PO₄⁻, H₂PO₄²⁻, H₃BO₃, H₂BO₃⁻</td>
<td>Esterification with native alcohol groups in plants. P-esters are involved in the energy transfer reaction (TPA to DPA).</td>
</tr>
<tr>
<td>K, Mg, Ca, Mn, Cl</td>
<td>K⁺, Mg²⁺, Ca²⁺, Mn²⁺, Cl⁻</td>
<td>Establishing osmotic potential, enzyme activation, balancing anions. Maintaining membrane permeability and electron potential.</td>
</tr>
<tr>
<td>Fe, Cu, Zn, Mo</td>
<td>Fe²⁺, Cu²⁺, Zn²⁺, MoO₄²⁻</td>
<td>Enable electron transfer by valency change. Present mainly in chelated* form incorporated in prosthetic** groups.</td>
</tr>
</tbody>
</table>

* A molecular structure in which a central polyvalent metal ion is combined into one or more rings by a chelating agent.

** A non-protein molecule which is combined with a protein, such as the haem group in haemoglobin.

Besides Table 2, which classifies nutrients into groups, some important functions of the micronutrients are:

- **Zinc, Zn:** Promotes growth hormones and starch formation, promotes seed maturation and production
- **Iron, Fe:** Important in chlorophyll formation, N fixation, NO₃⁻ and SO₄²⁻ reduction
- **Copper, Cu:** Important in photosynthesis, protein and carbohydrate metabolism, and probably N fixation
- **Magnesium, Mg:** Important in photosynthesis, N metabolism, and N assimilation
- **Boron, B:** Facilitates sugar translocation and synthesis of nucleic acids and plant hormones, essential for cell division and development
- **Molybdenum, Mo:** Essential for nitrogen fixation and assimilation because it is present in nitrogenase (nitrogen fixation) and nitrate reductase enzymes
- **Cobalt, Co:** Essential for nodule function and nitrogen fixation in legumes
- **Chloride, Cl:** Essential in photosynthesis, regulates water uptake in salt-affected soils.

It is clear from the functions of the nutrients that N, which is taken up by most higher plants in quantities more than any other essential element, would not be utilised by the plant without the presence of Mo which may be the element absorbed least. This emphasises the fact that all essential elements have the same importance for the plant. Figure 2 shows the average level of micronutrients in plants.
2. Soil physical properties

2.1 Soil texture

Soil texture is not readily subject to change, so it is considered a basic property of a soil. Soil texture refers to the size (diameter) of individual soil particles. There are three broad groups of textural classes: sand, loam and clay (Figure 3). The size differences between these classes give rise to significant differences in other physical properties such as pore size and cation exchange capacity, which play a vital role in storing and transporting water, gases and nutrients in soil (see Table 3).

Table 3. Some physical properties of the major soil texture classes

<table>
<thead>
<tr>
<th>Texture class</th>
<th>Size (mm)</th>
<th>Number of particles per gram</th>
<th>Specific surface area (cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse sand</td>
<td>2.0-0.2</td>
<td>5 x 10²</td>
<td>20</td>
</tr>
<tr>
<td>Fine sand</td>
<td>0.2-0.02</td>
<td>5 x 10⁵</td>
<td>200</td>
</tr>
<tr>
<td>Silt</td>
<td>0.02-0.002</td>
<td>5 x 10⁸</td>
<td>2,000</td>
</tr>
<tr>
<td>Clay</td>
<td>&lt; 0.002</td>
<td>5 x 10¹¹</td>
<td>20,000 (2 m²)</td>
</tr>
</tbody>
</table>
Table 3 shows clearly that the most important classes in soil texture are clay and to lesser extent silt, since they possess hundreds of times more surface area (hence more electrostatic adsorption capability) than sand. This enables the soil to store many more nutrients and also to buffer the harmful effect of sudden chemical changes in the soil. Most natural agricultural soils contain some clay. Even sandy soils at the lowest left hand corner of the triangle (Figure 3) may contain up to 10 per cent clay. This small fraction of clay is what makes such soils suitable for broadacre agriculture. For example, one gram of extremely sandy soil (95% sand + 5% clay or a ratio of 19:1 sand to clay) contains only 19 cm$^2$ surface area of sand but 1,000 cm$^2$ surface area of clay. The ratio for sand:clay surface area is 1:53.

Another important function of clay is to act as a binding agent, helping it to aggregate and maintain good soil structure (Figure 4).
Furthermore, clay and to a lesser extent silt, help to maintain bio-pores in soil by coating them, thus providing a network of conducting channels (Figure 5).

Soil texture is determined by establishing how much sand, silt and clay are in a soil sample. This is commonly done by a modified ‘plummet’ procedure. Soil is dispersed with a solution of ‘Calgon’ (sodium hydroxide), then silt (0.020-0.002 mm) and clay (<0.002 mm) are measured by density measurements using a plummet after standard settling times (Loveday 1974).

2.2. Soil structure

Soil structure refers to soil aggregation and is defined as the combination or arrangement of primary soil particles (sand, silt and clay) into secondary units or peds. The secondary units are characterised on the basis of size, shape and grade. Soil structure is the main soil physical fertility parameter that affects water and nutrient transport and storage in the soil.

There is a direct relationship between the dominant clay type in soil and the ability of the soil to form and maintain its structure. A brief discussion of clay minerals in soil may be helpful for understanding soil texture classes.
Clay minerals

Most clay minerals in soil are silicates. They carry negative charges which play a vital role in soil structure and plant nutrition. However, there are some non-silicate clays which do not carry electrostatic charges, such as iron and aluminium oxides and hydroxide clay, which is common in highly weathered soils like the ones in Western Australia (Gibbsite, Al(OH)₃ is a common non-silicate clay). Most silicate clay minerals are composed of microscopic sheets in a flake shape or hexagonal crystals (Figure 6). There are two dominant types of clay which influence soil structure: 1:1 clay which is common in the highly weathered soils of WA, and 2:1 clay which dominates less weathered soils in the rest of the world (see Figure 6).

![Figure 6. Two silicate clay minerals, kaolinite, 1:1 clay (left) and mica (illite), 2:1 clay (right) (Courtesy of Dr Bruce F. Bohor, Illinois State Geological Survey, Soil Science Society of America)](Image)

The basic molecular and structural components of silicate clays are:

- **Tetrahedron**: Four-sided building block composed of a silicon ion surrounded by four oxygen atoms
- **Octahedron**: Eight-sided building block in which Al or Mg ions are surrounded by six hydrogen groups or oxygen atoms (Figure 7).

The classification of clay minerals into the two main silicate groups 1:1 and 2:1 is based on the number and arrangement of tetrahedral (Si) and octahedral (Al, Mg) sheets contained in the crystal units or layer. In 1:1 silicate clay, each layer contains one tetrahedral and one octahedral sheet. In 2:1 silicate clays each layer has one octahedral sheet sandwiched between two tetrahedral sheets (Figure 8).
Figure 7. A single tetrahedron and octahedron, the two major building blocks for silicate clay mineral. In the clay crystal thousands of tetrahedral and octahedral building blocks are connected to give planes of Si and Al (or Mg) ions.

Figure 8. Schematic drawing illustrating 1:1 and 2:1 clay minerals.
Note that 1:1 clay, such as kaolinite is not an expanding clay because its layers are held together by hydrogen ions. Maximum interlayer expansion is found in smectite (Figure 9) and vermiculite (with somewhat less expansion) because of the moderate binding power of numerous Mg\(^{2+}\) ions. Expansion occurs when water enters the interlayer spaces forcing the layers apart. Some 2:1 clay minerals, such as fine-grained illite and chlorite do not expand because K\(^+\) ions (for example in case of fine-grained illite) or an octahedral-like sheet of hydroxide of Al, Mg, and Fe tightly bind the 2:1 layers together.

![Figure 9. 2:1 expanding clay mineral smectite. This clay mineral has a maximum swelling power (Courtesy of USDA Natural Resources Conservation Service)](image)

**Source of negative charges in silicate clay minerals**

During the weathering of rocks and minerals, many different elements coexist together in the weathered solution. As the clay minerals are crystallised, cations of comparable size may substitute for Si, Al and Mg ions in the tetrahedral or octahedral sheet causing unbalanced charges to occur in the clay lattice (Figure 10).

![Figure 10. Isomorphic substitution, here a magnesium or iron ions with +2 charges replacing an aluminium ion with 3+ charge causing the net charge to be -1.](image)
Soil compaction

Soil compaction is a major deterioration in soil structure. Even though large areas of Western Australia suffer from soil compaction, many farmers are not aware of the problem because it occurs in the subsoil and is seldom visible at the surface (Figure 11).

Figure 11. Soil erosion exposes soil compaction
(image courtesy of Chris Gazey, DAFWA).

Compacted soils usually have massive soil structure (sometimes called structureless) and high bulk density (Figure 12). In well structured soils, the pore spaces are relatively large and connected (Figure 13). Whereas in compacted soils, the pores are usually crushed and hydraulic continuity is disrupted. Compacted soils usually store much less soil solution and transport it more slowly than soils with good structure. In addition, roots need to exert more energy to penetrate the soil, energy which otherwise would be allocated for plant growth and yield. The limited amount of energy available leads to small, shallow root systems (Figure 14) and makes it difficult for seedlings to emerge (Figure 15). When soil strength exceeds 2.5 MegaPascals (MPa) most plant roots cease growing (Figure 16).

Figure 12. Compacted, massive clods brought up to the soil surface upon ripping a sandy soil in Tammin, Western Australia.
Figure 13. A three dimensional scan image of the network of pores in undisturbed soil (edges about 2 mm long). The pores (light in colour) show great variability in size and cross-sectional area. Not all pore channels are connected to each other leading to isolation of some tiny pockets of air and water, hence preventing them from moving readily downward or upward in the soil (Courtesy of Dr Isabelle Cousin, INRA Unite de Science du sol, SESCPF Centre de Research d’Orleans de Limere, Ardon, France).

Figure 14. Left: Corn crop with fibrous roots growing in compacted and uncompacted subsoils. Right: Black-berried nightshade weeds with tap roots growing in compacted and uncompacted subsoil (image B courtesy of Tim Overheu). Note the horizontal short growth of the primary tap roots in compacted soil compared to the vertical more extensive root growth in the uncompacted subsoil.
Figure 15. Plant seedlings must force their way through the soil surface as in this picture. In compacted soils this process is more difficult (Courtesy of R Weil).

Figure 16. Relationship between root growth and soil strength.

The presence of specific cations in the soil helps in forming and maintaining good soil structure because they help soil aggregation. To understand the role of cations in soil structure it is important to discuss how soil structure is formed.

**How soil structure is formed**

Soil structure depends on the ability of clay particles (flakes or crystals) to flocculate (form aggregated or compound masses of particles). Flocculation is a balance between two opposing forces which act on the clay particles: a repulsive force which prevents flocculation and an attractive force which causes flocculation. The repulsive force occurs between negatively charged clay particles, while the attractive force is Van Der Waal’s force.

Van Der Waal’s force is a weak attractive force between non-polar, electrically neutral molecules or parts of molecules when they lie close together. It acts over a very short range and is inversely proportional to the seventh power of the distance between the atoms or molecules. This microscopic distance coupled with the weakness of the force makes it easy for the repulsive force to be dominant, preventing flocculation and causing soil dispersion. To overcome this dominance, a large proportion of the negative charges on the clay particle must be neutralised to reduce the repulsive force and allow the attractive force to be active. This can be achieved by adding any cation (e.g. calcium) to the soil (Figure 17). The higher the cation valence (number of charges per ion) the higher the neutralising value of that ion.
Figure 17. Calcium ions help clay particles to flocculate by neutralising negative charges, thus reducing the repulsive forces between them.

For example, flocculation can be produced in the soil by addition of Al, Ca or Na in the relative amounts of approximately 0.04 Al³⁺, 2Ca²⁺ or 100 Na⁺ (Taylor & Ashcroft 1972). However, at these relative amounts both Na and Al will be harmful for both soil and plant, so Ca is the best practical choice to produce flocculated soil. It can be applied as gypsum (CaSO₄·2H₂O) and lime (CaCO₃) to address mild soil compaction. However, severe soil compaction must be removed by physical means, such as ripping after applying calcium. Ripping soil in the absence of an aggregating agent such as gypsum or organic material benefits the soil only for a short period, after which the soil becomes compacted again. Crops with strong, deep taproots could also be used to deal with soil compaction. Roots shrink (on transpiration) and swell (at night when transpiration has ceased) pushing and disturbing soil around them, thus helping to mitigate compaction (Hamza et al. 2001, Figure 18).

Figure 18. Scanning electron micrograph of a cross-section of a peanut root surrounded by soil. Plant roots shrink and swell diurnally, destabilising soil around them and loosening compaction.
3. Calcium to magnesium and other cation ratios

While the role of exchangeable Ca in maintaining soil structure especially in medium to heavy soils is well known and documented, it has proven difficult to establish critical levels of exchangeable Ca for plant growth that apply across a range of dissimilar soils (Bruce 1999). Pierre (1931) was one of the first to emphasise the importance of exchangeable Ca in acid soils and to suggest that base saturation (see Glossary for definition) was more important than the absolute amount of exchangeable Ca. He also concluded that the percentage base saturation of soils, and probably the proportion of the various bases present in the exchange complex and in the soil solution, are primary factors which directly influence plant growth on acid soils. This influence on plant growth comes from decreasing H, Al and Mn toxicities and it is only in the absence of these toxicities that Ca saturation becomes a useful measure of Ca availability to the plant (Adams 1984).

