Chapter 1
Micronutrients and Crop Production: An Introduction

Brian J. Alloway

Abstract Eight trace elements are essential for higher plants: boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni) and zinc (Zn). Whenever the supply of one or more of these elements is inadequate, yields will be reduced and the quality of crop products impaired, but crop species and cultivars vary considerably in their susceptibility to deficiencies. Zinc deficiency is the most ubiquitous micronutrient problem throughout the world affecting many crops including the staples maize, rice and wheat. Boron deficiency is the second most widespread micronutrient problem and dicotyledon species tend to be more sensitive to B deficiency than graminaceous crops. Iron deficiency is important in some regions, especially those with a Mediterranean climate and calcareous soils. Copper deficiency is important in some parts of the world, such as Europe and Australia where cereals are most affected. Likewise, Mn and Mo deficiencies vary in importance around the world. Acute micronutrient deficiencies in plants are accompanied by distinct symptoms, but hidden deficiencies without obvious symptoms are generally more widespread.

1.1 Introduction

Micronutrients are those trace elements which are essential for the normal healthy growth and reproduction of plants and animals. The trace elements essential for plants are: boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni) and zinc (Zn). Although, cobalt (Co) is known to be essential for the bacterial fixation of atmospheric nitrogen (N) in leguminous plants, it is not considered to be essential for all higher plants. Nevertheless, it has been shown to have beneficial effects on crops in other plant families, such as the *Graminae* (e.g., wheat, *Triticum* spp.) (Asher, 1991) and is referred to as a "beneficial" element. Other beneficial elements, which have not yet been proved to be "essential", include silicon (Si), sodium (Na), selenium (Se), vanadium (Va) and aluminium (Al) (Barker and Pilbeam, 2007).

The trace elements recognised as being essential for animals are: Co, Cu, chromium (Cr), fluorine (F), iodine (I), Fe, Mn, Mo, Se and Zn. However, an additional

B.J. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*.

seven elements are also regarded as being essential for humans (see Graham, Chap. 2 and Welch, Chap. 12).

For a trace element to be essential for either plants or animals (i.e., a micronutrient), it needs to satisfy three criteria: (1) the organism cannot grow and reproduce normally without the element, (2) its action must be specific and unable to be replaced by any other element, and (3) its action must be direct (Arnon and Stout, 1939). However, Epstein (1965) advocated that an element can also be regarded as essential if it is a component of a molecule known to be an essential metabolite, even if it cannot be demonstrated that it fulfils all of the criteria proposed by Arnon and Stout.

In geochemistry, the term "trace element" is given to elements which normally occur in trace amounts (usually <1,000 mg kg^{-1}) in rocks and soils. However, the biological use of the term "trace element" applies to elements occurring at relatively low concentrations (usually <100 mg kg^{-1}) in the dry matter of living organisms. The macro elements carbon (C), hydrogen (H), oxygen (O) and N, which form the main organic compounds in plants and animals, are present in the highest concentrations (at percentage levels). Potassium (K) tends to be present in similar concentrations to N (1.4–5.6%) but phosphorus (P), calcium (Ca), magnesium (Mg), Na and Cl are present in intermediate concentrations (0.1–2.5%) (Wild and Jones, 1988; Marschner, 1995).

It is very important that the micronutrient element requirements of crops are met as well as their macronutrient needs if they are to yield satisfactorily and bear products (e.g., grains and fruits) of acceptable quality. The dose response curves for all micronutrients show that, just as yields can be affected by deficiencies, they can also be reduced by toxicity due to excessive concentrations of the same elements. It is therefore important that soils and/or crops are monitored to ensure that the available micronutrient concentrations in soils are in the optimum range, being neither too low, nor too high. Typical dose–response graphs for micronutrients and non-essential elements are shown in Fig. 1.1.

It is only during the last 70 years that most micronutrient deficiency problems have been widely recognised and treated in the field. This has been largely due to the increased intensification of arable farming in many parts of the world and also to the cultivation of virgin and/or reclaimed land. Intensification involves the increased use of N, P, K and other fertilisers, growing new and higher yielding crop cultivars, liming to create more optimal soil pH conditions, increased use of agrichemicals to control pests and diseases and, in more arid areas, increased use of irrigation. Prior to this intensification, much lower crop yields were usually accepted as the norm in many parts of the world and the crop cultivars grown were generally well adapted to local soil and climatic conditions.

With the adoption of more intensive methods of crop husbandry, it was frequently found that crops began to exhibit various symptoms of stress which had not previously been known on the same area of land. Many of these micronutrient deficiencies were brought about by the increased demands of more rapidly growing crops for available forms of micronutrients. In some cases, several of the elements were rendered less available due to changes in soil conditions, such as increased pH through liming. Perhaps the most important and ubiquitous cause has been the

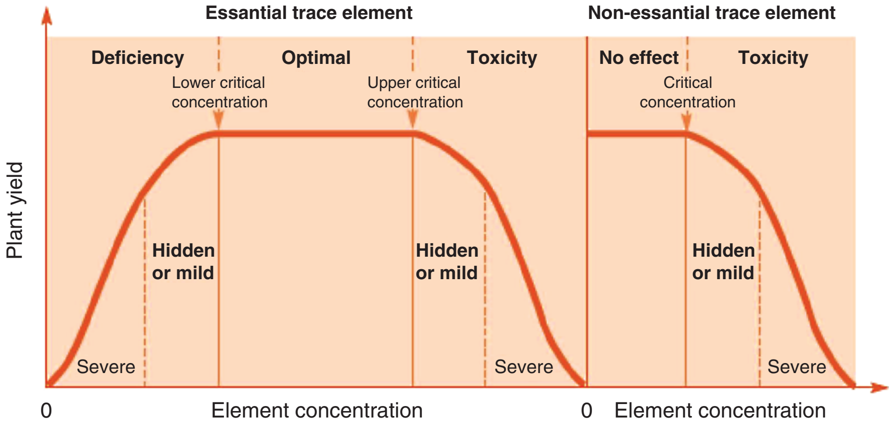

Fig. 1.1 Typical dose–response curves for essential and non-essential trace elements in crops (Alloway, 2004)

introduction of new species and/or cultivars of crops which have a greater requirement for certain micronutrients. The functions of the plant micronutrients are briefly summarised in Table 1.1 (see also Chap. 10).

Although the amounts of micronutrients required by plants are relatively low, individual species and varieties can vary considerably in their requirements for specific elements. Differences in the efficiency with which crop varieties are able to utilise low supplies of B, Cu, Mn, Fe and Zn have resulted in them being labelled as being either "efficient" or "inefficient" for a specific micronutrient. Under field conditions, where the available supply of a micronutrient may be marginal or low, efficient varieties will be better able to grow and yield more satisfactorily than inefficient ones.

When the supply of a micronutrient to plants is deficient, in addition to crop yields and quality being affected, there may also be visible symptoms of physiological stress, especially in cases of severe deficiency. Although plant species differ in the nature of the symptoms of micronutrient deficiencies which they display, there are several generalizations which can be made. In most cases, severe deficiencies will cause stunted growth, discoloration and, in some cases, necrotic spots on the leaves. The discolouration will usually commence as chlorosis when, instead of the normal green colour of chlorophyll, either all or part of the leaves turn yellow, even white, but leaves can also turn brown. Deficiency symptoms can also include smaller or twisted leaves, and loss of turgor. Leaf symptoms are usually seen only on old leaves in the case of Mo, on new leaves with Fe, Mn and Cu, on both young and old leaves with Zn, and on terminal buds with B deficiency. Green veins are seen on new leaves with Fe and Mn deficiency and yellow veins with Cu deficiency (Reddy and Reddi, 1997).

The stunted appearance of plants caused by some deficiencies, such as Zn, is due to reduced internodal expansion and this can give rise to a "rosette" appearance

Table 1.1 Brief summary of the essential functions of micronutrients in plants (Adapted from Srivastava and Gupta, 1996; Heckman, 2007; Xu et al., 2000.)

Element	Functions
Boron	Metabolism and transport of carbohydrates, regulation of, meristematic tissue, cell wall synthesis, lignification growth regulator metabolism, phenol metabolism, integrity of membranes, root elongation, DNA synthesis, pollen formation and pollination
Chlorine	Involved (as Cl^-) in the light reaction in photosynthesis, charge compensation and osmoregulation of the whole plant and individual cells, such as stomatal guard cells, and the activity of certain enzymes
Cobalt	Only proved to be essential in symbiotic N fixation (in roots of legumes) but has other beneficial roles in some other plant families
Copper	Constituent of several enzymes, with roles in photosynthesis, respiration, protein and carbohydrate metabolism, lignification and pollen formation
Iron	Constituent of cytochromes and metalloenzymes. Roles in photosynthesis, symbiotic N fixation, N metabolism, and redox reactions
Manganese	Photolysis of water in chloroplasts, regulation of enzyme activities, protection against oxidative damage of membranes
Molybdenum	N fixation, constituent of enzymes including nitrate reductase and sulphite oxidase
Nickel	Constituent of urease enzyme, role in N assimilation, protection of nitrate reductase against inactivation
Zinc	Constituent of several enzymes with roles in carbohydrate and protein synthesis; maintaining the integrity of membranes, regulating auxin synthesis and in pollen formation

where the whorls of leaves are situated more or less on top of each other. A summary of the main types of symptoms associated with each of the plant micronutrients is given in Table 1.2.

Less severe deficiencies may not manifest themselves until later stages in the development of the plant. In the case of mild to marginal Cu deficiency in cereals, leaf growth can appear normal and the only obvious symptoms appear when the ear, or spike, develops (anthesis). These symptoms can include late development of the ears and abnormal looking ears due to empty grain positions, giving a "rat tailed" appearance in the case of Cu-deficient wheat plants (Fig. 1.3 in Colour Section).