The ratio of Ca to Mg has been suggested for diagnostic purposes on the basis that it takes into consideration the competing effect of Mg on Ca availability (Carter et al. 1979, McLean 1981). However, experimental findings are conflicting in this respect because the Ca:Mg ratio overlooks the contribution of other cations, particularly Al in acid soils and Na in sodic soils (Bruce 1999). So it is not precise to talk only about the Ca:Mg ratio when we discuss plant nutrition because almost all cations tend to interact and compete against one another for uptake by roots. For example, because K⁺ ion absorption by plant roots is affected by the activities of other ions in the soil solution, some researchers prefer to use the ratio represented by the following equation:

\[
\left[ \frac{K^+}{Ca^{2+} + Mg^{2+}} \right]^{1/2}
\]

rather than the K concentration to indicate the available K level in the soil solution (Brady & Weil 2002). The major portion of cations that is absorbed by roots comes from the soil solution. However, the relative concentration of cations in soil solutions may bear no relationship to relative amounts of exchangeable cations. For example, sodium is often the dominant cation in soil solution in spite of a low exchangeable amount. For this reason it has been suggested that relative affinities of ions for exchange sites are more important than concentration (Bell & Gillman 1978). Table 4 shows a general guide for the desirable proportion of different cations ratio that suits different plants (Abbott 1989).

<table>
<thead>
<tr>
<th>Cations</th>
<th>% CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>65-80</td>
</tr>
<tr>
<td>Mg</td>
<td>10-15</td>
</tr>
<tr>
<td>K</td>
<td>1-5</td>
</tr>
<tr>
<td>Na</td>
<td>0-1</td>
</tr>
<tr>
<td>Al</td>
<td>&lt; 5</td>
</tr>
</tbody>
</table>
As far as plant nutrition is concerned, there is no universal or unique Ca:Mg ratio because:

- Plants differ in their absorption of Ca and Mg
- Ca and Mg have different affinity for clay minerals which affects their exchangeability and removal (leaching) rates
- Soils differ in their content of Ca and Mg.

Some duplex soils in WA show different Ca:Mg ratios for topsoils and subsoils. For example, a soil from Nyabing may have a 4.61 Ca:Mg ratio for the topsoil and half as much for the subsoil. Whereas some of the sodic soils from Salmon Gums have 12.20 exchangeable sodium percentage (ESP) and 0.92 Ca:Mg ratio at the topsoil, while in the subsoil the ESP increases to 46.30 and the Ca:Mg ratio decreases to 0.26.

It is desirable to have Ca as the dominant cation on the exchange complex (Bruce 1999), but Al may be dominant in acid soils and Na in sodic soils.

The Ca:Mg ratio is of greatest importance for good soil structure, particularly in clayey and loamy soils. Bearing in mind that it is difficult to determine an optimum ratio for Ca:Mg, many soil laboratories show in their soil report an ‘ideal’ ratio, based on the chemical analysis of individual soils. **It should not be used as the basis for making fertiliser recommendations, but simply as supplementary diagnostic information.**

**Gypsum, lime and dolomite – selection for particular soils**

Lime and dolomite have given similar responses at most sites tested (Cregan et al. 1989). It has been suggested that yield response was due to the lime effect on soil pH which allowed the plant to better exploit subsoil Mg and not to the Mg in dolomite. The selection of one or a combination of the materials for a particular soil should be based on the levels of calcium and magnesium found and on pH. The quality of lime, dolomite and gypsum vary depending on many factors. Purity, low salinity and absence of heavy metals are important in good quality materials. Ca should make up the following amount of the pure chemical component as:

<table>
<thead>
<tr>
<th>Material</th>
<th>Calcium</th>
<th>Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum (calcium sulphate)</td>
<td>23.2%</td>
<td>18.6% sulphur</td>
</tr>
<tr>
<td>Lime (calcium carbonate)</td>
<td>40%</td>
<td></td>
</tr>
<tr>
<td>Dolomite (calcium/magnesium carbonate)</td>
<td>21.7%</td>
<td>13.2% magnesium</td>
</tr>
</tbody>
</table>

* Calculations are based on pure chemical formula. When calculated on commercial formula the impurities would reduce the percentage.

**Note that:**

- Soils low in both calcium and magnesium are often lighter sandy soils and may require amelioration with dolomite.
- Soils low in calcium with high magnesium require lime or gypsum or a combination of both.

The addition of gypsum to soil will increase calcium, while at the same time displacing some magnesium. It is important to maintain a healthy ratio for good soil structure.

Some researchers have reported a decrease in lupin yield immediately after application of lime or gypsum. The causes of yield reduction are not fully understood due to contradictory
research results (Hamza & Anderson 2001), however the following causes have been reported:

- Competition between calcium (from gypsum or lime) and soil potassium
- Iron deficiency due to increasing soil pH after liming (Alami et al. 1998; Foy 1997; Birchall et al. 1995)
- An osmotic effect on lupin yield due to gypsum application (McLay 1997; Tang et al. 1995).

It has been recommended by some researchers that lupins should not be sown for at least two years after lime or gypsum applications (Tang et al. 1995; Hamza & Anderson 2001).

### 4. Soil reaction, pH

The H⁺ concentration in soil, as well as in plant fluids, is generally low and for this reason is expressed in terms of a logarithmic scale, or pH. The pH scale was suggested in 1909 by SPL Sorensen as a simple numerical expression of acidity of a solution. It has proven its importance in biology and is still in common use. The pH is defined as the logarithm of the reciprocal of H⁺ ion concentration in solution: \[ \text{pH} = \log \left[ \frac{1}{[H^+]} \right] \]. Pure water is neutral because it contains an equal amount of hydrogen ions (\( [H^+] = 10^{-7} \)) and hydroxyl ions (\( [OH^-] = 10^{-7} \)). Thus the ion product of the concentrations of H⁺ and OH⁻ ions is a constant equal to 10⁻¹⁴.

Since the product of the concentrations of H⁺ and OH⁻ ions must be equal, the increase in one of them must be accompanied by a decrease in the other. Thus, if the H⁺ concentration in an acid medium is 10⁻⁵, the pH is five, if it is 10⁻⁹ in an alkaline medium, the pH is nine. A soil pH 7 is regarded as neutral and a pH less than 7 is acidic, while a pH greater than 7 is alkaline.

The concentration of H⁺ ions in the soil represents actual acidity, while potential acidity also includes adsorbed H⁺ on the soil exchange sites (clay plus organic matter). Soils differ in their buffering capacity (the ability of a soil to resist changes in pH) for acidity, depending on the content of colloids. The higher the colloidal content of the soil, the higher the buffering capacity and the greater the difficulty for changing pH (clay soils have much higher buffering capacity than sandy soils).

The pH values of soils can differ widely from values of about three to as high as ten. In alkaline soils in particular, very high pH is commonly caused by the presence of weak acids (HCO₃⁻) and strong bases (Na⁺ or K⁺). The pH at the root surface (rhizosphere) may be as much as one unit different from that of the bulk soil, depending on OH⁻ or H⁺ effluxes from the roots (Nye 1977). If the plant absorbs more cations (positively charged ions such as K⁺) than anions (negatively charged ions such as Cl⁻), it releases H⁺ into the soil to maintain a negative potential across the root cell membrane (around -150 mV). If the plant absorbs more anions than cations, it releases OH⁻ or HCO₃⁻ into the soil to keep cell potential negative. In most cases, plants absorb more cations than anions and as a result release H⁺ ions to the soil lowering the value of pH at the root surface. The type of N fertiliser (whether NH₄⁺ or NO₃⁻) plays an important role in this regard.

The mix of plant species that dominates a landscape under natural conditions often reflects the pH of the soil (Brady & Weil 2002). The degree of soil acidity or alkalinity, expressed as soil pH, is a master variable that affects soil chemical, biological and indirectly its physical properties. Soil pH greatly influences the availability for root uptake of many elements, whether they are essential or toxic to the plant. A generalised idea of the relationships is shown in Figure 19. High H⁺ concentration (low pH value) favours the weathering of minerals resulting in a release of various ions such as K⁺, Mg²⁺, Ca²⁺, Mn²⁺, Cu²⁺ and Al³⁺. The solubility of salt minerals including carbonates, phosphates and sulphates is higher in the
lower pH range. The release and thus toxicity of Al in various forms from clay minerals is also pH dependent. However, Al solubility increases exponentially when soil pH drops below 4.5 (see Figure 19).

Soil pH also affects the mobility of many pollutants in soil by influencing the rate of their biochemical breakdown, their solubility and their adsorption on colloids.

Figure 19 shows that, when the correlation between soil pH and nutrient availability is considered as a whole, a pH range of about 5.5 to perhaps 7.0 seems to be best to promote the availability of plant nutrients. In short, if the soil pH is suitably adjusted for phosphorus, the other plant nutrients, provided they are present in adequate amounts, will be satisfactorily available in most cases (Brady & Weil 2002).

Figure 19. The relationships between soil pH, availability of plant nutrients and the activities of some soil micro-organisms. The width of the bands indicates the relative microbial activity or nutrient availability. The jagged lines between the P band and the Ca, Al and Fe bands represent the effect of these metals in restricting the availability of P (Courtesy of Brady & Weil 2002).
There are three methods in determining soil pH:

- **In water (pH<sub>w</sub>), where pure water is used to make a soil suspension.** In this method two major drawbacks may affect the pH reading: firstly, water dilutes the soil solution leading to values that are 0.2 to 0.5 units higher (for acid soils) than would be measured in the undiluted field soil solution. Secondly, small variations in soluble salt content of soil due to addition of fertilisers, or evaporative salt accumulation, can result in readings that differ by as much as 0.5.

- **In CaCl<sub>2</sub> (pH<sub>Ca</sub>), using a weak, unbuffered salt solution instead of pure water to make the soil suspension.** This would overcome the two problems mentioned in the previous method. A 0.01M CaCl<sub>2</sub> solution is used to provide a background electrolyte concentration that is similar in ionic strength to the soil solution in the field. The Ca<sup>2+</sup> added in the solution forces a portion of the exchange acidity to move into the active pool, giving CaCl<sub>2</sub> readings that are typically 0.2 to 0.5 units lower than pH<sub>w</sub> for the same soil (see Table 5 of conversion below).

- **In KCl (pH<sub>KCl</sub>), the soil is mixed with a more concentrated neutral salt solution such as 1M KCl.** This solution is concentrated enough to displace into the soil solution all the exchangeable acidity on the soil CEC by K<sup>+</sup>. The reading gives about one unit lower than the pH<sub>w</sub>, although the difference may be greater for soils with high pH level. The one unit difference indicates that the exchangeable pool is commonly about 10 times as great as the active pool of soil acidity.

When determined in the laboratory, the pH value is often measured by pH meter using a glass electrode on a 1:5 extract (Rayment & Higginson 1992a).

To convert pH<sub>w</sub> to pH<sub>Ca</sub> or vice versa (in a 1:5 soil solution) the following equation is used in general: pH<sub>w</sub> = pH<sub>Ca</sub> + (0.5 to 1.0). For more detailed conversion, use Table 5.

### Table 5. Conversion of pH<sub>Ca</sub> to pH<sub>w</sub>

<table>
<thead>
<tr>
<th>pH&lt;sub&gt;Ca&lt;/sub&gt;</th>
<th>Conversion factor add or subtract*</th>
<th>pH&lt;sub&gt;w&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3-7.8</td>
<td>0.5</td>
<td>7.8-8.3</td>
</tr>
<tr>
<td>6.6-7.2</td>
<td>0.4</td>
<td>7.0-7.6</td>
</tr>
<tr>
<td>6.0-6.5</td>
<td>0.5</td>
<td>6.5-7.0</td>
</tr>
<tr>
<td>5.4-5.9</td>
<td>0.6</td>
<td>6.0-6.5</td>
</tr>
<tr>
<td>4.4-5.3</td>
<td>0.7</td>
<td>5.1-6.0</td>
</tr>
<tr>
<td>1.0-4.3</td>
<td>0.8</td>
<td>4.9-6.0</td>
</tr>
<tr>
<td>3.8-4.0</td>
<td>0.9</td>
<td>4.7-4.9</td>
</tr>
<tr>
<td>&lt; 3.7</td>
<td>1.0</td>
<td>&lt; 4.7</td>
</tr>
</tbody>
</table>

*To convert pH<sub>w</sub> to pH<sub>Ca</sub> subtract the value of the conversion factor from the measured pH<sub>w</sub> value. For example if the measured pH<sub>Ca</sub> value was 6.8, then the pH<sub>Ca</sub> value should be 6.8 - 0.5 = 6.3. To convert the value of pH<sub>Ca</sub> to pH<sub>w</sub> add the conversion factor to the measured pH<sub>Ca</sub> values.

In general, each pH unit measured in water below 7.0 means that around 15 per cent of CEC (cation exchange capacity) is occupied by H<sup>+</sup>. For example H<sup>+</sup> ions at pH<sub>w</sub> = 7.0, occupies 0 per cent of the CEC while at pH<sub>w</sub> = 6.0, it occupies 15 per cent. Too much acidity decreases the nutrient-holding capacity of the soil because H<sup>+</sup> replaces other essential elements. However, acidification is a naturally occurring process in humid regions where the rainfall is sufficient to thoroughly leach basic cations from the soil profile. By contrast, in low rainfall (dry) regions such as the inland cropping regions of Western Australia, leaching is much less extensive, allowing soils to retain enough Ca, Mg, K and Na ions to prevent a build-up of acid.
cations, thus enhancing the process of alkalisation (that is, pH >7, Brady & Weil 2002). However, in arid areas, especially if extensively cropped, soil acidity may occur. The main causes beside parent materials are the high amount of basic cations exported from the soil and the acidity stemming from applying NH₄ fertilisers.

It should be mentioned that soil pH is only a measure of hydrogen ions, not an indication of soil fertility or mineral balance by itself. The ideal soil pH for most crops is from 5.8-6.5 (in CaCl₂).

Sources of soil acidity are:

- **Acids from plant roots**

  In most cases plants absorb more cations than anions and release H⁺ into the soil to keep the electrical potential negative across cell membranes (Clarkson 1984). Nutrients are absorbed by plant roots along their electrochemical gradient (electrical charge of the ion plus the concentration of the ion). Plant roots usually maintain a negative electrical potential across their root surface membrane (between root cell cytoplasmic solution and soil solution) which facilitates the absorption of cations.

- **Soil CO₂**

  Root respiration and the decomposition of soil organic matter by micro-organisms produces a high level of CO₂ in soil air. CO₂ dissolves in water to form carbonic acid (H₂CO₃). However, H₂CO₃ is a weak acid, and its contribution to soil acidity is very small when the soil pH is much below 5.

- **Acids from microbial activities**

  As microbes break down soil organic matter, many organic acids are released into the soil. Some of these organic acids, such as citric or malic acids, have a low molecular weight and weakly dissociate, thus producing only a small effect on soil pH. Others are more complex and stronger acids, such as the carboxylic and phenolic acid groups contained in humic substances.

- **Accumulation of organic matter**

  Organic matter tends to acidify the soil in two ways:

  (i) It forms soluble complexes with non-acidic cations (basic cations) such as Ca and Mg, thus facilitating the loss of these cations by leaching.

  (ii) Organic matter itself is a source of H⁺ ions because it contains numerous acid functional groups from which these ions can dissociate.

- **Oxidation of nitrogen (nitrification)**

  N is released from fertilisers into the soil solution as NH₄⁺ ions. NH₄⁺ ions in turn, are subject to oxidation, forming nitrate ions (NO₃⁻). The oxidation process is usually carried out by specific soil bacteria, but can also take place by a purely chemical reaction termed nitrification. The reaction releases two H⁺ ions for each NH₄⁺ ion oxidised:

  \[
  \text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{H}^+ + \text{H}^+ + \text{NO}_3^- \\
  \text{Dissociated nitric acid}
  \]
The long-term balance between the processes of acidification (production of H⁺) and alkalisation (consumption of H⁺) in soil systems reflects the pH level of the soil. Table 6 summarises these two major processes.

Table 6. Processes of acidification and alkalisation in soil systems

<table>
<thead>
<tr>
<th>Acidification processes</th>
<th>Alkalisation processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation of carbonic acid from CO₂</td>
<td>Input of bicarbonates or carbonates</td>
</tr>
<tr>
<td>Acid dissociation as:</td>
<td>Anion protonation such as:</td>
</tr>
<tr>
<td>RCOOH → RCOO⁻ + H⁺</td>
<td>RCOO⁻ + H⁺ → RCOOH</td>
</tr>
<tr>
<td>Oxidation of N, S and Fe compounds</td>
<td>Reduction of N, S and Fe compounds</td>
</tr>
<tr>
<td>Cation uptake, leaching and precipitation</td>
<td>Anion uptake by plant</td>
</tr>
<tr>
<td>Accumulation of acidic organic matter</td>
<td>Cations weathering from minerals</td>
</tr>
<tr>
<td>De-protonation of pH-dependent charges</td>
<td>Protonation of pH-dependent charges</td>
</tr>
</tbody>
</table>

**Liming**

Liming is the application of alkaline materials that provide conjugate bases of weak acids, such as carbonate (CO₃) and sometimes hydroxide (OH⁻). These are anions capable of reacting with H⁺ and converting it to weak acids such as water. When calcitic lime (CaCO₃) is applied to an acid soil, each molecule neutralises two H⁺ ions:

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

Usually, liming materials are supplied in their calcium and magnesium forms (see Table 7) and referred to as agricultural limes (lime sand, limestone or dolomite). Sometimes calcium oxide (CaO), also called burnt lime, is used to give OH⁻ upon dissolving in water (hydrolysed).

\[
CaO + H_2O \rightarrow Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-
\]

OH⁻ ions then react with H⁺ and are converted to water. CaO is corrosive and special precautions should be taken when using it. This includes using corrosion-resistant containers and protective clothing. However, it has more neutralising power per unit mass than the calcite limes. Furthermore, the pH of calcium hydroxide in water is about 11, which can be dangerous to eyes and skin compared to a pH of about 8.3 for calcium carbonate, which is about the same as seawater. Dissolving calcium oxide in water generates a lot of heat, which can burn or cause steam which may blow the caustic solution into the face and eyes. In practice it is not widely available in Western Australia.

Because lime is needed in large quantities, the cost of transporting it becomes an important issue in choosing the source of lime needed. However, the concentration of Ca and Mg in the soil is also important in choosing the liming material. If Mg is deficient in an acid soil, then dolomite, Ca Mg(CO₃)₂, can be used. Pure dolomite contains 21.7 Ca and 13.2 Mg by weight. However, commercial samples will be less pure than this. The nutrients supplied to plants by the liming material should not be overlooked. In some highly weathered soils like in Western Australia, small amounts of lime may improve plant growth, more because of the enhanced calcium or magnesium nutrition than from a change in pH.

Table 7 shows different liming material used in Western Australia. Calcitic limestone and dolomite are the most commonly used.
Table 7. Common types of liming material used in Western Australia

<table>
<thead>
<tr>
<th>Lime type</th>
<th>Chemical formula</th>
<th>% CaCO₃ equivalent</th>
<th>Solubility (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcitic limestone (lime sand)</td>
<td>CaCO₃</td>
<td>100</td>
<td>0.014</td>
</tr>
<tr>
<td>Dolomitic limestone</td>
<td>CaMg (CO₃)₂</td>
<td>95-108</td>
<td>0.32</td>
</tr>
<tr>
<td>Burned lime (oxide of lime)</td>
<td>CaO, MgO</td>
<td>178</td>
<td>1.85</td>
</tr>
</tbody>
</table>

How much lime is needed?

The action of liming is not instantaneous, but gradual depending on the solubility of lime. It may take weeks for hydrated lime, to a year or more for calcitic lime, to show some results. As Ca and Mg are removed from the soil by crops, or by leaching, they are replaced by acid cations and soil pH is continuously reduced. Eventually, another application of lime is needed depending on the starting pH and if the soil is in a maintenance phase or a recovery phase. However, in the low rainfall areas where both removal of Ca and Mg by crops and leaching is low, lime application is needed at longer intervals, as compared to high rainfall areas. In addition to economic considerations the amount of lime to add depends on:

- change required in the pH or exchangeable Al saturation
- buffering capacity of the soil
- type of liming material
- purity of neutralising value and fineness of the liming material.

Calculating how much lime is needed.

Most laboratories have buffer curves for the major types of soils in their service area to calculate how much lime is need to raise pH from the current value to the desired value. A calculation of the lime requirement similar to the example given below is done by the soil testing laboratory.

In the Nungarin Shire we have a loamy sand (a common soil type in WA) with a bulk density value of 1.3 mg/m³ and soil pH 4.9 and we want to increase the soil pH to 6.5. From the pH buffering curve of the soil we find that we need 2.1 cmolc of lime/kg soil. How much commercial lime with 90 per cent purity is needed to supply 2.1 cmolc/kg for 1 ha?

- Each CaCO₃ molecule neutralises 2H⁺ ions (CaCO₃ + 2H⁺ → Ca²⁺ + CO₂ + H₂O).
- The molecular weight of CaCO₃ = 100 g/mole, then the mass of 2.1 cmolc of pure CaCO₃ is:
  \[(2.1 \text{ cmolc} /\text{kg soil}) \times (100 \text{ g/mol CaCO₃}) \times (1 \text{ mol CaCO₃}/2 \text{ cmolc}) \times (0.01 \text{ molc/cmolc}) = 1.05 \text{ g CaCO₃/kg soil}.\]
- The weight of 1 hectare of soil with bulk density of 1.3 Mg/m³ to 0.15 m depth is:
  \[10,000 \text{ m}^2/\text{ha} \times 0.15 \text{ m} \times 1.3 \text{ Mg/m}^3 = 1950 \text{ Mg soil/ha} \text{ (or 1,950,000 kg soil/ha)}.\]
- Then the amount of pure CaCO₃ needed per hectare:
  \[(1.05 \text{ g CaCO₃/kg soil}) \times 1,950,000 \text{ kg soil/ha}) = 2,047,500 \text{ g CaCO₃/ha or} \]
  \[2,047 \text{ kg pure CaCO₃/ha}.\]

Since the purity of the limestone is 90 per cent, then we need:
\[(2047 \times 100) / 90 = 2,274 \text{ kg or 2.274 t/ha of commercial limestone}.\]
Note that not all limestone will react with soil in the field, so we might add more than the calculated material by one and a half to two times. It is better to split the application into two halves, adding the second half after a few years. Refer to a soil adviser for recommendation.

The main problem with calcitic lime is its low solubility (0.014 g/L), which means it moves very slowly in soil, so injecting lime to reduce subsoil acidity may be desirable. Development of tools to inject and mix lime into the subsoil is an important issue in addressing subsurface soil acidity.

**Role of aluminium in soil acidity**

Aluminium plays a central role in soil acidity and is responsible for much of the deleterious impact of soil acidity on plants. Most soil minerals contain Al as aluminosilicate and aluminium oxides (see Figure 7). When H⁺ ions are adsorbed on a clay surface they usually do not remain as exchangeable cations for long, but instead they attack the structure of the minerals, releasing Al³⁺ ions in the process. The Al³⁺ ions then become adsorbed on the colloid’s cation-exchange sites. These exchangeable Al³⁺ ions in turn, are in equilibrium with dissolved Al³⁺ in the soil solution. The exchangeable and soluble Al³⁺ ions play two critical roles in the soil acidity:

(i) Aluminium is highly toxic to most soil organisms and to plant roots.
(ii) Aluminium ion Al³⁺ reacts with water and splits to produce H⁺ (hydrolysis). In fact, a single Al³⁺ ion can release up to three H⁺ ions in a reversible reaction series which proceeds in a stepwise fashion. For this reason Al³⁺ and H⁺ together are considered acidic cations.

The positively charged hydroxy aluminium ions (Al(OH)²⁺ and Al(OH)⁺) form large polymers, which are tightly bound to the colloid’s negative charge sites, reducing the effective CEC of the soil. At the same time the formation of non-soluble Al(OH)₃ makes more negative sites on the colloids become available for cation exchange. This is why the cation exchange capacity of the soil increases as the pH is raised from 4.5 to 7.0.

**Pools of soil acidity**

Four pools of acidity are common in soils:

(i) **Active acidity**: Due to the H⁺ and Al³⁺ ions in the soil solution (this is the pH measured in field soil tests).

(ii) **Exchangeable acidity**: Involving the exchangeable Al³⁺ and H⁺ that are easily exchanged by other unbuffered salts, such as KCl. Once released to soil solution, the aluminium hydrolyses to form additional H⁺ thus increasing soil acidity. The exchangeable acidity in strongly to moderately acid soils is commonly thousands of times that of active acidity. The limestone needed to neutralise this type of acidity is commonly more than 100 times that needed to neutralise active acidity. However, since the common type of clay in WA soils is kaolinite, the exchangeable acidity is lower than that of both smectites and vermiculites (laboratory tests measure both active and exchangeable pH).

(iii) **Residual acidity**: This is commonly far greater than either the active or exchangeable acidity. It may be 1000 times greater than the soil solution or active acidity in a sandy soil and may be up to 100,000 times greater in a clayey soil high in organic matter. It is generally associated with hydrogen and aluminium ions that are bound in non-exchangeable form by organic matter and clay. As the pH increases, the bound hydrogen dissociates and the bound aluminium ions are released and precipitate as amorphous Al(OH)₃.
(iv) **Potential acidity from reduced sulphur.** This occurs only in certain acid sulphate soils and arises from the oxidation of sulphur compounds.

For most soils, except potential acid-sulphate soils, the total acidity that must be overcome to raise the soil pH to a desired value equals (Active acidity + exchangeable acidity + residual acidity).

Most farmers in Western Australia address soil acidity by applying one to two tonnes per hectare of lime sand to the topsoil. Some farmers inject this amount into the subsoil. Using an acidity tolerant species is a good way of co-existing with soil acidity.

5. **Sodicity**

Sodic soil is non-saline soil containing sufficient exchangeable sodium to adversely affect crop production and soil structure under most conditions of soil and plant type.

The stability of soil aggregates when wet is governed by forces operating both within the clay particles and from the surrounding soil solution. The presence of sodium ions on clay surfaces creates very high internal swelling pressures. This swelling keeps the clay particles apart and causes aggregates to break down and the clays to disperse. The presence of calcium ions on clay surfaces has the opposite effect.