In many cases, visible symptoms provide a convenient and low-cost means of identifying micronutrient deficiency problems, especially in areas where recurrent deficiency problems are found. However, these symptoms are usually only clearly expressed in cases of acute deficiency. These acute deficiencies will often be found for the first time when either new land is put into arable use or when new crop species or cultivars are grown for the first time. For example, Cu deficiency was called "reclamation disease" when it was observed in cereal crops grown on newly reclaimed peaty soils in the Netherlands and in Florida, USA. In the case of Zn, severe deficiencies were found in the Central Anatolia region of Turkey when new,

Table 1.2 Some common symptoms of micronutrient deficiency in widely grown crops (Adapted from Kabata-Pendias, 2001 with additions from Brown, 2007a and Heckman, 2007. See also Chap. 10, Table 10.9)

Element	Symptoms	Sensitive crops
Boron	Chlorosis and browning of young leaves; death of growing points; distorted blossom development; lesions in pith and roots ("heart rot") and multiplication of cell division. Empty grain positions in wheat ears	Legumes, *Brassicae*, beets, celery, grapes, fruit trees (apples and pears) and wheat
Chlorine	Wilting of leaves, especially at margins, shriveling and necrosis of leaves, frond fracture and stem cracking in coconut. Sub-apical swelling in roots	Oil palm, kiwi fruit, sugar, beet, wheat, barley, subterranean clover
Copper	Wilting, melanism, white twisted tips, reduction in panicle formation, disturbance of lignification and of development and fertility of pollen	Cereals, sunflower, spinach, onions, carrots and alfalfa
Iron	Interveinal chlorosis of young leaves	Fruit trees (citrus), grapes, peanut, soya bean, sorghum and calcifuge species
Manganese	Chlorotic spots and necrosis of young leaves and reduced turgor. Necrotic spots on cotyledons of peas	Cereals, legumes and fruit trees (apples, cherries and citrus)
Molybdenum	Chlorosis of leaf margins, "Whiptail" of leaves and distorted curding of cauliflower; "fired" margin and deformation of leaves due to NO_3 excess and destruction of embryonic tissues	*Brassiceae* and legumes
Nickel	Leaf tip necrosis (legumes), chlorosis and patchy necrosis (*Gramineae*)	Pecan, wheat, potato, bean, soya bean
Zinc	Interveinal chlorosis (mainly in monocotyledons), stunted growth, "little leaf". Rossette of trees and violet–red points on leaves	Cereals (especially maize and rice), grasses, flax/linseed and fruit trees (citrus)

high yielding varieties of wheat were grown with heavier applications of NPK fertilisers (see Cakmak, Chap. 7).

However, where the available supplies of micronutrients in the soil have been gradually depleted by repeated cropping, especially with higher yielding varieties, the degree of deficiency may be less severe and the manifestation of symptoms less distinct. Another problem with relying on visible symptoms to diagnose deficiencies is that they can often be confused with symptoms of deficiency of certain other micro or macronutrients, or with symptoms of disease, drought or heat stress and damage by herbicides. In most cases, it is advisable to carry out either soil or plant analysis to confirm the deficiency diagnosis.

In the case of marginal deficiencies, it is possible for the yields of many crops, especially cereals, to be significantly reduced (sometimes by 20% or more), and the quality of crop products to be impaired, without the manifestation of distinct visible symptoms. These are usually referred to as hidden deficiencies or "hidden hunger", latent, and/or subclinical deficiencies. In many parts of the world, this type of deficiency is likely to be more widespread and have a greater economic impact than more severe deficiencies. This is due to the fact, that without obvious symptoms, farmers are often not sure of the causes of the disappointing yields and quality in their crops. Poor yields are sometimes ascribed to inadequate supplies of N and P, with the result that more of these macronutrients may be applied to successive crops. This will often exacerbate the micronutrient deficiency and also lead to increased leaching of N and P into ground waters, possibly causing both ecological and water resource problems.

It is important to realize that the absence of symptoms of a deficiency of a particular micronutrient does not necessarily imply that the supply of this micronutrient is adequate. This is discussed in relation to possible deficiencies of micronutrients in the tropical cropping zone of Australia by Holloway et al. (Chap. 3). Another possibility is that more than one micronutrient may be deficient at a particular site (multi-micronutrient deficiencies). In correcting a diagnosed deficiency of one element, there is a risk that the available concentration of another micronutrient may be reduced in some way, thereby inducing a deficiency of this element instead. This has been found with Cu and Mn, Cu and Zn, and Mn and Fe and other combinations of micronutrients (Alloway, 1976).

As shown in Table 1.3, crop species vary considerably in their susceptibility to deficiencies of different micronutrients. However, intra-specific variations (between varieties/cultivars) can sometimes be even greater than differences in susceptibility between species. Nevertheless, all crops will be affected by a severe deficiency of any micronutrients. The main difference between genotypes is in the critical concentrations at which the supply of a particular micronutrient becomes inadequate. These will be significantly lower for the more tolerant genotypes. This is illustrated by Zn deficiency in wheat. Although, wheat is shown to be much less sensitive to Zn deficiency than other species, such as maize (as shown in Table 1.3), there is still a point at which the supply of available Zn becomes low enough to bring about the onset of physiological stress in wheat due to Zn deficiency. The widespread occurrence of Zn deficiency in wheat in Central Anatolia, Turkey, reported by Cakmak in Chap. 7 is a good example of this.

Cultivars which are able to grow normally in soils with marginally low available concentrations of a micronutrient are classed as being "efficient" for that particular micronutrient. Those cultivars which are unable to tolerate such low levels of this micronutrient are classed as "inefficient". The relative level of efficiency is usually expressed as an "efficiency index" and an example of this index for Zn is shown below (Graham and Rengel, 1993):

$$\text{Zn efficiency} = \frac{\text{Yield (without Zn)}}{\text{Yield (with Zn)}} \times 100$$

Table 1.3 The relative susceptibility of selected crop species to deficiencies of micronutrients (Martens and Chesterman, 1991; Loué, 1986; Prasad and Power, 1997; Follet et al., 1981 and others. The inclusion of two classes in a box reflects differences between sources of information. See also Chap. 6, Table 6.3)

Crop	B	Cu	Fe	Mn	Mo	Zn
Alfalfa	High	High	Medium	Medium/low	Medium	Low
Apple	High	Medium	–	High	Low	High
Barley	Low	Medium /high	High/ medium	Medium	Low	Medium
Bean	Low	Low	High	High	Medium	High
Cabbage	Medium	Medium	Medium	Medium	Medium	–
Carrot	Medium	High	–	Medium	Low	Low
Citrus	Low	High	High	High	Medium	High
Corn (maize)	Low/ medium	Medium	Medium	Low	Low	High
Cotton	High	Medium	Medium	Medium/low	–	High
Grass	Low	Low	High	Medium/low	Low	Low
Linseed/ flax	Medium	–	High	Low	–	High
Oat	Low	High	Medium	High	Low/ medium	Low
Pea	Low	Low/ medium	Medium	High	Medium	Low
Potato	Low	Low	–	High	Low	Medium
OS Rape/canola	High	Low	–	–	–	–
Rice	Low	Low	Medium/low	Med	Low	Medium/ high
Rye	Low	Low	Low	Low	Low	Low
Sorghum	Low	Medium	High	High/medium	Low	High/ medium
Soya bean	Low	Low	High	High	Medium	Medium
S. Beet	High	Medium	High	Medium/high	Medium	Medium
Spinach	Medium	High	High	High	High	Medium
Vine (grapes)	High	Medium	High	High	Low	Low
Tomato	High/ medium	Medium	High	Medium	Medium	Medium
Wheat	Low	High	Medium/ low	High	Low	Low

For a given genotype, nutrient efficiency is reflected by the ability to produce a high yield in a soil that is limiting in one of more nutrient elements (Graham, 1984)

Genotypic variations in efficiency have been reported for B, Cu, Fe, Mn and Zn in crop plants. It is claimed by Rerkasem and Jamjod (2004) that wheat shows a wider range of genotypically related B efficiency than any other crop for any other macro or micronutrient element.

1.1.1 Explanations for Variations in Micronutrient Efficiency

There are several possible explanations for the differences in micronutrient efficiency between cultivars and these are discussed by Graham and Rengel (1993) and Marschner (1995). These are briefly summarized below and comprise differences in:

- The volume and length of roots
- Presence, or not, of proteoid roots
- Root-induced changes in rhizosphere pH
- Increased absorption through vesicular mycorrhizae, if present
- Release of root exudates to facilitate uptake (e.g., phytosiderophores), triggered by low Fe or Zn, organic acids, such as malic acid (Gao et al., 2007)
- Efficiency of utilization of the micronutrients once absorbed into plants
- Recycling of elements within the tissues of the growing plant
- Tolerance of inhibiting factors, e.g., bicarbonate ions [$(HCO_3)^-$] inhibiting Zn uptake in rice

1.2 Individual Micronutrient Deficiencies

1.2.1 Boron

Over a period of nearly 70 years, B deficiency has been recognised in at least 80 countries on 132 plant species (Shorrocks, 1997). Boron is generally required in greater amounts by dicotyledon plant species than by monocotyledons (Srivistava and Gupta, 1996). Boron deficiency is often a problem in grape vines (*Vitis vinifera* L.) and in tree fruits, especially apple (*Malus sylvestris* Mill) and olive (*Olea europea* L.). In field crops, it affects sunflowers (*Helianthus annuus* L.), sugar beet (*Beta vulgaris* L.), black gram (*Vigna mungo* L.), and oilseed rape (canola) (*Brassica napus* L.). Although generally less sensitive to deficiency than dicotyledons, monocotyledon cereals including maize (*Zea mays* L.), sorghum (*Sorghum bicolor* L.), wheat, barley and oats can all be affected by B deficiency. Yield responses in wheat to B applications have been reported in Bangladesh, Brazil, Bulgaria, China, Finland, India, Madagascar, Nepal, Pakistan, South Africa, Sweden, Tanzania, Thailand, USA, Russia, countries of the former Yugoslavia and Zambia (Shorrocks, 1997; Rerkasem and Jamjod, 2004). The contiguous upland cereal growing areas of India, Nepal and Bangladesh comprise the world's largest known area affected by B-deficiency in wheat (Rerkasem and Jamjod, 2004).

Root elongation is usually the first effect of B deficiency in most plant species, but it is rarely seen in wheat. It is the reproductive phase which is the most sensitive to deficiency in wheat and this results in male sterility due to disrupted pollen formation. This causes a major reduction in the numbers of grain set and, thus a reduction in grain yield (Rerkasem and Jamjod, 2004). The lack of any obvious symptoms in the vegetative growth phase mean that many of the cases of male sterility caused by a shortage of B in wheat are hidden deficiencies, at least for a large part of the growth period. This implies that this condition can only be diagnosed by either soil or plant analysis or by yield responses to B fertilisation.

In addition to wheat, other crops known to be relatively sensitive to B deficiency, such as oilseed rape (canola) and sunflower, have been found to have a greater requirement for B during their reproductive phase than during their period of vegetative growth. The beneficial effect of B on grape vines is mainly due to its effect on flowering and fruit set. Rerkasem and Jamjod (2004) consider that wheat is more prone to B deficiency than rice, maize, soya bean or mung bean. In South Asia, where alternating rice and wheat is now the most common cropping system, the wheat in this system is generally more prone to B deficiency. The following rice crop on the same land is rarely affected by this deficiency. This may be partly due to wheat being grown in the coolest months in this subtropical region (Rekasem and Jamjod, 2004). Boron deficiency is a particular problem on alkaline and heavily limed soils and on highly leached sandy soils. The physiology of B in plants and the requirements of crops, especially high value tree crops are discussed by Brown in Chap. 11.

Excess B, causing toxicity is found in various low rainfall areas of the world, especially southern Australia, where it is of geochemical origin (Holloway et al., Chap. 3). Boron toxicity from excessive application of B fertilisers has also been reported in other low rainfall areas, including India and the Near East as discussed by Singh (Chap. 4) and Rashid and Ryan (Chap. 6). In low rainfall areas, there is insufficient percolation of water down the soil profile to leach away accumulations of soluble B salts.