Sodic soils are widespread in arid and semi-arid regions. In WA, 26% of soils are predominantly sodic. Sodic soils are subject to severe structural degradation and restrict plant performance through poor soil-water and soil-air relations (Rengasamy 1998). Sodicity is linked to salinity because it is associated with salt accumulation in the soil profile when evapotranspiration exceeds precipitation. When the salts present are predominantly sodium salts, the soil becomes sodic and plant growth is affected indirectly by degrading the physical behaviour of soils. Sodic clay particles when separated by hydration (wetting), repel each other and remain dispersed when wet. They are then free to block soil pores, thus significantly restricting water and gas movement into the soil. The dispersion of sodic clay and the swelling of soil aggregates can destroy soil structure, and so reduce porosity and permeability of soils and increase the soil strength even at low suction (that is, high water content). Plants cannot grow well because sodic soils are either too wet directly after rain or too dry within a short period after rain, so that duration of the soil water content range favouring plant growth is limited. Waterlogging, poor crop or pasture emergence and establishment, and soil erosion may indicate that the soil is sodic. However, these symptoms may be caused by several other problems such as soil compaction, and so a specific test for sodicity is needed. The coherence of soil aggregates in salt free water is almost the only way to test soil sodicity in the field, because clay is spontaneously dispersed by water when it is sodic.

Soil sodicity can be assessed by measuring the exchangeable sodium percentage (ESP):

\[
\text{ESP} = \left( \frac{\text{Exchangeable sodium}}{\text{Cation exchange capacity}} \right) \times 100
\]

where CEC refers to the sum of the cations (Ca, Mg, Na and K, etc.).

When ESP is greater than 15 the soil is regarded as sodic. However, sodic soils are sometimes described and classified according to their behaviour instead of using analytical criteria, because soils may exhibit sodic properties even though they have relatively low ESP values. This is the case in Western Australia where the soil is regarded as sodic when ESP is greater than 6.
Sodium absorption ratio (SAR) also can be used as indication of soil sodicity; it shows the relation between soluble sodium and soluble divalent cations which can be used to predict the exchangeable sodium fraction of soil equilibrated with a given solution. It is defined as:

\[ SAR = \frac{[Na^+]}{\sqrt{[Ca^{2+}] + [Mg^{2+}]}} \]

where the concentrations, denoted by bracket, are expressed in mmoles per litre.

Commonly the SAR of water is adjusted for precipitation or dissolution of Ca\(^{2+}\) that is expected to occur where water reacts with alkaline earth carbonates within a soil.

Classically, a sodic soil will respond to gypsum applications. By replacing sodium with calcium on the exchange sites, the clay particles will aggregate more readily and these aggregates will not cause the problems associated with dispersive, high ESP clays.

### Relationship between sodicity and soil pH

In general, high sodium concentration (high ESP) is usually associated with high soil pH because both Ca\(^{2+}\) and Mg\(^{2+}\) ions are commonly precipitated out of soil solution by carbonate and bicarbonate ions. A general relationship is shown in Table 8 (Gupta & Abrol 1990).

<table>
<thead>
<tr>
<th>pH in 1:2 soil:water suspension</th>
<th>ESP</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.2-9.0</td>
<td>&lt;20</td>
</tr>
<tr>
<td>9.0-9.4</td>
<td>21-35</td>
</tr>
<tr>
<td>9.4-9.6</td>
<td>35-50</td>
</tr>
<tr>
<td>9.6-9.8</td>
<td>50-65</td>
</tr>
<tr>
<td>9.8-10.0</td>
<td>65-85</td>
</tr>
<tr>
<td>&gt;10.0</td>
<td>&gt;85</td>
</tr>
</tbody>
</table>

### 6. Salinity (EC)

Salts accumulate in soils when, in general, rainfall is not enough to leach the salt out of the rooting zone or the drainage is not sufficient. Accordingly, salt has more chance to accumulate in low rainfall than the high rainfall areas. However, there can be exceptions in some high rainfall zones (e.g. Ferdowsian & Greenham (1992) found that at Upper Denmark (750 mm rainfall zone) high levels of salt stored in the soil profile.)

There are two main effects of salinity on crops. The first is the osmotic (total soluble salt) effect and the second is the specific ion effect. In the osmotic effect, the plant roots’ ability to absorb water decreases with increasing soil salinity, then stops altogether when the osmotic potential equals that inside the plant root. If soil solution salinity increases further, water moves along a water potential gradient from the root to the soil and roots start shrinking (Hamza et al. 2006). In the specific ion effect, ions such as Na\(^+\), Cl\(^-\), H\(_4\)BO\(_4\) and HCO\(_3\)\(^-\), are quite toxic to many crops when they exist in high concentration. Na\(^+\) for example causes soil dispersion and compete with K\(^+\) in the process of transport across the cell membrane during uptake (Brady & Weil 2002).

Salinity is measured as electrical conductivity (EC) by a conductivity meter at 25°C on a 1:5 soil:water suspension (Rayment & Higginson 1992b). To relate the effect of salinity on plant roots under field conditions, the suspension salinity (EC\(_{1:5}\)) must be converted to saturation salinity (EC\(_{e}\)):

\[ EC_e (mS/cm) = EC_{1:5} (mS/cm) \times \text{conversion factor} \]
where the subscript e refers to the saturation extract of the soil. The conversion factor depends on soil texture. The relationship in Table 9 can be used for converting EC\textsubscript{1.5} to EC\textsubscript{e}.

Table 9. Factors for converting EC\textsubscript{1.5} to EC\textsubscript{e} for different soil texture

<table>
<thead>
<tr>
<th>Soil texture</th>
<th>Conversion factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandy soils</td>
<td>21</td>
</tr>
<tr>
<td>Sandy loam soils</td>
<td>12</td>
</tr>
<tr>
<td>Sandy clay loam soils</td>
<td>9</td>
</tr>
<tr>
<td>Silty loam, silty clay soils</td>
<td>8</td>
</tr>
<tr>
<td>Clay soils</td>
<td>6</td>
</tr>
</tbody>
</table>

These values are based on field experience in Western Australia and may change to some degree from area to area.

Salinity is measured in a number of ways:

- mS/cm (milliSiemens per centimetre), which is equal to dS/m (deciSiemens per metre)
- mS/m, which is equal to mS/cm \times 100
- \( \mu \)S/m (microSiemens per metre), which is equal to mS/m \times 1000.

The following conversions might help in understanding the relationship between these units (Moore 2004):

\[
1 \text{ mS/m} = 10 \mu \text{s/cm} = 1000 \mu \text{S/m} = 0.01 \text{ dS/m} = 0.01 \text{ mS/cm} = 5.5 \text{ mg/L or ppm}
\]

\[\text{dS/m} = \text{mS/cm} = \text{mmho/cm}\]

Concentration of salt (mg/L) = 550\* \times EC

* This factor is for Western Australian soils. For other soils this factor may be as high as 640.

To convert EC\textsubscript{1.5} to total soluble salt (TSS) in the soil:

\[
\text{TSS (mg/L)} = \text{EC}_{1.5} \times 550
\]

Where EC\textsubscript{1.5} is in dS/m and TSS is in mg/kg (ppm)

The Soil and Water Salinity Calculator published by the Department of Agriculture and Food, provides a handy conversion table for the various units.

Crops differ in their tolerance to salinity, but in general soil EC\textsubscript{e} above 4 mS/cm is regarded as salt affected soil. Table 10 gives an estimate for yield reduction due to salinity under different salinity levels (electrical conductivity of saturated soil extract) for some crops (Ayers 1977).
Table 10. Estimation for yield reduction at different salinity levels

<table>
<thead>
<tr>
<th>Crop</th>
<th>Expected yield reduction at ECₐ indicated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>Barley</td>
<td>8.0</td>
</tr>
<tr>
<td>Cotton</td>
<td>7.7</td>
</tr>
<tr>
<td>Wheat</td>
<td>6.0</td>
</tr>
<tr>
<td>Safflower</td>
<td>5.3</td>
</tr>
<tr>
<td>Soybean</td>
<td>5.0</td>
</tr>
<tr>
<td>Sorghum</td>
<td>4.0</td>
</tr>
<tr>
<td>Rice</td>
<td>3.0</td>
</tr>
<tr>
<td>Beans (field)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

7. Cation Exchange Capacity (CEC)

CEC is expressed as the number of moles of positive charge adsorbed per unit mass (cmol+/kg = centimoles/kg). Some laboratories still use the older unit milliequivalent per 100 grams (me/100 g) which gives the same value as cmol+/kg (1 me/100 g = 1 cmol+/kg). For example, a soil which has a CEC of 12 cmol+/kg indicates that 1 kilogram of the soil can hold 12 centimole of H⁺ ions, and can exchange this amount of charges for the same number of charges from any other cation. This means that the exchange reaction takes place on a charge-for-charge (not an ion-for-ion) basis. Accordingly, two Na⁺ ions can exchange for one Ca²⁺ ion. This also may indicate to some degree how strongly an individual cation is held on the soil colloids. For example, Al³⁺ is held on the soil exchange sites more strongly than Ca²⁺ and this in turn more strongly than Na⁺. So the order of adsorption strength can be:

Al³⁺ > Ca²⁺ > Mg²⁺ > K⁺ = NH₄⁺ > Na⁺.

This order is important when a particular cation used as soil amendment is replacing another cation on the exchange complex.

CEC can be determined using different methods. However, in all methods the adsorbed cations must be replaced by a single exchanger cation such as Ba²⁺, NH₄⁺ or Sr²⁺ and then the CEC is calculated either from the amount of the exchanger cations used for replacement or from the amounts of each of the replaced cations originally held on the soil exchange sites (usually Ca²⁺, Al³⁺, Mg²⁺, K⁺ and Na⁺). Most laboratories determine CEC in a buffered solution using one M NH₄Cl at pH 8.5 in 60 per cent ethanol, or ammonium as the exchanger cation at pH 7.0, or barium as the exchanger cation at pH 8.2. If the soil pH is less than the pH of the buffered solution then the pH-dependent exchange sites that would become negatively charged at pH 7.0 or 8.2 will be measured too.

The CEC of a given soil is determined by the relative amount of different colloids in that soil and by the CEC of each of these colloids. The major soil colloids are clay and organic matter. Silt may contribute a little to soil CEC, while the contribution of sand is very small and in most cases negligible. In sandy soils most of the CEC comes from the clay and organic fractions of the soil. Table 11 shows the CEC of some of the soil constituents.
Table 11. CEC of some soil constituents (cmol(+)/kg)

<table>
<thead>
<tr>
<th>Soil constituents</th>
<th>CEC, cmol(+)/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>5-15</td>
</tr>
<tr>
<td>Chlorite</td>
<td>10-40</td>
</tr>
<tr>
<td>Illite</td>
<td>20-50</td>
</tr>
<tr>
<td>Transitional minerals</td>
<td>40-80</td>
</tr>
<tr>
<td>Montmorillonite (smectite)</td>
<td>80-120</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>100-150</td>
</tr>
<tr>
<td>Organic material (humic acid)</td>
<td>200-500</td>
</tr>
</tbody>
</table>

In Western Australia many duplex soils have sandy topsoil and clayey subsoil. These soils are commonly low in CEC, particularly in the topsoil, because they are often composed of leached sands that might contain some highly weathered soils with kaolinite as the dominant clay silicate (Table 12). The magnitudes of CEC, ionic composition and base saturation of soils are related to organic matter, clay content, pH and soil origin.

Table 12. Subsoils from Geraldton (north), Wickepin (middle) and Esperance (south-east) in Western Australia showing some soil properties

<table>
<thead>
<tr>
<th>Soil property</th>
<th>Geraldton</th>
<th>Wickepin</th>
<th>Esperance</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEC, cmol(+)/kg</td>
<td>2.81</td>
<td>2.88</td>
<td>32.39</td>
</tr>
<tr>
<td>Base saturation, %</td>
<td>67</td>
<td>67</td>
<td>100</td>
</tr>
<tr>
<td>Organic matter, %</td>
<td>0.71</td>
<td>0.59</td>
<td>0.62</td>
</tr>
<tr>
<td>pHw</td>
<td>5.40</td>
<td>5.40</td>
<td>9.00</td>
</tr>
<tr>
<td>Exchangeable Ca, %</td>
<td>40.00</td>
<td>38.20</td>
<td>9.60</td>
</tr>
<tr>
<td>Exchangeable Mg, %</td>
<td>13.60</td>
<td>13.80</td>
<td>37.10</td>
</tr>
<tr>
<td>Exchangeable K, %</td>
<td>3.70</td>
<td>2.20</td>
<td>4.70</td>
</tr>
<tr>
<td>Exchangeable Na, %</td>
<td>3.10</td>
<td>6.20</td>
<td>46.30</td>
</tr>
<tr>
<td>Exchangeable H, %</td>
<td>33.00</td>
<td>33.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 12 shows that the value of base saturation gives direct insight into the amount of acidity/alkalinity in the soil and which cations are deficient or in excess. If the soil base saturation is low, as in the Geraldton or Wickepin soils, it is difficult to get a good yield before increasing the base saturation (removing excess acidity). Removing excess acidity through application of lime would in most cases improve the soil base saturation.

The CEC will determine the fertiliser practices that are appropriate and the amount of nutrients needed to correct imbalances. It will take more fertiliser to balance high CEC clay than low CEC sand. Sand will need smaller but more frequent applications of nutrients.