1.2.1.1 Treatment of Boron Deficiency

The fertiliser compounds available for the treatments of B deficiency are given in Table 1.4.

Table 1.4 Boron compounds used for treating boron deficiency in plants (Martens and Westerman, 1991; Borax Ltd.)

Compound	Formula	Boron content (%)
Boric acid	H_3BO_3	17.5
Disodium tetraborate decahydrate (borax)	$Na_2B_4O_7.10H_2O$	11.3
Disodium tetraborate pentahydrate (borax, Granubor II)	$Na_2B_4O_7.5H_2O$	14.8
Anhydrous sodium tetraborate	$Na_2B_4O_7$	21.5
Sodium pentaborate	$Na_2B_{10}O_{16}.10H_2O$	18.3
Solubor	$Na_2B_8O_{13}.4H_2O$	20.9

Boron compounds can be mixed with fertilisers to produce "boronated fertilisers" which tend to be used in areas of high rainfall, such as South America and parts of north-western Europe where there is marked leaching of B and little danger of this highly soluble element accumulating to possibly harmful levels.

Foliar sprays of B compounds are widely used throughout the world on perennial crops such as nuts, vines and fruit orchards because they consistently give better results than soil applications. Rates are usually 10–50% of broadcasting rates: 0.08–0.38 kg B ha^{-1} or 0.4–1.9 kg Solubor ha^{-1} for grapes (Martens and Westerman, 1991). Solubor is normally applied to crops at concentrations of up to 1% (w:v) (Shorrocks, 1997). Foliar sprays have the advantage that they enable an existing deficiency problem to be treated rapidly. They overcome problems of low availability in soil and tend not to make a significant input of B (or any other micronutrient) to the soil.

In India, B fertilisers are broadcast and cultivated into the soil before seeding, or banded (0.5–2 kg B ha^{-1}) (Singh, Chap. 4). In China, B fertilisers are applied either to the seeds, the soil, or to foliage of oilseed rape and cotton (Zou et al., Chap. 5).

1.2.2 Chlorine

Although classed as a micronutrient, Cl is often found in relatively high concentrations in plants (Heckman, 2007). Symptoms of deficiency of Cl are rarely seen in field crops and are most likely to be found in plants grown in solution culture in the greenhouse. Rainfall is usually an adequate source of Cl but in regions remote from the sea, inputs from this source are generally much lower and deficiencies can occur in sensitive cultivars. Amounts of Cl deposited from rain range from 18 to 36 kg ha^{-1} in continental areas to greater than 100 kg ha^{-1} in coastal areas (Heckman, 2007). In the Great Plains of the USA, where chloride salts, such as KCl are rarely used as fertilisers and where the input from rainfall is low, crops have been found to respond to Cl fertilisation. In general, soils do not adsorb chloride ions in significant amounts. therefore regular inputs of this element in rainfall, from weathering minerals, groundwater or fertilisers are necessary to maintain an adequate supply for crops. Symptoms of Cl deficiency are wilting, marginal chlorosis, followed by bronzing and stunting. Chlorine-deficient sugar beet shows interveinal chlorosis and stunting of secondary roots (Srivastava and Gupta, 1996). Kiwi fruit, sugar beet and coconut have relatively high Cl requirements (Marschner, 1995; Xu et al., 2000).

Highly leached, permeable, sandy texture soils such as Arenosols, Ferralsols, and Acrisols, with no weathering minerals releasing Cl, in areas remote from the sea, are the most likely to give rise to Cl deficiency in sensitive crops. In a recent review, Xu et al. (2000) reported that the concentration range below which deficiencies can occur varies from 0.1 to 6 mg g^{-1} (Dry Matter – DM) or between 0.03 and 0.17 mmol L^{-1} of the plant tissue water content for different species. In wheat at heading, the critical concentration lies between 1.5 and 4 mg g^{-1} (DM) with no response above this value. In pot experiments, positive responses to Cl have been found in potato, peanuts, tomato and sugar beet. Yield increases have been found in maize and in wheat. There is also a beneficial effect of Cl in reducing foliar and root diseases of wheat (Xu et al., 2000).

1.2.2.1 Treatment of Chlorine Deficiency

The fertiliser compounds available for treating chlorine deficiency are shown in Table 1.5.

Table 1.5 Chlorine compounds used for treating chlorine deficiency in plants (Heckman, 2007)

Compound	Formula	Cl content (%)
Potassium chloride	KCl	47
Sodium chloride	NaCl	60
Ammonium chloride	NH_4Cl	66
Calcium chloride	$CaCl_2$	64
Magnesium chloride	$MgCl_2$	74

1.2.3 Copper

Copper deficiency can be a major problem in cereals, especially wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), oats (*Avena sativa* L.), and a wide range of other crops, including alfalfa (*Medicago sativa* L.), oilseed rape (canola) (*Brassica napus* L.), onions (*Allium cepa* L.), spinach (*Spinacea oleracea* L.) and lettuce (*Lactuca sativa* L.). In cereals, vegetative growth can be affected by Cu deficiency and symptoms shown, but in cases of marginal or hidden deficiency, male sterility resulting in grain yield losses of up to 20% or more, without the appearance of obvious symptoms is commonly found. This hidden deficiency, like the male sterility caused by B deficiency in wheat in South Asia, is of major economic importance because it is relatively difficult to detect before yields are affected.

In addition to reduced yields, Cu deficiency can also adversely affect the quality of crop products. These include shrivelled grains and reduced viability of seeds in cereals. In citrus, abnormal shaped fruits with a rough exterior, low juice content and poor flavour and in apples, small fruits of poor quality are found due to Cu deficiency. In sugar beet, juice purity is reduced due to elevated concentrations of nitrogenous compounds. In vegetables, small size, chlorotic leaves, apparent wilting and discolouration of edible portions tend to render them less marketable (Alloway and Tills, 1984).

An example of acute Cu deficiency, with characteristic symptoms, in a mature wheat crop on a Rendzina soil in north-western France is shown in Figs. 1.2 and 1.3 (in Colour Section).

In the foreground of Fig. 1.2, the Cu-deficient wheat plants are shorter, darker in colour and have a lower density of ears (spikes) per unit area than the blocks of

Fig. 1.2 View of a field trial with copper on wheat growing on a Rendzina soil in France showing the copper-treated area (taller and pale coloured) in the distance. The copper-deficient crop in the foreground shows a lower density of ear-bearing tillers and a darker colour due to melanism (From B.J. Alloway) (*See Colour Plates*)

Cu-treated crop in the distance. Figure 1.3 (Colour Section) shows ears of both the Cu-treated and the Cu-deficient wheat from the two areas shown in Fig. 1.2. The ears from the Cu-treated plants are larger and full of grains. In contrast, the ears from the deficient plants are smaller, with empty grain positions at each end due to the failure to set grain due to pollen sterility. They also show some dark pigmentation (melanism) which is characteristic of Cu deficiency in wheat on Rendzinas (organic-rich calcareous soils) (Shorrocks and Alloway, 1985).

Significant losses in grain yield of up to 20% without prior symptoms are recognized as an important feature of Cu deficiency in cereals (Graham and Nambiar, 1981). Pollen sterility and impaired carbohydrate metabolism (reduced starch formation) are two of the major causes of the yield reductions associated with hidden Cu deficiency in cereals on soils with marginally low concentrations of available Cu (Jewell et al., 1988).

The soils most often associated with Cu deficiency include sandy and highly leached soils (Arenosols, Ferralsols, Acrisols) with low total Cu contents, calcareous (Calcisols, especially Rendzinas) and other high pH soils, such as saline soils (Solonchaks) and soils with high contents of organic matter (Histosols, Podzols), where the Cu is relatively unavailable. Other factors which can cause or exacerbate Cu deficiency include high N and P applications leading to dilution of Cu in tissues, and relatively high concentrations of other micronutrients, including Zn, Fe and Mn (e.g., from the treatment of other deficiencies).

Fig. 1.3 Ears of wheat from the field experiment shown in Fig. 1.2. Normal ears from copper-sufficient plants on the left and partially filled ears showing some melanism from copper-deficient plants on the right (From B.J. Alloway) (*See Colour Plates*)

Copper deficiency occurs in many parts of Europe, due to the widespread occurrence of sandy, calcareous, eluviated and organic-rich soils in this region, There are also favourable growing conditions for cereals and a high level of intensive crop management in many areas. It is estimated that around 30% of arable soils in Scotland are Cu-deficient, with 25% deficient in Germany and Denmark and 20% in Finland (Sinclair and Edwards, Chap. 9). On the basis of soil analysis data, up to 40% of soils in Ireland and Poland are potentially Cu-deficient (Alloway, 2005). Copper deficiency is found in all states in Australia on calcareous and acid soils. The largest areas of Cu deficiency (millions of hectares) are in Western Australia, South Australia and western Victoria and generally coincide with those affected by Zn and Mn deficiency (Holloway et al., Chap. 3). Copper deficiency occurs on the tropical red soils (Ferralsols) in Brazil and is often associated with intensive cropping and associated pH increases due to liming (Fageria and Stone, Chap. 10). Copper deficiency is generally not considered to be a major problem in many parts of Asia and the Near East (Singh, Chap. 4; Zou et al., Chap. 5; Rashid and Ryan, Chap. 6).

1.2.3.1 Treatment of Copper Deficiency

The fertiliser compounds available for the treatment of Cu deficiency are shown in Table 1.6.

In Europe, cereal land is normally treated with between 2 t and 15 t Cu ha^{-1} as $CuSO_4$ applied to the soil at infrequent intervals of between 5 and 15 years. Copper oxychloride is often applied to soils at rates of 10 kg ha^{-1}. Foliar treatments include $3Cu(OH)_2.CuCl_2$ at 0.5–2.2 kg ha^{-1} or 100 g ha^{-1} of Cu EDTA applied to each crop (Sinclair and Edwards, Chap. 9). In Brazil, 1–2 kg Cu ha^{-1} either broadcast, or banded is used, or a 0.1–0.2% Cu solution of copper sulphate in 400 l water/ha as a foliar spray (Fageria and Stone, Chap. 10). In Australia, Cu is applied mixed with phosphatic fertilisers but there is an increasing trend to using liquid fertilisers for both macronutrients and micronutrients (Holloway et al., Chap. 3).

Table 1.6 Copper compounds used for treating copper deficiency in plants (Gilkes, 1981; Martens and Westerman, 1991)

Compound	Formula	Copper content (%)
Copper sulphate	$CuSO_4.5H_2O$	25
Bordeaux mixture	$CuSO_4.3Cu(OH)_2 + 3CaSO_4$	12–13
Basic copper sulphates	$CuSO_4.3Cu(OH)_2$[a]	13–53
Copper oxychloride	$3Cu(OH)_2.CuCl_2.4H_2O$	52
Cuprous oxide	Cu_2O	89
Cupric oxide	CuO	75
Copper EDTA chelate	Na_2EDTA	14
Copper HEDTA chelate	NaCuHEDTA	9
Copper lignosulphonate	–	5–8
Copper polyflavonoid	–	5–7

[a] General formula of basic copper sulphates.

1.2.4 Iron

Iron deficiency is mainly a problem on calcareous and other alkaline soils with pH values of greater than 6 or 7, in which Fe has a low availability. The availability of Fe can also be reduced by relatively high concentrations of P, NO_3-N, high organic matter contents, and root infections (Fageria and Stone, Chap. 10). In general, C_4 plants have a higher requirement for Fe than C_3 species (Marschner, 1995). Fruit trees, grape vines (*Vitis vinifera* and *Vitis labrusca*), cereals, beans (*Vicia* and *Phaseolus* spp.), potato (*Solanum tuberosum* L.), soya (*Glycine max* L.) and sorghum (*Sorghum bicolor* L.) all tend to be susceptible to Fe deficiency in high pH soils. Iron is most available in acid or waterlogged (gleyed) soils and toxicity can occur on these soils. This is a particular problem in flooded (paddy) rice soils where rice yields can be severely reduced by Fe toxicity.

On Mediterranean-type soils in the Middle East, Fe deficiency is the second most important micronutrient deficiency problem, after that of Zn, due to the high pH calcareous soils. Legumes, citrus tree species and deciduous fruits are more susceptible to Fe deficiency than cereals (Rashid and Ryan, Chap. 6).

In China, peanuts are highly susceptible to Fe deficiency when grown in monoculture on calcareous and alkaline soils. However, intercropping peanuts with maize improves the uptake of Fe by peanuts due to root secretions from the maize (Zou et al., Chap. 5).

In addition to soil properties affecting the availability of Fe, the widely used herbicide Glyphosate is known to induce Fe deficiency (and also other micronutrient deficiencies) in some crops growing on soil with residues of this chemical (Eker et al., 2006).

1.2.4.1 Treatment of Iron Deficiency

The fertiliser compounds available for the treatment of Fe deficiency are shown in Table 1.7.

Table 1.7 Iron compounds used for treating iron deficiency in plants (Martens and Westerman, 1991)

Compound	Formula	Iron content (%)
Ferrous sulphate (heptahydrate)	$FeSO_4.7H_2O$	19
Ferrous sulphate (monohydrate)	$FeSO_4.H_2O$	33
Ferrous ammonium sulphate	$(NH_4)_2SO_4.FeSO_4.6H_2O$	14
Iron HEDTA chelate	NaFeHEDTA	5–9
Iron EDDHA chelate	NaFeEDDHA	6
Iron DTPA chelate	NaFeDTPA	10
Iron lignosulphonate	–	5–8
Iron polyflavonoid	–	9–10
Iron methoxypropane	FeMPP	5

In the USA, the most Fe-deficiency sensitive crops are soya bean and high-value crops, such as citrus species, grape vines and peaches. These crops receive the major proportion of Fe fertilisers which are usually applied as foliar sprays (Brown, Chap. 11). On high pH soils in China, acid ferrous sulphate is used as a fertiliser on soils and for soaking soya bean seeds. In fruit trees, neither soil, nor foliar, applications of Fe compounds are very effective so alternative methods of treatment have been developed (Zou et al., Chap. 5). In Brazil, foliar applications of Fe salts are used (1–2% solution of $FeSO_4.7H_2O$) in 4001 of water ha^{-1}. Iron chelates, such as FeEDDHA and FeEDTA, can also be used, but they are more expensive (Fageria and Stone, Chap. 10).

1.2.5 Manganese

Manganese deficiency problems occur on soils with low total contents of Mn (heavily weathered tropical and sandy soils), on peaty soils, or organic-rich soils with a pH above 6, and on mineral soils with pH values of 6.5 or above, such as calcareous soils, or acid soils which have been heavily limed. In addition to the available Mn status of soils, temperature, soil moisture and light intensity can all affect the incidence and severity of Mn deficiency in crops (Moraghan and Mascagni, 1991). According to Marschner (1995), Mn deficiency symptoms include: interveinal or blotched chlorosis in mature and young leaf blades and interveinal necrosis in young leaf blades. Deficiency problems are worst when crops are developing in wet and cold conditions (i.e., worse in spring than later in the growing season). Manganese deficiency is widespread in northern Europe, with its generally cool and humid climate. In the United Kingdom, Mn is the most commonly encountered micronutrient deficiency in field crops. Although it is most severe on organic soils with a pH above 6 and on sandy soils, it can also occur on a wider range of soils in some years, depending on weather conditions and the crops grown. Cereals, sugar beet, potatoes, oilseed rape and peas are the field crops most commonly affected. Cereal crops on ploughed-up grassland are particularly prone to Mn deficiency (Sinclair and Edwards, Chap. 9)

Manganese is more mobile in imperfectly drained (gleyed) soils and so rice grown in paddy fields tends not to be affected by deficiency. With regard to light, Mn deficiency is more likely to occur under low light conditions. The availability of Mn is strongly influenced by reactions in the rhizosphere. Root exudates, including phytosiderophores (which also mobilise Fe and Zn), have the ability to render Mn^{2+} available for uptake into the roots.

Many crops are highly sensitive to Mn deficiency, including: apple (*Malus domestica* Borkh.), cherry (*Prunus avium* L.), raspberry (*Rubus* spp. L.), pea (*Pisum sativum* L.), bean (*Phaseolus Vulgaris* L.), sugar beet (*Beta vulgaris* L.) potatoes (*Solanum tuberosum* L.), soya bean (*Glycine max* Merr.), oat and wheat (Humphries et al., 2007). However, maize (*Zea mays* L.) and rye (*Secale cereale* L.) are considered to be relatively tolerant (Marschner, 1995).

In recent years it has become apparent that prolonged use of the herbicide Glyphosate, is causing increased incidence of deficiencies of Mn and other micronutrients, such as Fe in some crops, including soya, sunflower and citrus, compared with controls grown under organic farming conditions on adjacent land. Research by Neumann et al. (2006) has shown that foliar-applied glyphosate to target (weed) plants can be released into the rhizosphere after translocation through the plant and inhibit the acquisition of micronutrients such as Mn, Zn and B by non-target plants. Glyphosate is widely used around the world and this potential deficiency problem is likely to be of increasing importance with the development of transgenic glyphosate-resistant crops (Brown, Chap. 11). The problem can be overcome by increased use of foliar applications of Mn and any other micronutrient found to be in short supply. Foliar applications are necessary because of the inhibition of root uptake caused by glyphosate. An interesting variation on the problem of glyphosate and Mn nutrition is that the efficacy of glyphosate used on soya beans in the USA can be reduced when it is tank mixed with certain types of Mn fertilisers for foliar application. However, it was found that Mn-EDTA did not interact with the glyphosate (Bernards et al., 2002).

The incidence of Mn deficiency in India is relatively low, with only 4% of advisory soil samples indicated as having low available Mn contents. However, it is becoming an increasing problem in rice–wheat cropping systems on sandy and alkaline soils (Singh, Chap. 4). In some countries, soil testing is not considered to be reliable for predicting Mn deficiency (Sinclair and Edwards, Chap. 9).

1.2.5.1 Treatment of Manganese Deficiency

Fertiliser compounds used for the treatment of Mn deficiency are shown in Table 1.8.

In most parts of the world, $MnSO_4$ is the most widely used Mn fertiliser due to its low cost, high solubility and easy availability. In Brazil, soil applications of 5–50 kg Mn ha^{-1} are used with larger amounts applied by broadcasting and smaller amounts when banding. Foliar applications of 0.1–0.2% $MnSO_4.H_2O$ in 4001 of water/ha are normally used but sometimes several applications may be required (Fageria and Stone, Chap. 10). In India, foliar sprays have generally been found to be more efficient in correcting Mn deficiency in wheat, berseem clover (*Trifolium*

Table 1.8 Manganese compounds used for treating manganese deficiency in plants (Martens and Westerman, 1991; Walter, 1988)

Compound	Formula	Manganese content (%)
Manganese sulphate	$MnSO_4.n\ H_2O$[a]	20–36.4[a]
Manganese oxide	MnO	41–68
Manganese EDTA chelate	$Na_2MnEDTA$	5–12
Manganese lignosulphonate	–	5
Manganese polyflavonoid	–	5–7
Manganese frits	Fritted glass	10–35

[a] Mn content depends on the degree of hydration of $MnSO_4$.

alexandrinum L), oat, sunflower, green gram (*Phaseolus aureus* Roxb.) and other crops (Singh, Chap. 4). In China, Mn deficiencies are corrected either by foliar application of Mn, or by banding Mn with an acid starter fertiliser. With wheat, it has been found that the most effective fertiliser regime is seed treatment with Mn, followed by foliar spraying (Zou et al., Chap. 5). Manganese deficiency in UK crops is usually treated by foliar applications of $MnSO_4$ (5 kg $MnSO_4$ ha^{-1}) but Mn-EDTA and other formulations are also widely used. Although Mn-EDTA is generally more efficient, on the basis of Mn applied, and more convenient to use, it is much more expensive than $MnSO_4$ (Sinclair and Edwards, Chap. 9). In the USA, Mn-EDTA is being used increasingly on crops treated with glyphosate herbicide because $MnSO_4$ and some of the other forms of Mn have been found to interact with this herbicide in tank mixes, rendering it less effective (Brown, Chap. 11).

1.2.6 Molybdenum

Unlike the other plant micronutrients, Mo is most readily taken up by plants in soils with a pH above 7 and is relatively unavailable in acid soils. Molybdenum deficiencies are most likely to occur on acid and severely leached soils and are mainly a problem in brassicas, legumes, such as peanuts, subterranean clover and soya beans, but other crops, including wheat and sunflowers can also be affected.

In Australia, Mo deficiency is the second most ubiquitous micronutrient deficiency problem, after zinc, affecting large areas of cropland with acid soils (Holloway et al., Chap. 3). In China too, Mo deficiency has become an important factor limiting yields in winter wheat and soya beans. Molybdenum-efficient cultivars of both these species have been identified, and growing these on deficient soils would help to reduce yield loss due to deficiency (Zou et al., Chap. 5). On the predominantly acid soils in Africa, Mo deficiency is a widespread problem, particularly in maize, sunflower, groundnuts, dry beans and peas (van der Waals and Laker, Chap. 8). In India, Mo deficiency is not very common but occurs in rice, wheat, soya bean and other legumes on Fe oxide-rich soils (Singh, Chap. 4). In the USA, deficiencies of Mo occur on acid sandy soils of the Atlantic, gulf and Pacific coasts. Legumes, cruciferous crops, grasses and several vegetable crops have responded to Mo fertilisation (Martens and Westerman, 1991).

1.2.6.1 Treatment of Molybdenum Deficiency

Fertiliser compounds used for the treatment of Mo deficiency are shown in Table 1.9.

Although deficiencies in some acid soils can sometimes be corrected by liming, deficiencies in strongly leached soils, with low total and available Mo contents, need to be fertilised with suitable compounds, usually either ammonium or Na-molybdate.