The ideal CEC range for soil fertility is around 10-18 cmol(+)/kg, however most WA soils are sandy and have low to very low CEC. In duplex sand over clay or loam soils, ripping the soil may improve CEC if the clay is not too deep. Hamza and Anderson (2002) were able to increase clay content of the topsoil by about 10 per cent in Merredin through ripping.
Exchangeable cation determinations

Cations such as Ca, Mg, K and Na are usually measured by one of three procedures:

- **1M NH₄Cl at pH 7.0** – Used for neutral soils (pHₜw between 6.5 and 8). Here, cations Ca, Mg, Na and K are measured by ICP-AES (inductively coupled plasma – atomic emission spectrometry). Soluble salts must be removed from soils with EC₁:₅ > 20 mS/m by washing with glycol-ethanol.

- **0.1 M BaCl₂ (unbuffered)** – Used for acid soils only (pH <6.5). This method is based on a modification of Gillman et al. (1984). Cations Ca, Mg, Na, K, Al and Mg are measured by ICP-AES. Soluble salts are removed from soils with EC(1:5) > 20 mS/m by washing with glycol-ethanol.

- **1M NH₄Cl, pH 8.5** - Used for calcareous soils. This is a modification of Rayment and Higginson (1992c). Ca, Mg, Na and K are measured by flame AAS (atomic absorption spectrophotometry).

Conversions

To convert cmol(+)/kg to t/ha, use the following equation (Hazelton & Murphy 2007):

\[
1 \text{ cmol}(+) /\text{kg} = \frac{(0.001 \times \text{MW} \times \text{D} \times \text{BD})}{\text{C}}
\]

where MW is the molecular weight of the cation or anion in grams, D is the depth of the soil in cm, BD is the bulk density of the soil in g/cm³ and C is the charge of cation or anions.

For example, if you want to convert the Ca in 1 cmol(+) /kg to t/ha with soil depth of 10 centimetres and BD of 1.4 g/cm³, then:

\[
1 \text{ cmol}(+) /\text{kg} \text{ of Ca} = \frac{(0.001 \times 40.08 \times 10 \times 1.4)}{2} = 0.28 \text{ t/ha of Ca.}
\]

8. Organic Matter (OM)

Soil organic matter comprises all the living, dead and decomposing plants, animals and microbes along with the organic residues and humic substances they release. Organic matter is the major pool of terrestrial carbon in soil and provides major soil energy and nutrient reserves (Carter 1996). The type of organic matter is also important, for example readily oxidisable soil organic matter seems to be more relevant than total organic matter in determining mechanical behaviour of the soil (Ball et al. 2000).

Three different types of soil organic matter are recognised (Lickacz & Penny 2001):

- Raw plant residues and micro-organisms (1-10 per cent)
- 'Active' organic fraction (10-40 per cent)
- Resistant or stable organic matter (40-60 per cent) also referred to as humus.

Soil organic matter is a complex mixture of materials that vary in size, chemistry, degree of decomposition and interaction with soil minerals.

Besides the nutritional value of soil organic matter, it provides a good way of protecting soil from erosion. For example, plant residues on the soil surface help reduce water runoff, thus decreasing soil erosion. It also reduces wind erosion by providing plant cover. Removal or burning of residues predisposes the soil to serious erosion. It is highly recommended that stubble is retained and not burned unless necessary, such as in case of epidemic disease.
Micro-organisms (especially fungi) with the 'active' and some resistant soil organic components, are involved in binding small particles into larger aggregates. Aggregation is important for good structure, aeration, water infiltration and resistance to erosion and crusting.

The resistant or stable fraction of soil organic matter contributes mainly to cation exchange capacity and colour. This fraction of organic matter decomposes very slowly and therefore has less influence on soil fertility than the 'active' organic fraction.

Organic matter in soil serves several functions, but from a practical agricultural standpoint, it is important for two main reasons: 'nutrient recycling'; and as an agent to improve structure, maintain tilth, and minimise erosion.

The nutrient recycling function has two main actions:

- Since soil organic matter is derived mainly from plant residues, it contains all of the essential plant nutrients. Accumulated organic matter, therefore, is a storehouse of plant nutrients. Upon decomposition, nutrients are released in a plant-available form.
- The stable organic fraction (humus) adsorbs and holds nutrients in a plant-available form.

Organic matter does not add any 'new' plant nutrients, but releases nutrients in a plant available form through the process of decomposition. In order to maintain this nutrient cycling system, the rate of addition from crop residues and manure must equal the rate of decomposition.

Soil organic matter will decline if the rate of addition is less than the rate of decomposition, and conversely, soil organic matter will increase if the rate of addition is greater than the rate of decomposition. The term steady state has been used to describe a condition where the rate of addition is equal to the rate of decomposition. Fertiliser can contribute to the maintenance of this nutrient recycling by increasing crop yields and consequently the amount of residues returned to the soil.

Organic matter plays a vital role in biological, chemical and physical soil fertility. In dryland areas such as Western Australia, where soil biological and physical fertilities are degraded, the contribution of organic matter in invigorating soil micro-organisms and improving soil physical properties, especially of topsoil, is very important. The evidence that soil structure improves and becomes more resistant to degradation as soil organic matter content increases is overwhelming (Cochrane & Aylmore 1994; Thomas et al. 1996; Hamza & Anderson 2005). Maintaining an adequate amount of organic matter in the soil helps regulate air and water infiltration, increases resistance to erosion, stabilises soil structure, increases water and nutrient storage, decreases bulk density and soil strength, invigorates soil micro-organisms and restores crop productivity to levels proportional to high-input agricultural systems (Sparovek et al. 1999; Carter 2002). Losses of soil organic matter and aggregate stability are regarded as standard features of non-sustainable land use (Håkansson 2000; Carter 2002). The positive correlation between soil organic matter content and physical properties is attributed to their mutual effects, where organic matter binds soil particles (Figures 20 and 21), while soil aggregates protect organic matter from decomposition (Carter 1996). This is related to the contribution of organic matter to wet aggregate stability (Zhang 1994). Organic matter also retains a greater amount of moisture, thus helping soil to rebound against compaction (Paul 1974).

Increase in soil organic matter is desirable because the various components provide a multitude of beneficial functions for the soil, such as:
• Providing energy and nutrients to soil micro-organisms. Much of the impact of organic matter on soil health is achieved by stimulating soil micro-organisms
• Binding soil mineral particles (Theng & Oades 1982; Zhang 1994)
• Reduction of aggregate wettability (Zhang & Hartge 1992)
• Influencing the mechanical strength of soil aggregates, which is the measure of coherence of inter-particle bonds (Quirk & Panabokke 1962).
• Prevents transferring soil compaction to subsoil
• Leads to better plant nutrition, ease of cultivation and seedbed preparation.
• Greater aggregate stability, reduced bulk density, improved water-holding capacity, enhanced porosity and earlier warming in spring.

Figure 20. Soil high in organic matter is granulated and has significantly lower bulk density compared to soil low in organic matter.

Figure 21. Organic matter (light colour) binds clay particles (dark colour) hence improving soil aggregation.
Organic matter is estimated from measurements of organic carbon. Organic carbon is usually determined, on soil ground to less than 0.15 mm, by Metson's colorimetric modification of the Walkley & Black method. The procedure is based on oxidation of soil organic matter by dichromate in the presence of sulphuric acid. In general, organic matter contains around 50 per cent organic carbon, so multiplying organic carbon (OC) by two gives a good estimation of organic matter. Most soil laboratories measure only the fine (less than 2 mm) or colloidal organic matter, which does not include bulk material like straw and roots. It is therefore a good indicator of soil humus levels. In some soils the organic carbon may contain large amounts of charcoal. Although charcoal is no longer actively decomposing (non-labile) it can still play a role in holding and supplying nutrients and water for plant growth. The lability of organic matter depends on the degree of decomposition, which exposes more surface area for interaction. However, partially decomposed organic matter provides an important source of energy and nutrients for soil micro-organisms and also helps soil aggregation.

Soils with low organic matter require more artificial nitrogen than soils rich in organic matter.

Ideal organic matter content is around 4 to 6 per cent, but this is hard to achieve in the low rainfall areas where the average organic matter is commonly in the range of 1 to 3 per cent.

The following sections discuss nutrients that have been proven essential for plants. There are many published visual guides that illustrate deficiencies or toxicities (Snowball & Robson 1983; Bennett 1993).

9. Nitrogen (N)

Extensive cropping has led to severe decline in soil N in cereal soils throughout Western Australia (Strong & Mason 1999). To sustain high grain yield of the quality sought in competitive markets, N must be supplemented as fertiliser. However, a soil test is of little use in determining the soil N status accurately, or the plant requirement for fertiliser. Measurement of total soil nitrogen or total organic carbon can give a general idea of N status, but not an accurate idea of its availability to the plant. Soil tests along with other information such as soil type, field history and crop yield potential can be used for determining a recommendation for N fertiliser.

Total nitrogen is measured by Kjeldahl digestion of soil (copper sulphate-potassium sulphate catalyst). Ammonium and nitrate are usually determined in the soil by extracting them by 1M KCl solution and measured by automated colorimetry (ammonium by salicylate; chlorine and nitrate by reduction, diazotisation and coupling with N-1-naphthylethylenediamine dihydrochloride).

Soil nitrogen is usually calculated by commercial laboratories from the organic matter present. If organic matter is relatively low (e.g. 1-2 per cent) then there may not be enough natural nitrogen in the soil for adequate crop growth and extra N fertiliser should be applied. Plants have a higher requirement for nitrogen than for any other nutrient, but the amount that needs to be applied in fertilisers will depend on the yield targeted and the supply from natural sources like organic matter breakdown and atmospheric fixation by legumes. If plants have a good supply of all other nutrients, then growth can be controlled with nitrogen applications.

Only enough nitrogen to support the production target should be applied, because excess growth may exhaust water supply too early and result in 'haying off'. Too much nitrogen will produce excess lush (soft) shoot growth at the expense of root growth. Excessive shoot growth may be more susceptible to disease and insect attack. Too little nitrogen will result in limited pale shoot growth and the crop or pasture will tend to thin out and be prone to weed invasion. N is also important in increasing protein level in cereals.
For good N utilisation by plants, micronutrients, particularly molybdenum, should be adequate. Mo is essential for N assimilation in plants because it is a constituent of nitrate reductase enzymes which are responsible for reduction of NO$_3^-$ to NH$_4^+$ for subsequent assimilation into amino acids and protein.

**Nitrogen deficiency symptoms in cereals**

Symptoms first occur on the oldest leaves. Pale green plants change to yellow, then to almond white as the deficiency becomes more severe. However, leaves may not die for some time. N deficiency symptoms are similar to K and P deficiency symptoms, but the plants die more slowly.

10. Sulphur (S)

The most important function of S in plants is its involvement in protein synthesis. Sulphur is present in the structure of the amino acids cysteine and methionine, both of which are important components of proteins. As much as 90 per cent of the total sulphur in plants may be present as protein-S.

Sulphur soil testing in Australian soils is treated with caution due to the lack of awareness of responses to S (Lewis 1999). This may be due to a substantial seasonal variation in plant-available S when measured with the more common techniques. This variation is caused by temperature and moisture changes in the soil, which in turn affects the rate of mineralisation of organic S, as well as S losses due to leaching. Sulphate adsorption capacity or the measurement of a soil's ability to hold sulphate against leaching (Barrow 1975), has been given much priority over the supply of available S when interpreting tests in WA. Fine textured soils and soils with high organic matter have much greater ability to adsorb sulphate.

In Western Australian soils S deficiency is usually confined to sandy and sandy loams (Clark & Lewis 1974). In the Geraldton area where sandplain soils predominate, 35 per cent of wheat samples were S deficient (Robson et al. 1995). S in the soil is either immobilised or mineralised, depending on the soil environment. Organic S accumulates in the soil from stubble, pasture and animal residues and to some extent from reduced tillage, leading to an increase in the S pool. For example, the accumulation of S in a Coolup sand can reach 4.4 kg/ha/year (Barrow 1969). Soil micro-organisms are primarily responsible for mineralisation of organic S. Therefore those factors that affect micro-organism populations, such as temperature, moisture, pH and food supply will determine organic S availability. Temperature in the range 20-40°C and moisture in the range 15-40 per cent appear to favour mineralisation. Development of soil testing procedures that characterise net S mineralisation as well as determining the residual amount of SO$_4^{2-}$ within the root-zone is needed. A simple procedure for assessing the SO$_4^{2-}$ retention in subsoil will assist the prediction of SO$_4^{2-}$ movement in soil profiles and thus the likely fate of residual SO$_4^{2-}$ (Anderson et al. 2006).

Brennan and Bolland (2006) have identified responses of canola when soil test values (KCl procedure) were less than 7 mg/kg in the 0-30 cm soil depth in sandy duplex soils.

**Sulphur deficiency symptoms in cereal**

Pale green plants have greater yellowing in the newest leaves. Whole leaves are light yellow with no strips or green veins. Leaf tips of old leaves can die in cases of severe deficiency. P deficiency may look similar to N deficiency except that in N deficiency only old leaves are affected first, not the whole plant.
11. Phosphorus (P)

Phosphorus is important for cell division and growth. It is needed for photosynthesis, sugar and starch formation, in energy transfer and movement of carbohydrates around the plant. It is concentrated in the growing tips. A deficiency of phosphorus will greatly reduce the growth of plant tops and roots. It is essential for early root development and plants need a readily available source of P in the early growth stages, or crop yields will be reduced.

The phosphorus pool in the soil consists of several interacting sources. The soil solution is the immediate source of P for the plant root, and the rhizosphere is the zone in which the interaction between the plant and soil solution occurs. Diffusion from bulk soil continuously replenishes depleted P at the soil. However, because roots take up P in the orthophosphate (mineral) form, organic P must be mineralised by extracellular micro-organisms (using the phosphatase enzyme) before uptake can occur.

\[
\text{Organic P} \xrightarrow{\text{Microbes}} \text{H}_2\text{P}_4\xrightarrow{\text{Fe}^{3+}, \text{Al}^{3+}, \text{Ca}^{2+}} \text{Fe, Al, Ca Phosphates} \xrightarrow{\text{Mineralisation}} \text{Soluble P} \xleftarrow{\text{Immobilisation}} \text{Organic P}
\]

Increasing Al and Fe oxides in soil increases P adsorption, which in turn makes it less available to the plant.

The ability of plants to recover P from the soil is dependent on a symbiotic relationship between the roots of most crops and soil fungi (mycorrhiza), the hyphae of which greatly increase the surface area for P absorption by roots (Figure 22).

![Fungus hyphae greatly increase the surface area for P absorption.](image)

There are three problems with natural P in soil. First, the total level of most soils is usually low, at about 1000 kg/ha in the upper 15 cm. In WA soils it is much lower, at < 500 kg/ha, which is no more than one-tenth to one-fourth that of N and one-twentieth that of K (Brady & Well 2002). Second, most of the P compounds in the soil are unavailable because they are highly insoluble. Third, when soluble sources of P are added to the soil as fertilisers and manures, they are fixed and in time form highly insoluble compounds.

Most laboratories express phosphorus as kg/ha of P rather than as P\(_2\)O\(_5\). This makes it easier to calculate the amount of fertiliser required to meet an identified deficiency. For example, if the deficiency is 50 kg/ha P then it will require:

- 250 kg DAP (20% P)
- 500 kg rock phosphate (10% P)
556 kg Superphosphate (9% P).

Although the actual application rate will depend on economic considerations, the soil test will give a good basis for fertiliser planning. There are different procedures for P test in the soil. However, researchers in Western Australia have found that they all predict yield equally (Bolland et al. 1988, Kumar et al. 1994). Accordingly the Colwell (1963) sodium bicarbonate soil test is commonly used. Some laboratories also use Olsen or Recovery methods.

Colwell method

Bicarbonate P is measured by the method of Colwell (1963), viz. 1:100 soil:solution ratio, extractant is 0.5 M sodium bicarbonate (pH 8.50), 16 hours extraction at 23°C.

P-Recovery method

P-Recovery is the proportion of P that is available to plants following fertiliser application after interaction with the soil. For example a P-Recovery of 50 per cent means that if 10 kg of phosphorus is applied to the soil as fertiliser, only 5 kg would be available to the plants. P-Recovery can be used to assist determination of the desired level of P for a particular soil. A high P-Recovery means a lower reading of P is acceptable, but if P-Recovery is low (< 40%), then a higher level of available P is required.

Phosphorus Retention Index

Phosphorus Retention Index is used to rank the soil's ability to either leach or 'fix' phosphate applied as water-soluble fertiliser. The plant yield response curve for Colwell P (see below) varies with the soil type, especially influenced by the P adsorption properties. For example, critical levels (soil test P required for 90 per cent of maximum yield) vary from less than 10 ppm P on grey sands up to greater than 40 ppm P for clay loams. This means that it requires both a Colwell-P soil test value and a PRI value to come up with a phosphate fertiliser recommendation (Allen & Jeffery 1990, Allen et al. 2001).

Two points should be considered when dealing with the profitability of P fertilisers:

(i) The relationship between the amount of freshly applied fertiliser and yield (yield response curve)

(ii) The relationship between soil test and yield (Soil P test calibration).

Both the yield response and soil test calibration must be determined locally via field experiments.

Because plant root systems differ in their physiological P uptake, mycorrhiza dependence and root surface area, the critical soil test value which is applicable to one crop may not be applicable to another. A soil test may be correlated with P availability to a crop, but this does not mean it is also correlated with P fertiliser requirement. The buffering capacity of the soil for P must be considered before judging the correlation. Thus, for a soil at the same level of extractable P, the higher the P buffer capacity, the greater the fertiliser requirement. Broadcasting or dispersing the fertiliser also depends on the buffering capacity of the soil. Banding fertiliser is much less affected by the buffering capacity while dispersing it is highly affected by the buffering capacity.

When the P-fixing capacity of a soil is not saturated, a great portion of the applied P will be fixed by the soil and for optimum crop yield it will take far higher rates of P fertilisers than the plant actually takes up. It is better in this case to band P fertilisers to reduce the amount fixed by the soil. In alkaline soils, combining P with ammonium would increase P uptake by the plant because the nitric acid produced through the oxidation of the ammonium ions slows
the formation of the more insoluble calcium phosphate compounds. Addition of organic matter would also increase the availability of P for the plant. Maintaining soil pHw at about six to seven would optimise the availability of P in most agricultural systems.

P deficiency symptoms in cereals
Reduced early growth and vigour, dull dark green or purple leaves. Tips begin to yellow and then the yellow area moves down the leaf. Leaves then die quickly, with the tip becoming orange to dark brown. P yellowing symptoms of the oldest leaves are similar to N. However, yellow areas in P die much more quickly.

12. Calcium (Ca)

Calcium is essential for the proper growth and function of root tips. It is also found in large quantities in leaves where it is a constituent of the cell wall. Calcium is thought to encourage earthworm activity and thus can increase the natural aeration of the soil. A good level of calcium is also associated with aggregation and stable soil structure. This is due to an increase in flocculation of the clay particles and to less extent, to the increased activity of soil organisms. Both an excess and a deficiency of calcium will create a phosphate deficiency. Factors contributing to Ca deficiency may include alkaline sodic soils and high soluble Al.

Absolute deficiency of calcium for plants is not common in Australian soils. However, many Australian soils show inadequate concentration for healthy soil structure. Acid soils with low CEC in high rainfall environments are most likely to be low in Ca.

Ca is the fifth most plentiful element and the third most plentiful metal (after Fe and Al) in the earth’s crust. Its content in the lithosphere (earth’s crust and upper mantle) is about 3.6 per cent. However, Ca in non-calcareous soils is much lower ranging from about 0.1 to about 1 per cent. Ca is lost through crop removal, leaching and soil erosion, but is replenished by weathering and dissolution, by decay of organic matter, and by addition of fertilisers and amendments such as lime, dolomite and gypsum. Under humid conditions, particularly with highly weathered soils, removal exceeds replenishment and base unsaturation of the exchange complex develops. Under such conditions soil becomes strongly acid and Ca deficiency may develop (Bruce 1999). The level of exchangeable Ca reflects the interacting effects of the total amount and the solubility of Ca sources, CEC, competition from Al, Mg or Na, and the extent of the Ca-removing processes. In general, neutral and alkaline soils possess higher concentrations of exchangeable Ca relative to acid soils.

Calcium saturation is the percentage of the CEC occupied by exchangeable Ca and can vary widely (Table 13). Ca saturation is correlated with soil pH and inversely related to Al saturation. Ca saturation is very important for soil structure. Low Ca saturation commonly results in deteriorated soil structure. In this case soil amendment such as gypsum or lime is required to increase the saturation percentage.

Exchangeable Ca level commonly exceeds that of exchangeable Mg level, except in humid and sub-humid regions where exchangeable Mg increases relative to exchangeable Ca as soil age and degree of development increases (Buol et al. 1973).

Since exchangeable Ca is the principal source of soluble Ca, the concentration of Ca in soil solution is influenced by the amount of exchangeable Ca and also by factors which affect its release from exchange sites. These include the nature of the exchange complex, the degree of Ca saturation, and the type and ratio of complementary ions (mainly Mg, K and Na). Ca, like almost all other nutrients, undergoes temporal changes where the concentration is reduced by crop removal but restored by the next season. Ca concentration also varies with soil moisture and seasonal conditions.
Table 13. Analytical data for topsoil and subsoil of acid soils (Bruce et al. 1989)

<table>
<thead>
<tr>
<th>Soil (91 sites)</th>
<th>Topsoil</th>
<th>Subsoil</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH&lt;sub&gt;w&lt;/sub&gt;</td>
<td>5.29</td>
<td>5.21</td>
</tr>
<tr>
<td>pH&lt;sub&gt;Ca&lt;/sub&gt;</td>
<td>4.47</td>
<td>4.37</td>
</tr>
<tr>
<td>Exch. Ca, cmol/kg</td>
<td>2.4</td>
<td>0.74</td>
</tr>
<tr>
<td>Ca saturation, %</td>
<td>41</td>
<td>20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Soil solution (48 sites)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca concentration, μM</td>
<td>308</td>
<td>790</td>
</tr>
<tr>
<td>Ca activity ratio</td>
<td>0.107</td>
<td>0.054</td>
</tr>
</tbody>
</table>

**Calculus in the plant**

The nutritional effects of Ca can be explained by the following aspects of the physiology:

- Plants do not have a highly efficient uptake mechanism for Ca
- Ca uptake by the root occurs just behind the tip
- The upward movement of Ca from the roots is controlled by the rate of transpiration
- Redistribution of Ca from old to young leaves is negligible because very little Ca is remobilised or translocated downward in the plant as the concentration of Ca in the phloem is very low.

Calcium can be supplied as agricultural gypsum, lime or dolomite and also in calcium and rock phosphate fertilisers. Dolomite is used where there is also a magnesium requirement, or where gypsum application will create a soil magnesium deficiency.

**Soil tests for Ca**

Measurement of exchangeable and soil solution Ca are the bases for diagnostic soil tests for Ca. Calcium level may be used directly or expressed relative to other soil attributes. For example, exchangeable Ca can be expressed as a percentage of the CEC (Ca saturation) or as the ratio of Ca to Mg. Soil solution Ca is often expressed as the Ca activity ratio, which is the ratio of Ca activity to the sum of the activities of all major cations in solution.

**Calcium/pH**

Calcium recommendation is usually based on soil deficiency, not on pH. This recommendation will be for calcium carbonate (lime), dolomite or gypsum, depending on the percentages of calcium and magnesium present in the soil. Note that applied calcium will displace soil magnesium, so dolomite will often be recommended if exchangeable soil magnesium is low (usually below 1 per cent base saturation). Calcium will also suppress the uptake of manganese, so a deficiency may be induced by the application of gypsum, especially if soil manganese is low. However, there is no unique or universal Ca:Mg ratio applied to all crops and/or soils that gives the highest yield, because different soils and different crops show different Ca:Mg requirements for highest yield.

**Calcium deficiency symptoms in cereals**

Spots in the middle of the newest leaf die. This area quickly expands and the leaf collapses in the middle before it even unrolls. Terminal growth is distorted. Deficiency symptoms are seldom observed in Western Australia.
13. Magnesium (Mg)

Magnesium is essential for both animal and plant production. Magnesium is the eighth most common element in the earth’s crust (Barber 1995). The relative abundance in plant matter is similar to that of S and P but less than that of N, K and Ca. The bulk of Mg in the soil is usually in a form of primary and secondary minerals that is not readily available to the plant.

Despite an Australia-wide recognition of the soil acidity problem, with an associated implication of declining soil Mg levels, there is little documentation in Australia of the effect of applied Mg on yield or the relationship between soil test values and yield response to applied Mg (Aitken & Scott 1999). For this reason, Mg is only applied occasionally as a fertiliser.

Exchangeable Mg has proved to be a good estimate of total plant-available Mg and soil tests based on this are likely to be successful in identifying the soil Mg status. Soil tests are usually reliable because Mg in soil changes little over time. The major Mg inputs to the soil are from the breakdown of certain minerals, rain and fertilisers, while the major losses include crop removal and leaching. Both inputs and losses are relatively small.

The desired level of base saturation percentage for Mg is around 10-20 per cent (which depends on the soil CEC).

Magnesium deficiency symptoms in cereals

Leaves are pale and soon yellow, remaining unopened with a twisted appearance. With time yellowing becomes mottled (spots/beads) and in old leaves may turn reddish along the leaf margins. In severe deficiency the entire length of the leaf will remain folded or rolled.

14. Potassium (K)

As an essential macronutrient, K is required for photosynthesis, translocation, cellulose formation, enzyme activities, cation-anion balance and stomatal control (Marschner 1986). Crops require a large quantity of K, which has to be supplied from the soil. Potassium is one of the most abundant elements in the soil. Soil K is a function of the parent material, the extent of weathering and leaching of soil minerals, the type of soil minerals, organic matter content and K fertilisers. The total K content of soil generally increases with increasing clay content, giving texture an important role influencing both total and exchangeable K (Table 14).

Potassium deficiency in Australian agricultural soils has been long recognised (Gourley 1999), particularly in the south-west of WA (Williams & Raupach 1983). A reliable soil test is based on ‘exchangeable K’ or ‘extractable K’. There is little evidence that one test is better than another.