Table 1.9 Molybdenum compounds used treating molybdenum deficiency in plants (Martens and Westerman, 1991)

Compound	Formula	Molybdenum content (%)
Ammonium molybdate	$(NH_4)_6MoO_{22}.4H_2O$	54
Sodium molybdate	$NaMoO_4.2H_2O$	39
Molybdenum trioxide	MoO_3	66
Molybdic acid	$H_2MoO_4.H_2O$	53
Molybdenum frits	Fritted glass	2–3

In Australia, Mo is added to superphosphate fertilisers in many areas and is also applied with Cu and Zn fertilisers on acid, sandy and gravely soils in the south-west of Western Australia (Holloway et al., Chap. 3). In India, soil application of foliar sprays containing 0.05–1% Na molybdate are applied three times to green gram. Basal applications of Mo are applied to peanuts on calcareous soils and the seeds of soya beans and peanuts are also treated with an Mo formulation (Singh, Chap. 4).

1.2.7 Nickel

The first reported evidence of a response to Ni in field crops (potatoes, wheat and beans) was in 1945, but its essentiality was not conclusively demonstrated until 1987 (Brown, 2007a; Brown et al., 1987). A requirement for the use of nickel fertilisers has been established for perennial crops in the south-east of the USA. It has been found that Pecan trees could benefit from the application of Ni because it is effective in controlling pecan scab disease which affects yields. However, there have been few reports of the occurrence of acute Ni deficiency problems in field crops but it is likely that undiscovered (hidden) deficiencies may be important in some areas (Brown, Chap. 11). In contrast to deficiencies, there is generally more concern about the development of Ni toxicity in crops on soils contaminated with Ni from sources such as atmospheric deposition and the recycling of biosolids (sewage sludge).

Like the other cationic elements, Ni will be less available under alkaline conditions and most available in acid soils. Symptoms of Ni deficiency in graminaceous plants include chlorosis, similar to Fe deficiency and patchy necrosis in the youngest leaves. With Ni deficiency there is also a marked enhancement in senescence and reduced tissue Fe concentrations (Brown, 2007a).

1.2.7.1 Treatment of Nickel Deficiency

There are few fertiliser compounds used for the treatment of Ni deficiency owing to the general lack of information about the occurrence of the problem. However, Ni-sulphate ($NiSO_4.7H_2O$, 21% Ni) and other nickel compounds have been used.

Organic complexes containing Ni have also been used and many compound fertilisers and pesticides contain significant concentrations of Ni which may make them effective sources of the element. Biosolids (sewage sludges) can also contain appreciable concentrations of Ni, but must conform to the statutory limits for the state, or country concerned (e.g., $<420\,mg$ Ni kg^{-1} dry matter for the USA) (USEPA, 1993). However, biosolids contain elevated concentrations of whole suites of micronutrient and non-essential elements (e.g., Cd) and also organic pollutants. Therefore their use as a source of micronutrients has to be carefully planned and based on a broad-spectrum analysis of the biosolid product from the local sewage treatment plant.

1.2.8 Zinc

Zinc deficiency is by far the most ubiquitous micronutrient deficiency problem in the world as a whole. All crops can be affected by Zn deficiency, but maize (corn), beans, cotton, linseed and citrus fruits are the most sensitive. Although shown to be relatively tolerant to Zn deficiency, yields of rice and wheat, the world's two major staple food crops, are restricted by Zn deficiency over millions of hectares worldwide. It is estimated that up to 50% of the rice grown under lowland (flooded) conditions (paddy rice) may be affected by Zn deficiency (Scharpenseel et al., 1983). In addition to optimising crop yields to produce adequate amounts of food crops, the Zn contents of the crop products, especially cereal grains and beans are of major importance in human nutrition (Hotz and Brown, 2004). There is increasing interest in fortifying crop products with zinc and other micronutrients often in short supply for humans such as Fe, as discussed by Graham (Chap. 2) and Welch (Chap. 12).

Many of the soil and crop management changes involved in the intensification of arable farming increase the risk of Zn deficiency occurring on soils of marginal to low available Zn status. Apart from growing different plant varieties, one of the most common changes with intensification is the application of larger amounts of N, P, K, and S fertilisers. It is widely recognised that high levels of available P in soils of low Zn status can cause Zn deficiency (Loneragan and Webb, 1993).

The soil conditions which are most commonly found to be associated with Zn deficiency in crops include:

- Low total Zn contents (such as in highly weathered and leached tropical soils with low pH, and sandy soils with low contents of organic matter)
- Neutral or alkaline soil pH (including limed soils)
- High salt concentrations (saline soils)
- High calcium carbonate content (calcareous soils with high pH)
- Peat and muck (organic soils)
- High available P status (closely linked with intensive production)
- Prolonged period of waterlogging or flooding (paddy rice soils)
- High magnesium and/or bicarbonate concentrations (in soils and irrigation water)

- Foliar and soil fertilisation with Cu
  Low inputs of livestock manures
  (Alloway, 2004)

For rice grown in flooded (paddy) soils, the possible causes of Zn deficiency can be summarised as:

- Low total Zn content in soil
- Growing highly susceptible (Zn-inefficient) rice varieties (e.g., IR 26)
- High pH (≥7 under anaerobic conditions)
- High bicarbonate (HCO_3^-) concentrations in soils and irrigation water
- Depressed Zn uptake due to increased availability of other micronutrients and P after flooding
- Formation of organic Zn complexes in soils with a high pH and high organic matter contents (e.g., manures/straw)
- Zinc sulphide precipitation when pH decreases in alkaline soil after flooding
- Excessive liming (elevated pH and adsorption of Zn on $CaCO_3$ and $MgCO_3$)
  Wide Ca:Mg ratios (<1.0) (often due to excess Mg from ultrabasic soil parent material)
  (Dobermann and Fairhurst, 2000)

Soil testing in both India and China has shown that 48% and 51% of soils, respectively, are potentially deficient in available Zn. In India, cereals, millet, oilseed rape, fodder crops, vegetables, fruit trees and plantation crops are most affected (Singh, Chap. 4). In China, maize, rice, lentil, pea, cotton, sorghum, apple and peach trees are amongst the crops most affected (Zou et al., Chap. 5). In Australia, Zn deficiency affects crops on sandy and calcareous soils and there are millions of hectares of Zn-deficient land in Western Australia and South Australia. The problem is increasing due to more intensive methods of production and the change from comparatively Zn-rich superphosphate to more pure forms of P fertiliser (Holloway et al., Chap. 3). In South America, Zn deficiency is widespread mainly due to the low total Zn contents of the strongly weathered and leached tropical red soils (Ferralsols). The low Zn status of many of the soils is further exacerbated where the soils are limed and heavily fertilised with P for growing high yielding cultivars of cereals and other crops (Fageria and Stone, Chap. 10).

1.2.8.1 Treatment of Zinc Deficiency

Fertiliser compounds used for the treatment of Zn deficiency are shown in Table 1.10.

The history of the use of Zn fertilisers goes back to 1934 when $ZnSO_4$ was used to treat "white bud" (leaf chlorosis) in maize in Florida. It is generally recognised that, at least in the short-term, the more highly water-soluble Zn fertiliser compounds, such as $ZnSO_4$ (98% soluble), Zn lignosulphonate (91% soluble) and ZnEDTA (100% soluble) are more effective in correcting deficiencies than less soluble compounds, such as ZnO.

Although some traditional fertilisers, such as single superphosphate, are a valuable source of Zn (<600 mg Zn kg^{-1}), the trend towards high analysis fertilisers has necessitated the use of either Zn-fortified fertilisers, or "straight" Zn compounds

Table 1.10 Zinc compounds used for treating zinc deficiency in plants (Martens and Westerman, 1991)

Compound	Formula	Zinc content (%)
Zinc sulphate (monohydrate)	$ZnSO_4.H_2O$	36–37
Zinc sulphate (heptahydrate)	$ZnSO_4.7H_2O$	22–23
Zinc oxysulphate	$xZnSO_4.xZnO$	40–55
Basic zinc sulphate	$ZnSO_4.4Zn(OH)_2$	55
Zinc oxide	ZnO	50–80
Zinc carbonate	$ZnCO_3$	50–56
Zinc nitrate	$Zn(NO_3)_2.3H_2O$	23
Ammoniated zinc sulphate solution	$Zn(NH_3)_4SO_4$	10
Disodium zinc EDTA	$Na_2ZnEDTA$	8–14
Sodium zinc HEDTA	NaZnHEDTA	9–13
Zinc polyflavonoid	–	5–10
Zinc lignosulphonate	–	5–8

being applied to the seedbed directly (Holloway et al., Chap. 3; Cakmak, Chap. 7). Foliar applications can be of $ZnSO_{4,}$ but this can carry a high risk of scorch unless a neutraliser, such as calcium hydroxide is added, or the spray solution is made up in hard water. Chelated forms of Zn are becoming more commonly used for foliar applications and have the advantage of being compatible with many herbicide and fungicide formulations in spray tank mixes, but they are more expensive than inorganic compounds.

In China, $ZnSO_4$ and ZnO are the most widely used fertilisers but $ZnCl_2$ and chelates are also used. The maize crop receives the largest proportion of Zn fertilisation, followed by rice, but lentil, pea, sorghum, cotton, apple and peach trees are also treated widely (Zou et al., Chap. 5). Soil applications of 9–22 kg Zn ha^{-1} on calcareous soils in South Australia have been found to have a beneficial residual effect for about 10 years. More recent practices have been to spray zinc sulphate onto seedbeds at a rate of 1 kg Zn ha^{-1} and cultivate it into the topsoil or as a foliar spray mixed with a compatible cereal fungicide at a rate of 0.2 kg Zn ha^{-1}. The inclusion of urea in foliar sprays of $ZnSO_4$ increases leaf penetration and addition of a sticker can reduce wash off (Holloway et al., Chap. 3).

In South America, application rates of $ZnSO_4.7H_2O$ are 30–50 kg ha^{-1} as a top dressing on both upland and lowland rice (Fageria and Stone, Chap. 10). In India, application rates Zn fertilisers (usually of $ZnSO_4.7H_2O$) are typically 11 kg Zn ha^{-1} for wheat and rice, 5.5 kg Zn ha^{-1} for maize, soybean and sugarcane and 2.5 kg Zn ha^{-1} for peanuts, soya bean and other selected crops (Singh, Chap. 4).

1.3 Hidden Micronutrient Deficiencies in Crops

Hidden deficiencies of micronutrients (also called subclinical, latent, or "symptomless" deficiencies) are often more widely occurring and economically important than severe forms of deficiencies because they are difficult to detect. Nevertheless, subtle differences in colour, height and time of maturity can often be seen in field experiments, on marginally Zn-deficient soils, where control and micronutrient-treated plots are located side by side. In the case of hidden Cu deficiency, numerous second growth tillers can often be found in cereal crops. The farmer is usually aware that crops on some of his land have relatively poor yields, but there are often other possible explanations for this apart from a marginal micronutrient deficiency stress. These can include drought, soil structural problems, herbicide damage, disease and shortage of macronutrients. The same soil and plant causal factors are responsible the onset of both hidden and acute deficiency but, usually, the magnitude of the factor is smaller and the effect more marginal in hidden deficiencies. In most cases, it is the micronutrient-inefficient genotypes which are affected by hidden deficiencies.