Table 14. Total and exchangeable K in some Western Australian soils (after Cox 1973)

<table>
<thead>
<tr>
<th>Location</th>
<th>Texture</th>
<th>Total K, %</th>
<th>Exchangeable K, mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Busselton</td>
<td>Coarse sand</td>
<td>0.02</td>
<td>16</td>
</tr>
<tr>
<td>Walpole</td>
<td>Fine sand</td>
<td>0.06</td>
<td>14</td>
</tr>
<tr>
<td>Cundinup</td>
<td>Loam</td>
<td>1.8</td>
<td>120</td>
</tr>
<tr>
<td>Bridgetown</td>
<td>Clay</td>
<td>1.4</td>
<td>160</td>
</tr>
</tbody>
</table>

Most of the widely used soil tests have had some level of field calibration which has resulted in suggested critical values that form the basis of K fertiliser decisions for many crops and
pastures. Surprisingly, these critical values in surface soils are similar for most agronomically important plant species and are generally around 0.2-0.5 cmol(+)/kg or 80-200 ppm for Australia in general, and around 60 ppm for mostly duplex soils in WA (Gourley 1999). The desired level of K depends on the exchange capacity (CEC) of the soil. Light soils (less than six CEC) require a higher percentage of K (6 per cent). Heavier soils (greater than 20 CEC) require 3 per cent K. This is due to the fact that there are more exchange surfaces in a high CEC soil so there is also a higher amount of potassium available. Plants require relatively large amounts of potassium.

Furthermore, high Ca and Mg levels in the soil solution may reduce K uptake by the plant roots. Due to the competition between K and Ca, K deficiency frequently occurs in calcareous soils even when the amount of exchangeable K present would be adequate for plant nutrition (Brady & Weil 2002).

The desired level of K in the soil is around 2 to 5 per cent base saturation.

**Potassium deficiency symptoms in cereals**

Symptoms first appear on the oldest leaves, speckled along their whole length, quickly spreading to the tip and margins in severe cases. As leave die back from the tip and margins a spear shaped pattern of green remains.

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**15. Cobalt (Co)**

Co is an essential trace element for animals, but not for plants except legumes, where it is required by rhizobia in legume nodules for N fixation (Peverill & Judson 1999). Cobalt deficiency in legumes is shown by reduced and undeveloped nodules.

Soluble or available Co is determined by various extractants including 2.5 per cent acetic acid (pH 2.5), neutral N ammonium acetate, or 0.05 M EDTA (Mengel & Kirkby 1982).

Co absorbed through the leaves is particularly immobile, while that absorbed by the roots follows the transpiration stream and is concentrated at the margins and tips. Excess Co may induce Fe deficiency.

Co is more likely to be deficient during wet periods and periods of rapid, fresh growth because the Co taken up is distributed through a larger plant mass. Deficiency occurs in highly leached sandy soils derived from acid igneous rocks or in highly calcareous or peaty soils. Co deficiency can be controlled by applying cobalt salt, usually sulphate, to the soil.

In Western Australia, the critical level for Co has not been determined yet.

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**16. Boron (B)**

Boron is essential for photosynthesis and energy production in plants. It also acts as a modifier in helping to maintain the balance between calcium, potassium and magnesium, especially when one of these major cations is in excess and creating a major imbalance. It is needed for the development and growth of new cells, and since it is not readily translocated within the plant, boron increases calcium absorption in plants and animals, increases fruit quality and shelf life and also increases the oil percentage in canola. Boron is also involved in many other essential plant processes, including the translocation of sugars and other bio-chemicals, protein synthesis, nodule formation in legumes and the regulation of carbohydrate metabolism (energy). In pastures, B helps to balance nitrogen levels and prevents the excess accumulation of nitrate nitrogen, thus reducing excess protein in spring and autumn pasture. This is also the case in fruit crops.
The absorption of B by plant roots is determined by its concentration in the soil solution and it is correlated well with assessing toxicity and plant response on a wide range of soils (Aitken & McCallum 1988).

Soil testing is difficult because of high spatial variability and the high B concentrations that occur in the subsoil which is more difficult to sample. Boron toxic patches scattered in the field occur irregularly, impairing growth and causing yields to be low. Soil samples can be collected from such patches for analysis.

In Australia three methods are in use in testing for B:

- Hot water soluble extraction method (Haddad & Kaldor 1982) which does not work well in sodic or alkaline clay soils
- CaCl₂-Mannitol extraction method (Cartwright et al. 1983)
- Hot CaCl₂ (Spouncer et al. 1992).

The CaCl₂ is mainly used to assess B toxicity on alkaline and sodic soils for which the hot water soluble B test is unsatisfactory.

In WA, B toxicity rather than B deficiency is a widespread constraint to cereal and legume crop and pasture production in alkaline soils. However B deficiency has been reported on some sandy soils (Bell 1999). The B absorption rate by plant roots is determined by concentration in the soil solution. For assessing B toxicity, soil solution B appears to correlate well with plant response on a wide range of soils (Aitken & McCallum 1988).

Generally, soil analysis gives a reasonable prediction of B deficiency when tests are calibrated for particular soil groups and crop species. Both hot water and hot 0.01M CaCl₂ extractant are used for soil B analysis in Australia. In soils with low B, the two extractants remove similar amounts of B and correlate well with plant response. Most values of the critical concentration for deficiency range from 0.15 to 0.5 mg B/kg soil. In very sensitive crops and in alkaline clay soils these values can be doubled (Bell 1999). The capacity of soil to buffer soil solution B against losses by plant uptake is determined by soil texture, soil mineralogy, pH and organic matter. B reacts more strongly with clay than with sandy soils, making clay soils buffer B in the soil solution better than sandy soils. B is also less likely to leach through clay soils or clay-rich horizons than sandy soils or horizons (Pinyerd et al. 1984). Higher organic matter also increases the B-sorption capacity of soil (Yermiyahu et al. 1995).

**Boron deficiency symptoms in cereals**

The first visual sign of boron deficiency is often the cessation of growth of buds or shoots. This is followed by the death of young leaves, so deficiency often gives plants a bushy appearance. Wheat heads can also have a bushy appearance and show white tips. Newer leaves split along the leaf close to the midrib and a saw tooth effect on edges of young leaves may be seen. Shoots wither similarly to Cu and Ca deficiencies.

**Boron toxicity**

In contrast to all other essential plant nutrients, B is mainly present in the soil solution as non ionised boric acid, B(OH)₃ which under high soil pH conditions is only slightly de-protonated (dissociated). This is the main reason why B is easily leached from the soil. However, in compacted, poorly drained soils or soils with a subsoil hard pan, B can accumulate to a toxic level. Boron toxicity symptoms include the yellowing and death of leaf tips, starting with the oldest leaves first. These symptoms often do not appear in early vegetative growth.
17. Iron (Fe)

Iron has many important functions in plants such as involvement in the synthesis of chlorophyll.

Iron is the fourth most abundant element in the earth’s lithosphere after oxygen, silicon and aluminium. Many extraction methods have been developed for use in soil taxonomy systems, but they are inappropriate for the assessment in nutrient availability because they extract not only the most reactive forms of Fe, but also varying amounts of less reactive forms of little use to plants. It is difficult to recommend a particular soil analysis for predicting deficiency in plants. In Fe deficiency, soil environment factors such as pH, moisture content, temperature and bicarbonate concentration and the genetic variability within and between plant species with respect to Fe uptake, make any Fe soil-testing procedure very difficult to calibrate for reliable interpretation (McFarlane 1999). Fe solubility is the most important factor responsible for Fe deficiency in plants, especially on calcareous soils. Fe solubility decreases significantly in aerated soils especially at soil pHw 7-8, where most of the Fe is present as low soluble Fe$^{3+}$ oxides and hydroxides. Soil pH is the most important soil parameter influencing Fe solubility and hence availability to plants. The concentration of Fe in soil solution within common soil pH levels ranges from 30 to 550 g/L, whereas in strongly acid soil it can exceed 2000 g/L. When a soil is submerged, Fe$^{3+}$ compounds are directly and indirectly reduced to the more soluble (more available) Fe$^{2+}$, and large amounts of Fe are brought into solution. The concentration of water-soluble Fe$^{2+}$ increases to a peak value and then declines or reaches a plateau. These changes depend on the pH and organic matter content, temperature and the salt content of the soil. However poor aeration, especially in compacted soils which lead to higher solubility of Fe, may intensify Fe deficiency because many smaller roots are injured or destroyed, which in turn reduces the absorptive capacity of the whole root system.

The content of soluble Fe in soil is extremely low in comparison with the total content. Most available Fe is the reduced ferrous Fe$^{2+}$ which decreases availability in well aerated soil. Furthermore, Fe in general and Fe$^{3+}$ in particular, are highly soil pH dependent, where the activity of Fe$^{3+}$ falls with increasing pH. At higher pH level Fe$^{3+}$ activity in solution decreases 1000 fold for each pH unit rise and reaches its minimum at 6.5-8.0. Since Fe is more soluble in acid soils, Fe deficiencies can be caused by over-liming.

The critical Fe level in WA has not been determined but can range from 100 to 400 ppm.

Iron deficiency symptoms in cereals

Pale green to yellow leaves. Interverinal chlorosis (usually yellow colour turning white under severe deficiency). Similar symptoms to N and P deficiencies, usually seen in youngest leaves.

18. Manganese (Mn)

Manganese is essential for many important plant functions, including photosynthesis, nitrogen metabolism and nitrogen assimilation. Manganese is essential for calcium uptake by plants. Deficiency symptoms are common in cereals growing on highly alkaline soils and generally appear as a yellowing of the leaves. Roots are covered by a thick film which is easily wiped off, leaving a thin white strand. There are pale green strips on young leaves, which are weak and tear easily.

It is almost impossible on the basis of soil test alone to correctly diagnose either Mn deficiency or toxicity of field-grown plants. Although much is known of the nature and reaction of Mn in soil and of its absorption and functioning in plants, our ability to predict the
level of plant-available Mn in soil is limited (Uren 1999). Determination of the Mn status of field soils for adequate plant growth requires measurement of water-soluble plus exchangeable Mn, easily reducible Mn, soil pH and Mn concentration in the plant. Time of sampling, field conditions at the time of sampling, time taken for and conditions of drying and storage before analysis can all affect test values. Standard protocols for sampling, preparation and storage need to be established and adhered to strictly in routine soil analysis (Uren 1999).

Mn deficiency was first reported in WA by Carne in 1927. Toxicity is not as widespread as deficiency. The availability of Mn in soil is determined by soil and plant factors. Soil factors include microbial activity, pH and the reducibility of Mn oxides. The reducibility of the oxides is related to the exposed surface area of these oxides. Amorphous oxides with small particle size (large specific surface area) are the most reactive. Plant factors are related to the surface area and reducing capacity of the roots. Quite large differences between species and cultivars of the same species exist in their tolerance of toxicity and deficiency. However there is no apparent link between the mechanism of tolerance to toxicity on one hand and tolerance to deficiency on the other.

Mn concentration in plants can also be suppressed in high potassium soils or following calcium or potassium applications.

The desired Mn level (total) in soil is between 80 to 140 ppm.

**Mn toxicity**

Gray flakes or yellow or brown spots develop on leaves. Note that the flecking symptoms are similar to insect damage, while the yellow spots are similar to some leaf diseases or herbicides. Brown spots in barley can be confused with leaf disease.

**19. Copper (Cu)**

Copper is involved in many plant processes. It is essential for photosynthesis and for protein and carbohydrate metabolism. Copper also appears to be required for nitrogen fixation by *Rhizobia*. In severe deficiencies leaf tips turn almost white and leaves become narrow. In cereal grains the seeds fail to develop leaving blind ears. Yellow bleached spots on the surface of leaves may occur, similar to the symptoms of Mn toxicity. Copper is an essential nutrient for animals and is often deficient when they graze pastures low in copper.

Many empirical methods have been used to test for Cu in soil. We call them empirical because there is no guarantee that the Cu extracted in soil is necessarily the one that will be absorbed by the roots. Most soil tests extract much more Cu than is accumulated by the shoots and roots of the annual crops. The most reliable method in showing the amount of Cu that can be available to the plant is when Cu is extracted with ammonium oxalate. Using this method in WA, it has been shown, for example, that 0.3 ppm Cu or less in the topsoil (top 10 centimetres) is certainly indicating a deficient Cu level for wheat, while greater than 0.8 ppm is almost adequate.

Deficiency level of Cu, Zn, Mn and Fe can be identified by the DTPA procedure, but this test has not been calibrated adequately for acidic WA soils.

Copper deficiency of cereals in Western Australia was first recognised in late 1930s and early 1940s (Teakle 1942). Researchers have reported widespread Cu deficiency on the red gum country, sandy, gravelly soils of the wheatbelt, Great Southern soils and coastal soils high in lime (Teakle 1942, Dunne 1948). Soil factors causing deficiency or toxicity include soil pH, organic matter, clay, iron and aluminium oxides as well as soil moisture and
Copper deficiency can be induced by excess soil molybdenum, and iron and copper availability to plants is affected by the soil pH. As the pH increases, so copper availability decreases.

The desired level of Cu in soil extracted by ammonium oxalate is greater than 0.8 ppm. The desired level in soil extracted by DTPA is around 0.2-0.3 ppm (Ross Brennan, DAFWA, pers. comm.).

20. **Zinc (Zn)**

Zinc is an essential nutrient for both animals and plants. In plants it promotes growth hormones and starch formation and is involved in seed maturation and production. Grain seed heads often fail to completely fill if zinc is deficient. It is essential for root membrane permeability and moisture absorption into roots.