Examples of hidden Cu deficiency, where yield responses were obtained with Cu fertilisers in crops not showing obvious symptoms, include:

1. In 20 field experiments with cereals on sandy soils in North East Scotland, Reith (1968) found distinct deficiency symptoms ("white tip") in only 3 of the 18 trials which gave significant positive responses to Cu treatment. The mean yield response was 20% over all the trials. Some untreated control plants showed numerous second growth tillers in the crops and in the stubble after harvest.
2. Experiments by the Agricultural Development and Advisory Service (ADAS) in southern England on shallow chalk soils (Rendzinas/Rendic Leptosols) showed significant increases in yield of around 4% with foliar applications of copper on controls yielding 6.96 t ha^{-1} without any symptoms being apparent (Sinclair and Withers, 1995).
3. An increase of 22.4% (giving a yield of 3.21 t ha^{-1}) was obtained with foliar-applied copper hydroxide before the end of tillering in spring barley growing on a brown sand soil in eastern England. The yield increase was due to a significant increase in the number of grains per ear. The untreated control had received a non-metallic fungicide application (Alloway et al., 1985).
4. Foliar-applied $CuSO_4$ gave a grain yield response of 15.6% (6.68 t ha^{-1} increased to 7.72 t ha^{-1}) in winter wheat growing on an organic-rich Rendzina. The untreated control had received a non-metallic fungicide application. Soil tests indicated a marginal deficiency, but no symptoms of deficiency were observed in the untreated crop (Tills, 1981).
5. Sugar beet (a crop with medium susceptibility to Cu deficiency), growing on a brown sand soil developed on drift over Chalk, gave a significantly increased root yield of 18% and improved juice purity when 12.5 kg Cu ha^{-1} was applied to the seedbed (as $CuSO_4$). No visible symptoms of Cu deficiency were shown by the untreated sugar beet plants (Tills and Alloway, 1981).
6. "Symptom-less" Cu deficiency was reported by Vetter et al. (1985) in 21 field trials with cereals growing on sandy soils, loams developed on loess and on peat soils in the Hanover and Weser-Ems regions of northern Germany. Mean yield responses of up to 30% were obtained with Cu fertilisers, especially when N fertilizers were used and P levels in the soils were optimal.

In parts of India, Nepal and Bangladesh, B deficiency in wheat mainly affects pollen formation and pollination and is hidden during the early stages of growth (Rerkasem and Jamjod, 2004). The yield response of grapevines, on low-B soils in Hungary, to B fertilisation is also indicative of a hidden deficiency since the applied B has the effect of reducing flower-shedding and thereby increasing the amount of fruit set (Györi and Palkovics, 1983).

In addition to physiological responses to micronutrient treatments bringing about increased yields, indirect effects of micronutrients, such as reducing susceptibility of crops to fungal infections, can also help to give increased yields and product quality. This includes the effects of Zn and of Cl on root diseases in wheat (Grewal et al., 1996; Xu et al., 2000). Apart from these specific effects, healthy plants are generally less likely to be infected than those under physiological stress due to micronutrient deficiencies. It is important to note that foliar applications of many micronutrient compounds can have fungicidal, as well as a nutritional, effects. In field experiments to investigate yield responses to micronutrient treatments, it is essential to apply a non-metallic fungicide to control plots in order to rule out this confusing factor. This is not necessary in experiments where fertiliser has been applied to the seedbed.

Finally, it is important to recognize that the absence of symptoms of nutrient deficiency does not necessarily imply optimum nutrition. Unsatisfactory crop performance could still be due to a hidden micronutrient deficiency and these can progress to acute deficiencies with changes in cultivars grown and crop management. The only reliable diagnosis for a hidden deficiency is by soil/plant analysis, or fertiliser responses.

1.4 Worldwide Occurrence of Micronutrient Deficiencies

Details of the occurrence of micronutrient deficiency problems in crops in many different countries or continents are given in Chaps. 2–11 of this volume. However, the amount of information and data available for different countries varies considerably, as do some of the methods used in analytical surveys of soils and crops. However, an analytical survey of the macro- and micronutrient status of arable soils in 30 countries around the world was conducted for the FAO by Sillanpää (1982). The data from this survey, and a subsequent follow-up study, provide a very useful reference with which data from individual countries can be compared. This FAO study was carried out between 1974 and 1982 and comprised a total of 3,538 soil samples collected from representative sites in all 30 participating countries (shown in Table 1.11, except for Ecuador). After collection, the soil samples were sent to The Institute of Soil Science at the Agricultural Research Centre in Jokoinen, Finland where they were prepared and analysed. A cultivar of spring wheat (*Triticum aestivum* cv. “Apu”) was grown on samples of each soil under controlled conditions (in a greenhouse at the Institute) to act as an “indicator” of the plant availability of the nutrients. Unfortunately, there was insufficient soil to grow this wheat on the soil samples from Ecuador.

Table 1.11 Percentage distribution of the soil × crop concentration products for six micronutrients in Zones I and II (0–5% and 5–10%, respectively) for wheat grown on soil samples from 29 countries in the study by Sillanpää (1982)

	Element Zone	B		Cu		Fe		Mn		Mo		Zn	
Country	No. of samples	I	II	I	II	I	II	I	II	I	II	I	II
Belgium	36	0	0	0	0	0	0	3	0	0	0	0	0
Finland	90	3	1	6	13	0	0	1	1	0	1	0	0
Hungary	201	0	1	0	0	0	0	4	4	1	3	0	0
Italy	170	0	0	0	0	1	1	12	9	0	2	3	4
Malta	25	0	0	0	0	60	8	80	16	0	0	0	0
New Zealand	35	0	0	17	11	0	0	0	0	9	29	0	0
Argentina	208	0	0	4	19	0	0	0	0	0	0	0	0
Brazil	58	0	0	0	0	0	2	2	0	45	26	0	0
Mexico	242	0	2	2	3	0	2	6	4	1	1	0	0
Peru	68	1	3	1	1	0	3	1	4	1	3	0	0
India	258	12	8	0	0	3	9	14	11	0	2	11	7
Korea	90	3	13	1	7	2	0	8	6	0	2	11	7
Nepal	35	46	23	0	3	0	0	0	9	20	14	3	3
Pakistan	237	2	1	0	0	1	8	11	15	0	0	8	12
Philippines	194	30	25	0	1	0	0	1	1	3	9	0	0
Sri Lanka	18	0	11	0	0	0	11	0	0	0	6	0	0
Thailand	150	10	13	3	1	4	3	0	0	1	2	1	2
Egypt	198	0	0	0	0	0	1	8	13	0	0	0	2
Iraq	150	3	3	0	0	2	7	2	5	0	1	34	23
Lebanon	16	0	0	0	0	13	0	13	0	0	0	6	6
Syria	38	3	0	0	3	8	13	13	11	0	0	5	11
Turkey	298	1	1	0	0	14	9	2	5	0	2	17	18
Ethiopia	125	4	6	21	6	0	1	0	0	0	4	0	1
Ghana	93	0	0	23	24	1	0	0	0	16	22	0	2
Malawi	97	9	14	7	6	0	4	0	0	7	24	1	1
Nigeria	153	11	14	12	20	5	12	1	3	20	12	0	1
S. Leone	48	0	2	68	21	0	4	0	2	81	10	0	0
Tanzania	163	0	1	14	9	6	7	0	0	6	7	3	2
Zambia	44	2	11	36	16	16	11	0	0	50	9	0	2

The soil and wheat samples were analysed for a range of macro- and micronutrients and six key soil properties were measured (pH, organic matter and $CaCO_3$ contents, electrical conductivity, texture and bulk density). From the analytical results, the products of soil concentration × plant concentration were calculated for each nutrient (from here on called “concentration products”). The lowest 5% of these concentration product values were allocated to Zone I and the next lowest 5% to Zone II. The middle 80% of the concentration products were allocated to Zone III, the top 90–95% of concentration products to Zone IV and the uppermost 95–100% of the concentration product values were put in Zone V. This implies that concentration product values in Zones I and II represent low available concentrations of nutrient elements and those in Zones IV and V high available concentrations. Therefore those soil samples with a high probability of severe deficiencies, would be in Zone I and less severe, possibly hidden deficiencies in Zone II. The soils with the greatest risk of crops accumulating high, possibly even toxic, concentrations of some of the nutrient elements monitored would be found in Zone V.

The percentage distribution of concentration products for the soil and wheat sample analyses for six micronutrients in the two lowest zones (I and II) are shown in Table 1.11. From this data, several generalizations can be made regarding the countries with the higher percentages of soils having potentially deficient concentrations of available micronutrients. Owing to insufficient soil in the samples from Ecuador to grow wheat in pots, no concentration products were produced for this country and so the data in Table 1.11 is only for 29 countries.

1.4.1 Countries in the Sillanpää (1982) Study Shown to Have Significant Numbers of Potentially Micronutrient-deficient Soils

1.4.1.1 Boron

From Table 1.11 it can be seen that B deficiencies are most likely to occur in the Far East/South Asian countries included in the survey, especially India, Nepal, Philippines, and Thailand. Significant percentages of low concentration products for B were also found in soil samples from Korea, Nigeria, Malawi, Korea, Zambia and Sri Lanka with smaller numbers of potentially B-deficient soils in Finland, Peru, Pakistan, Iraq, Syria, Turkey and Ethiopia.

1.4.1.2 Copper

All of the African countries in the study had high, or relatively high, percentages of potentially Cu-deficient soils (in Zones I and II). These soils were predominantly acid and some had relatively large organic matter contents. Countries in other regions with significant percentages of potentially Cu-deficient soils include: Finland, New Zealand, Argentina and Korea. It is interesting to note that, in follow-up field trials in some of the same African countries, responses to Cu were not as high as expected in the light of these low concentration products (Sillanpää, 1990).

1.4.1.3 Iron

Many of the countries with high percentages of Fe concentration products in Zones I and II have calcareous and/or high pH soils and these are: Malta, Lebanon, Syria, Turkey and Iraq. Potentially deficient Fe values were also found in Zambia, Nigeria, Tanzania, India, Sri Lanka, Pakistan and Thailand. However, the African countries differ from the others in having predominantly acid soils which render Fe more available.

1.4.1.4 Manganese

Some of the countries with relatively high percentages of Mn concentration products in Zones I and II were the same as those shown to have potentially Fe-deficient soils, especially Malta and Syria, and the high soil pH is one of the main causes of both low available Mn and Fe. However, higher percentages of potentially Mn-deficient soils were found in India, Egypt, Pakistan, Italy and Korea than were found with Fe.

1.4.1.5 Molybdenum

Molybdenum deficiency is usually associated with acid soils and the countries with the highest percentages of potentially Mo-deficient soils are Sierra Leone, Brazil, Zambia, New Zealand, Ghana, Nepal and Malawi, which all have high percentages of acid soils.

1.4.1.6 Zinc

Zinc is indicated as being most deficient in Iraq, Turkey, Pakistan, India, Korea, Syria and Italy and, with the exception of Italy, these countries all had generally high pH soils. It is interesting to note that follow-up field trials in a second project for FAO (Sillanpää, 1990) in some of the countries included in this study confirmed that Zn deficiency was the most ubiquitous micronutrient problem of all. As shown in Table 1.12, 49% of the 190 field trials in 15 counties showed a response to applications of Zn and, of these, half were "latent" or hidden deficiencies without obvious symptoms.

The data of Sillanpää (1982) only relate to 29 countries which are probably not fully representative of the continents in which they are located. Nevertheless, given

Table 1.12 Summary of the occurrence of acute and latent micronutrient deficiencies in 190 field trials in 15 different countries[a] (Sillanpää, 1990)

Deficiencies	Micronutrients					
	B	Cu	Fe	Mn	Mo	Zn
% Acute	10	4	–	1	3	25
% Latent	21	10	3	9	12	24
Total %	31	14	3	10	15	49

[a]Countries included Ethiopia, Finland, Iraq, Malawi, Mexico, Nepal, Pakistan, Philippines, Sierra Leone, Sri Lanka, Tanzania, Thailand, Turkey, Zaire, Zambia

the logistical problems of carrying out such a large study, this project and its follow-up field experiments in 15 countries is a vitally important source of information on the soil fertility of a large part of the world and it complements the more intensive national surveys carried out in countries such as China (Chap. 5), India (Chap. 4) and various European countries (Chap. 9).

In 1990, Sillanpää reported the results for a series of 190 field trials conducted in 15 countries which, with the exception of Zaire, were surveyed in his earlier 1982 study of soil and plant concentrations of micronutrients. A summary of his results is shown in Table 1.12.

From Table 1.12, it can be seen that the percentage of field experimental sites where deficiencies of the micronutrients were significant, decreased in the order: Zn > B > Mo > Cu > Mn > Fe. Hidden (or "latent") deficiencies of micronutrients were more widespread than acute forms for all the elements except Zn. This helps to confirm the international importance of hidden micronutrient deficiencies as discussed in Sect. 1.3 above.

All of the 18 field experiments conducted in Iraq showed some degree of Zn deficiency, which confirms the predictions from the concentration products derived from the soil and wheat analysis by Sillanpää (1982). In Turkey, 75% of the 21 field trials showed some degree of Zn deficiency (see Cakmak, Chap. 7, for details Zn deficiency problems in Central Anatolia, Turkey).

Either acute or latent Zn deficiencies were found in all of the 15 field experiments in Thailand. Copper was also deficient at many sites but the response of the maize test crop to Cu was not very marked. Maize is only moderately sensitive to Cu deficiency, and so its significance may possibly have been underestimated. However, maize is highly sensitive to Zn deficiency.

In the Philippines, almost half of the 15 trials showed some degree of Zn deficiency. In the five trials conducted in Tanzania, shortages of Cu and/or B were the most common micronutrient deficiency problems. Sri Lanka (10 trials) had relatively few acute micronutrient deficiency problems, but at most sites there were latent deficiencies of B or Zn and occasional latent deficiencies of Cu, Mn or Mo. A majority of the 18 field trials in Nepal showed indications of B and Zn deficiencies. Rerkasem and Jamjod (2004) have discussed the widespread B deficiency in wheat in Nepal and adjacent countries. In Finland, indications of both deficiencies and excesses of B, Cu and Mn were found. The excesses were probably due to the placement of micronutrient fertilisers near to the seed.

The order of occurrence of deficiencies shown in Table 1.12 is Zn (49%) » B (24%) > Mo (15%) ≈ Cu (14%) > Mn (10%) » Fe (3%). This cannot be extrapolated to the whole world because only a relatively small number of countries were involved in the field experiment study (although they had been selected from the earlier survey involving more countries). The countries involved, with the exception of Finland, were all developing nations in tropical or semi-arid regions and therefore not truly representative of the full range of crop production systems around the world. Nevertheless, these data do provide a very important indication of the relative importance of the different deficiency problems in the countries included in the study and many others like them. Many of the more technologically developed countries around the world have more humid, temperate conditions and markedly different soils to those found in the majority of countries involved in this study. In general, crop production techniques in the more developed parts of the world are more intensive and the combination of different soils, crops and farming practices has resulted in individual micronutrient deficiency problems differing locally in importance from the order given in Table 1.12. For example, Zn deficiency is not so important in Europe as in many other parts of the world, but Cu deficiency occurs to a greater extent in many parts of Europe (Sinclair and Edwards, Chap. 9), Australia (Holloway et al., Chap. 3) and some regions in the USA (Brown, Chap. 11) and Canada than was found in the Sillanpää (1992) study. On the more intensively managed farms in the technologically developed countries, both acute and hidden, deficiencies are more likely to have been recognised or detected and treated, so the micronutrient status of many soils is likely to be higher.

These two related studies by Sillanpää (1982, 1990) are particularly useful because they involved standardised sampling and analytical procedures for all of the countries involved and therefore allow comparisons to be made. There are several other valuable sources of information on the percentages of agricultural soils in different countries found to be potentially deficient in micronutrients and these are reported in the chapters on India (Singh, Chap. 4), China (Zou et al., Chap. 5) and Europe (Sinclair and Edwards, Chap. 9).

1.5 Soil Types Commonly Associated with Micronutrient Deficiencies

The available concentrations of micronutrients in soils are determined by several factors, which include:

- Geochemical composition (total micronutrient contents) of the soil parent material
- Pedogenic soil type
- Inputs of trace elements from anthropogenic sources (e.g., atmospheric deposition, pesticides, manures, fertilizers)
- Adsorptive properties of the soil for retaining elements in available/unavailable forms (pH, redox status, organic matter content, calcium carbonate content and salinity)
- Available concentrations of macronutrients and other micronutrients

Table 1.13 Typical total concentrations of micronutrients in soils of different types (mg kg^{-1} DW) (Kabata-Pendias, 2001)

Element	Podzols (sandy)		Cambisols (silty/loamy)		Rendzinas (calcareous)		Histosols (organic)		Chernozems etc. (humus-rich, semi-arid)	
	Range	*Av.*	*Range*	*Av.*	*Range*	*Av.*	*Range*	*Av.*	*Range*	*Av.*
B	<0.1–134	(22)	<1–128	(40)	1–210	(40)	4–100	(25)	11–92	(45)
Cu	1–70	(13)	4–100	(23)	6.8–70	(23)	1–113	(16)	6.5–140	(24)
Mn	7–2000	(270)	45–9200	(525)	50–7750	(445)	7–2200	(465)	100–3907	(480)
Mo	0.17–3.7	(1.3)	0.1–7.2	(2.8)	0.3–7.35	(1.5)	0.3–3.2	(1.5)	0.4–6.9	(2)
Ni	1–110	(13)	3–110	(26)	2–245	(34)	0.2–119	(12)	6–61	(25)
Zn	3.5–220	(45)	9–362	(60)	10–570	(100)	5–250	(50)	20–770	(65)

Typical ranges and average contents of most micronutrients in different types of soils are given in Table 1.13 (Kabata-Pendias, 2001). These show wide ranges in concentrations of most elements in the different soil types, which are largely due to differences in the geological parent material that the soils are derived from. Total contents do not provide an indication of the available concentrations apart from the fact that when the total concentration is low there is a higher chance of sorptive mechanisms holding the elements in unavailable forms. In Table 1.13, the sandy Podzol soils are shown to contain the lowest average total contents of all elements and the Cambisols, with higher clay and silt contents, contain the highest average contents of Mn and Mo. Rendzinas contain the highest average Ni and Zn contents. However, cationic forms of metals tend to have a relatively low availability in these shallow, organic-rich calcareous soils. Likewise, Cu and Mn will tend to have a low availability in Histosols due to binding by organic matter and also in Chernozems, which also tend to have higher pH values than Histosols.

Sometimes, there appear to be no clear links between the incidence of certain deficiencies and soil type, as in the case of low Cu soils in China (Zou et al., Chap. 5). This is likely to be due to variations in the geochemical composition of the soil parent material.

1.5.1 Effects of Soil Parent Material and Pedological Soil Type on the Availability of Micronutrients

The following generalizations can be made with regard to the links between soil parent materials and the geochemical composition and adsorptive properties of the soils derived from them. The equivalent soil groups in the two main international classification systems, the FAO-UNESCO/World Resources Base (ISSS, 1998 a,b) and the USDA Soil Taxonomy (Soil Survey Staff, 1999), are given in Appendix 2.

1.5.1.1 Sandy Soils

Sandy soils developed on sandstones or sandy drift deposits, tend to be have low concentrations of all micronutrients (B, Cl, Cu, Fe, Mn, Mo, Ni, Zn) and can often show multiple micronutrient deficiencies (as shown in Table 1.13). The main world soil types (FAO–UNESCO/World Reference Base classification) comprising sandy soils are Arenosols, Leptosols, Regosols, Podzols and Ferralsols.

1.5.1.2 Tropical Soils

Soils formed on heavily weathered parent materials, such as tropical forest soils will tend to be highly acid and have low available concentrations of almost all micronutrients. However, the low pH favours the availability of cationic forms of elements, especially Fe, but not anionic forms, such as molybdates. Liming of these acid soils will reduce the availability of cationic micronutrient elements and often lead to deficiencies of B, Cu, Mn, and Zn. The natural vegetation of these soils is usually tropical rain forest, or scrub in less humid areas. When the vegetation is cleared to create arable land, after the initial flush of micronutrients present in the ash of the burnt vegetation, both macro and micronutrients often become deficient. The requirement for N, P, K and S is widely recognized but if any micronutrients are deficient, crop performance will be suboptimal. This problem is widely encountered in Brazil and other countries with rain forest (see Fageria and Stone, Chap. 10). The main soil types involved, include: Ferralsols, Acrisols, Lixisols (previously called Red–Yellow Podzols), Nitisols and Plinthosols. In the USDA Soil Taxonomy classification the equivalent orders are: Ultisols, Oxisols and Latosols, and Lateritic soils in other classifications.

1.5.1.3 Organic Soils

Organic soils, such as peats and mucks and humic variants of mineral soils with relatively high contents of organic matter tend to be deficient in Cu, Mn, and Zn and this can often occur over a wide range of pH. The main world soil types comprising organic soils include: Histosols, Chernozems, Kastanozems, Phaeozems, Podzols, Rendzinas (Rendic Leptosols and Calcisols) and Umbrisols and humic variants of several different other types, including: Cambiols, Fluvisols and Gleysols.