There is no single reliable soil test for Zn in Australia (Armour & Brennan 1999). DTPA is the most widely used test particularly in recent research. Calibration data are only available for a limited number of plant species and soil types. Plant species and selections within species vary widely in their tolerance to Zn deficiency as well as toxicity (Graham & Rengel 1993).

The most important soil factor associated with Zn deficiency is pH, because availability is markedly reduced with increasing soil pH over the agriculturally important range of 5.5-7.0. For this reason over-liming acid soils may severely reduce the Zn availability for the plant. Highly available P and prolonged waterlogging also reduce availability. Zn is present in soil in different forms, including in soil solution as Zn$^{2+}$, ZnCl$^+$, and ZnOH$^+$. These ions are immediately available for plants as exchangeable Zn, in complex with organic matter, occluded by or co-precipitated with oxides and hydroxides of iron, aluminium and manganese held in clay minerals.

DTPA extraction is widely used in testing Zn in soil; however, wide variation exists between soils due to different clay content, pH and organic matter. The desired level for Zn in soil extracted by DTPA is around 0.2 to 0.6 ppm depending on the soil type (Armour & Brennan 1999).

**Zn deficiency symptoms in cereals**

Young to middle leaves develop yellow patches between the mid-vein and the edge of the leaf and extend lengthways towards the tip and base of the leaf. These areas eventually die, turning pale grey or brown. Plants take on a water- or diesel-soaked appearance. Symptoms are similar to leaf spot.

21. **Molybdenum (Mo)**

Molybdenum is essential for both plants and animals. In plants, Mo is part of enzymes needed for nitrogen fixation by clovers and lucerne, as well being essential for nitrogen utilisation, especially in brassicas. Deficiencies occur mostly at a pH <5. In livestock, excess levels in pasture can adversely effect stock health by reducing the absorption of copper and so induce copper deficiency. This problem has been caused by the excessive use of molybdenum fertilisers.

Molybdenum was first established as an essential element for higher plants by Arnon and Stout (1939). Acid ammonium oxalate extraction of soil Mo has received the most attention.
of all tests. In soil, Mo occurs in clay minerals, bound to organic matter and in soil solution. The soil solution Mo is readily available for the plant, followed by MoO$_4$$^2$ held weakly on the surface of clay or secondary minerals, while Mo held in primary mineral structure is only sparingly soluble and considered unavailable to the plant.

At the time of sampling, tissue tests may be able to diagnose Mo deficiency in some crops. There is no current reliable soil test for Mo.

**Mo deficiency symptoms in cereals**

Mo deficiency symptoms are difficult to detect in the field, however middle leaves show speckled flecking or yellow stripes and appear limp and water stressed. At high N levels the old leaf tips are scorched. Under severe deficiency maturity is delayed and heads are empty. Cu deficiency may look similar to Mo deficiency. Physiological effects such as crimping of the flag leaf, are often confused as a symptom of Mo deficiency.

### 22. Sodium (Na)

Excess sodium causes dispersion and destruction of soil structure. Dispersed clay particles block soil pores resulting in restricted water and air movement. If surface soil pores are blocked by dispersed clay, the soil becomes massive and when dry may form a surface crust or hard-setting layer. This will inhibit seedling emergence and water penetration. Subsoil dispersion results in reduced water movement down the profile. Following heavy rainfall, waterlogging of the surface soil could also result. The consequent lack of oxygen in the root zone will detrimentally affect the crop. During hot weather, there may also be excessive evaporation due to the restriction of drainage through the profile. On sloping land, lateral water movement may occur above the relatively impermeable subsoil horizon. Subsoil dispersion also results in the structural breakdown of aggregates and increased soil density and hardness. Plant root movement will be restricted by the dense subsoil and much of the moisture and nutrients stored in the subsoil will not be used.

In Australian soils, when the exchangeable Na percentage (ESP), exceeds 5 per cent of the cation exchange capacity, soil structure starts to degrade especially in soils with low Ca. This degradation of structure significantly reduces water infiltration and percolation. Gypsum is usually applied to address soil sodicity. However, lack of rain and drainage may impose serious problems in improving sodic soils because there is not enough water to help calcium replace sodium and there is no outlet for the leached sodium. Sodic topsoils can also benefit from addition of organic matter, because organic matter increases cation exchange capacity and helps bind soil particles together.

Acceptable Na level in soil is between 0.5 to 2 per cent of the CEC.

**Note:** Often a preferred index or measure of sodicity is the Sodium Adsorption Ratio (SAR) rather than Exchangeable Sodium Percentage (ESP), because ESP values can vary depending on whether CEC or the sum of the major cations is used as the divisor. SAR is often reported in horticultural analyses.
23. **Aluminium (Al)**

Aluminium is not an essential nutrient for most higher plants, but can still be taken up and accumulated through passive transports such as osmosis or with the flow of transpiration water, possibly through damaged membranes. The importance of Al in soil stems from its abundance where 15 per cent of the earth’s crust is made of Al₂O₃, thus making Al an important constituent of the soil. Furthermore, Al and Si, are the major elements making up the lattices of soil clay minerals. The solubility of Al increases sharply when soil pH decreases below 5.5 and more than half the cation exchange sites may be occupied by Al.

The first observable effect of Al toxicity on plants is a limitation in root growth. Root tips and lateral roots become thickened and turn brown. Frequently P uptake and translocation to the upper parts of the plant are decreased. There is a wide variation in Al tolerance between species. Lucerne, barley, medics and canola are highly sensitive, while oats, triticale and lupins are very tolerant. Aluminium is only a problem in low calcium soils, so addressing the lime or dolomite requirements is the priority and will usually overcome toxicity challenges. Soil aluminium levels reported from soil analysis are generally not a reliable indicator of lime requirement and it is better to apply lime based on the level of exchangeable calcium present.

Acceptable 0.01 M CaCl₂ Al level in soil is less than 4 ppm, frequently depending on the sensitivity of the plant species (Slattery et al. 1999).

**Symptoms of Al toxicity**

Poor lateral root development and the main root is thickened and distorted in taprooted species. Early in the season all leaves become pale, particularly the oldest, which turn yellow and die. Leaf symptoms are similar to P deficiency. Late in the season plants appear to be drought stressed despite adequate soil moisture. However, tolerant crops do not display clear symptoms.
Glossary of soil science terms

**Acid cations:** Cations principally Al³⁺, Fe³⁺, and H⁺, that contribute to H⁺ ion activities either directly or through hydrolysis reaction with water.

**Acid soil:** Soil with a pH value <7.0.

**Active acidity:** The activity of hydrogen ions in the aqueous phase of a soil. It is measured and expressed as pH value.

**Adsorption:** The process by which atoms, molecules, or ions are taken up from the soil solution or soil atmosphere and retained on the surface of a solid by chemical or physical binding.

**Aggregates:** A group of primary particles that cohere to each other more strongly than to other surrounding particles, such as a clod, crumbs, block, or prism.

**Agronomy:** The theory and practice of crop production and soil management.

**Alkaline soil:** Soil with a pH value >7.0.

**Antagonism:** Production of a substance by one organism that inhibits one or more other organisms. The terms antibiosis and allelopathy have also been used to describe such cases of chemical inhibition.

**Available nutrient:** (i) The amount of soil nutrient in chemical forms accessible to plant roots or compounds likely to be convertible to such forms during the growing season; and (ii) The contents of legally designated 'available' nutrients in fertilisers determined by specific laboratory procedures which in most states constitute the legal basis for guarantees.

**Base saturation percentage:** The extent to which the adsorption complex of a soil is saturated with exchangeable cations other than hydrogen and aluminium. It is expressed as a percentage of the total cation exchange capacity

**Bulk density:** The mass of dry soil per unit volume of soil with units of g/cm³, mg/m³ or t/m³. The bulk volume is determined before drying to constant weight at 105°C.

**Cation Exchange Capacity, CEC:** The sum of exchangeable bases plus total soil acidity at a specified pH value (usually 7 or 8). The unit is centimoles of charge per kilogram of exchanger (cmolc/kg).

**Colloid:** A particle, which may be a molecular aggregate, with a diameter of 0.1 to 0.001 μm. Soil clays and soil organic matter are often called soil colloids because they have particle sizes that are within, or approach colloid dimensions.

**Dolomite:** A mineral consisting of CaCO₃ (Ca = 21.7) and MgCO₃ (Mg = 13.2) used to supply Ca and Mg ions.

**Essential elements:** Any plant nutrient that is required for the completion of the life cycle.

**Exchangeable sodium percentage:** The extent to which the adsorption complex of a soil is occupied by sodium. It expressed as follows: ESP = [Exchangeable sodium (cmolc/kg soil)/total cation exchange capacity (cmolc/kg soil)] X 100.
Green manure: Green plant material incorporated with the soil by cultivation, chemical desiccation or mulching for improving soil organic matter.

Gypsum: Calcium sulphate, CaSO$_4$.2H$_2$O, is used to improve compacted soils and increase soil permeability and help soil flocculation, which is a prelude for soil aggregations. It is also used to treat sodic soils where Ca ions can replace Na ions. It has a moderate solubility of 2.41 g/L in cold water and 2.22 g/L in hot water. Similarly, gypsum is commonly used as a sulphur fertiliser at rates much lower than that required for soil structure improvements.

Kaolinite: An aluminosilicate mineral of the 1:1 crystal lattice group consisting of single silicon tetrahedral sheets alternating with single aluminium octahedral sheets. A very common clay mineral in Western Australia.

Lime: CaCO$_3$, mainly used to remove acidity (H$^+$) from the soil by converting the hydrogen ions to water and releasing CO$_2$ gas. It has low solubility of 0.014 g/L (cold water) and 0.018 g/L (hot water).

Macronutrients: Essential plant element needed by the plant in relatively large quantities such as N, P, K, Ca, Mg, S and Cl.

Micronutrients: Essential plant elements needed in small quantities such as Fe, Mn, B, Cu, Zn, Co, and Mn.

Mineral soil particles: Minerals particles $<$2.0 mm in equivalent diameter ranging between specified size limits. The International Society of Soil Science recognises the following soil separates: coarse sand 2.0 to 0.2 mm; fine sand 0.2 to 0.02 mm; silt 0.02 to 0.002 mm and clay $<$0.002 mm.

Mineralisation: The conversion of an element (for example, N and S), bound in an organic form, into an inorganic state as a result of microbial decomposition.

Montmorillonite: An aluminosilicate clay mineral in the smectite group with a 2:1 expanding crystal lattice, with two silicon tetrahedral sheets enclosing an aluminium octahedral sheet. Isomorphous substitution of magnesium for some of the aluminium has occurred in the octahedral sheet. Considerable expansion may be caused by water moving between silica sheets of contiguous layers.

Muriate of potash: A potassium fertiliser, potassium chloride, containing 49 per cent of potassium element.

Oxidation: The loss of one or more electrons by an ion or molecule.

Ped: A unit of soil structure such as a block, column, granule, plate, or prism, formed by natural processes (in contrast with a clod, which is formed artificially.

Pedon: A three dimensional body of soil with lateral dimensions large enough to permit the study of horizon shapes and relations.

Permeability, soil: The penetration of water and gases through a bulk mass of soil or a layer of soil. Since different soil horizons vary in permeability, the particular horizon under question should be designated.

Pore space: The portion of soil bulk volume occupied by soil pores.
**Potential acidity:** The acidity that could potentially be formed if reduced sulphur compounds in a potential acid sulphate soil were to become oxidised.

**Protonation:** Attachment of proton (H+) to exposed OH group on the surface of soil particles, resulting in an overall positive charge on the surface.

**Reduction:** The gain of one or more electrons by an ion or molecule.

**Saline soil:** A non-sodic soil containing sufficient soluble salt to adversely affect the growth of most crop plant. The lower limit of saturation extract electrical conductivity of such soils is conventionally set at 4 dS/m (at 25°C). Sensitive plants may be affected at half this salinity while highly tolerant ones may be affected at about twice this level.

**Soil erosion:** The detachment and movement of the soil surface by water, wind, ice or other geological agents including gravitational creep.

**Soil horizon:** A layer of soil or soil material approximately parallel to the land surface and differing from adjacent genetically related layers in physical, chemical, and biological properties or characteristics such as colour, structure, texture, consistency, kinds and number of organisms present, degree of acidity or alkalinity, etc.

**Soil strength (cone index):** It is a transient localised soil property which is a combined measure of a given pedon or other subunit’s solid phase adhesive as well as cohesive status. It is highly influenced by soil moisture and bulk density. Other soil factors such as organic matter and soil texture may also affect it.

**Soil structure:** The arrangement or combination of primary soil particles into secondary units or peds. These secondary units are characterised on the basis of size, shape and grade.

**Soil test interpretation:** Using soil data to improve or mitigate a problem(s) in the soil and that leads to increase net yield and profit. Some interpretations may take environment into account.

**Soil texture:** It refers to the relative proportion of the soil primary particles of different size ranges - sand (S), loam (L) and clay (C).

**Subsoil:** It is located just beneath topsoil and extended from 10 centimetres to include almost all soil rooting depths. It is usually low in organic matter and high in leached nutrients.

**Topsoil:** The surface soil layer that is about zero to 10 centimetres in depth and separates the subsoil from the atmosphere. It usually has a darker colour because soil organic matter is highest.

**Total acidity:** Approximated by the sum of the salt-replaceable acidity plus the residual acidity.
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