1.5.1.4 Calcareous Soils

Calcareous soils have a relatively high content of free $CaCO_3$ (>15%) and include soil developed on limestones of various types and also soils in which $CaCO_3$ has been deposited in voids through the evaporation of Ca-rich groundwater

(Calcification). These calcareous soils tend to give rise to deficiencies of B, Cu, Fe, Mn, Ni and Zn. Several micronutrients can be deficient simultaneously in crops on these soils (multi-element deficiencies). The world soil types comprising these soils include Calcisols, Leptosols, Rendzinas (also included in Calcisols) and calcic variants of several other soil types including Cambisols. Vertisols have a high pH and $CaCO_3$ content and can give rise to deficiencies of Fe and Zn.

1.5.1.5 Saline Soils

Saline soils are characterized by having high concentrations of soluble salts and are normally found in arid and semiarid regions. Inappropriately managed irrigated soils can also become saline (salinisation) due to the accumulation of salts. Where cropped, saline soils can cause deficiencies of Cu, Fe, Mn and Zn. The world soil types comprising saline soils are mainly the Solonchaks and Solonetz. In the USDA Soil Taxonomy classification they include Natrargids, Natrustalfs and Natrixerolls and other soil types which have become salinised through irrigation.

1.5.1.6 Gleyed Soils

Gleyed soils, are soils which are affected by waterlogging (“gleying”) for at least part of the year and can occur naturally in low-lying situations in humid regions where groundwater accumulates. Gleying can also occur as a result of impermeable conditions in the upper part of the soil profile, usually in clay-rich soils and can be caused, or exacerbated by poor soil management, leading to compaction. Gleying is characterised by reducing conditions which cause the dissolution of oxides of Fe and Mn and the release of any trace elements sorbed in or on them. Thus, the availability of Fe and Mn can be high in gleyed soils but the total content is usually comparatively low owing to depletion of the mobile Mn^{2+} and Fe^{2+} ions. Zinc (and possibly other micronutrients) may be relatively unavailable in gleyed soils due to the elevated pH and formation of insoluble sulphides (e.g., ZnS). The main soil groups comprising gleyed soils are the Gleysols, Fluvisols, Planosols and gleyed variants of a wide range of soil types, including Cambisols.

The most widely occurring cropping system involving gleyed soils is lowland (flooded) rice production. In this system, many soils which were not naturally gleyed have been converted to gleys in the construction of paddy fields with standing water for most of the growing period of the rice crop. Some of the soils are both calcareous and gleyed and thus the availability of elements like Zn is affected by both pH and redox conditions. Possibly, up to 50% of paddy rice-growing land is affected by Zn deficiency (Scharpenseel et al., 1983).

1.5.1.7 Clay-rich Soils

Clay-rich soils can often show gleying in their uppermost horizons due to impermeability. Most of the clay minerals making up clay-textured soil, except kaolinite, tend to have relatively high adsorptive capacities for many micronutrients and therefore tend to retain trace element inputs (including micronutrients) from various sources, including livestock manures, agrichemicals and atmospheric deposition. In contrast to the low concentrations of most micronutrients found in sandy soils developed on sandstones and sandy drift materials, some parent materials of clay-rich soils can be relatively rich in several micronutrients. Soils developed on shales and clay formations tend to be relatively enriched in a range of trace elements, both essential and non-essential, including: Cu, Mo, Zn and also As, Se, Cd and other elements (Alloway, 1995). The availability of these elements in clay-textured soils will depend on soil factors, including redox conditions, pH, organic matter content and available P status. Soils developed on basalts and other basic igneous rocks can also be relatively enriched in several micronutrients but the high content of adsorptive iron oxides in the soils may affect the availability of some elements. The main groups of clay-rich soils are: Alisols, Chernozems, Luvisols, Vertisols and argic variants of other groups including Cambisols.

1.5.1.8 Contaminated Soils

Any type of soil can become contaminated with micronutrient elements. However, the higher the cation-adsorptive capacity of the soil, the longer the contaminants are likely to be retained against leaching. Some of the main sources of contaminants are atmospheric deposition of localized and long-distance transported industrial air pollutants, recycling and disposal of biosolids (sewage sludges) and animal manures (e.g., Cu and Zn), metal-containing fungicides (e.g., Cu, Zn and Mn), contaminants in agrichemicals and fertilisers (e.g., Zn in superphosphate) and residues of micronutrient fertilisers. Many of these accumulations can be beneficial sources of micronutrients and counteract the risk of deficiencies occurring as they would on similar but uncontaminated soils. However, there is a danger of elements accumulating to potentially toxic levels and also the problem that non-essential elements in the same micronutrient-rich materials may also be accumulating to undesirable levels (e.g., Cd in sewage sludges and P fertilizers) (Alloway, 1995b).

1.5.2 Effects of Soil Conditions on the Availability of Micronutrients to Crops

1.5.2.1 Soil pH

Soil pH is perhaps the most important soil property affecting the availability of trace elements in soils (Alloway, 1995a). Elements existing as cations (e.g., Cu^{2+}, Zn^{2+}) in the soil solution will be more available at low pH, whereas elements in anionic form (MoO_4^{2-} and $HMoO^{4-}$) will be more available at high pH. In humid environments, most mineral soils, except calcareous types, will tend to be naturally acid due to the leaching of bases and higher contents of organic matter. Gleyed soils will normally have slightly higher pH values than their freely drained counterparts. In arid environments, soils will tend to be neutral to alkaline. Although it can be expected that farmers will often attempt to raise the pH of acid soils. Where soils are acid, the micronutrient most likely to be deficient will be Mo. In contrast to deficiency, the availability of Fe and Mn may be so high that some sensitive crops may be affected by toxicity of these elements on acid soils.

In contrast, where soils are neutral to alkaline, the micronutrients likely to be deficient include: B, Cu, Fe, Mn, Ni and Zn (as found on calcareous soils). Apart from naturally calcareous soils, farmers in many areas will have limed their soils to raise the pH and this can have the effect of reducing the availability of the elements listed above, with Mn and Fe being particularly sensitive to liming.

1.5.2.2 Soil Organic Matter Content

Trace elements, including Cu, Mn and Zn can be bound in relatively unavailable forms in soil humic matter. This implies that crops growing on naturally organic-rich soils are likely to be deficient in these elements (Alloway, 1995a). Copper deficiency in particular is strongly correlated with peaty and organic-rich soils (Alloway, 2005). However, mineral soils with relatively high organic matter contents due to land use and/or manure spreading can also give rise to deficiencies of these elements. However, the application of readily decomposable organic material can have the effect of rendering some micronutrients more available as a result of forming water-soluble organic complexes with the elements (Barrow, 1993). Zinc deficiency problems in paddy soils have been rectified by applying manure to the soils to act in this way.

1.5.2.3 Soil Drainage Status (Redox Conditions)

As stated above for gleyed soils, poorly drained soils tend to have higher available concentrations of Fe and Mn and elements such as Co (essential for animals) that are sorbed in iron and manganese oxides. However, gleyed soils also have higher pH values than their more freely drained equivalents and this can affect available concentrations and, to a certain extent, offset the increased availability resulting from the absence of Fe and Mn oxides due to the reducing conditions. In strongly gleyed soils, such as paddy rice soils, some micronutrient elements, including Zn may be present as insoluble sulphides, which renders them virtually unavailable.

The soil properties and the associated micronutrient deficiency problems are summarized in Table 1.14.

1.6 Plant Factors Associated with Micronutrient Deficiencies

The physiological mechanisms and plant stresses involved in causing micronutrient deficiencies in crops are discussed in many of the chapters. However, Table 1.15 provides a brief list of the key factors involved.

Table 1.14 Soil types and properties commonly associated with micronutrient deficiencies

Soil/soil Properties	Micronutrient deficiency
Sandy texture and strongly leached	B, Cl, Cu, Fe, Mn, Mo, Ni, Zn[a]
High organic matter content (>10% OM)	Cu, Mn, Zn
High soil pH (>7)	B, Cu, Fe, Mn, Ni, Zn
High $CaCO_3$ content (>15%) (calcareous soils)	B, Cu, Fe, Mn, Ni, Zn[a]
Recently limed soils	B, Cu, Fe, Mn, Ni, Zn
High salt content (salt-affected soils)	Cu, Zn, Fe, Mn
Acid soils	Mo, Cu, Zn
Gleys	Zn
Heavy Clay	Cu, Mn, Zn

[a] Multi-element deficiencies can occur on sandy and calcareous soils.

Table 1.15 Plant factors associated with micronutrient deficiencies

- Plant genotype (i.e., micronutrient-efficient/inefficient cultivars)
- Nitrogen supply (effects on growth rate, dilution, elements locked up in proteins in foliage)
- Phosphate supply (effects on growth rate – dilution, e.g., Cu and metabolism, e.g., Zn)
- Moisture stress (uptake reduced in drought conditions)
- Temperature stress (high and low temperatures)
- High/low light intensity
- Rooting conditions (restrictions in rooting zone will reduce the volume of soil explored by roots)
- Mycorrhizal infection (increases the effective volume of roots)
- Secretion of root exudates (e.g., phytosiderophores)
- Pathological disease
- Agrichemicals (e.g., glyphosate-induced deficiencies of Mn, Zn, etc.)
- Antagonistic effects of other micronutrients (e.g., Cu–Zn, Fe–Cu, Fe–Mn, and Cu–Mn)
- Previous crop species – there is some evidence that the mineralisation products of some plant species can render certain micronutrients less available in the soil. An example of this is Cu deficiency in wheat following oilseed rape (canola)

1.7 Future Trends in Micronutrient Requirements for Crops

The global incidence of micronutrient deficiencies is likely to increase due to the intensification of arable farming. In many cases, this will necessitate regular applications of micronutrient fertilisers either to the soil, foliage or seed and, ideally, these should be based on regular soil or plant tissue testing. However, this is not likely to be possible in many developing countries so agricultural extension workers will need to be able to advise farmers how often they will need to repeat applications, depending on type of soil, crops and climatic zone, (as discussed by Singh in Chap. 4).

In countries or regions where there is little systematic information available on the micronutrient status of soils, there is a need for rapid surveys to be conducted in order to find out where deficiency, or even toxicity, problems may occur with changes in cropping (as discussed in Chap. 6).

Advances in plant physiological research are likely to provide a better understanding of the importance of hidden deficiencies and lead to increased use of micronutrient fertilisers to ensure optimum yields and quality, especially in high value crops (Brown, Chap. 11). Horticultural crops will probably continue to receive proportionately more micronutrients than field crops owing to their generally greater susceptibility to deficiencies and the relatively high value of their products (Brown, Chap. 11; Zou et al., Chap. 5).

In most parts of the world, especially developing countries, simple trace element compounds such as sulphate salts (e.g., $ZnSO_4.7H_2O$ and $MnSO_4.nH_2O$), will continue to be the most widely used forms of micronutrient fertilisers because they are relatively inexpensive, highly water soluble and easily applied (Chaps. 4 and 10). However, with the trend to intensification, there will be an increasing demand for micronutrient products which can be integrated into arable farming operations, such as compounds which are compatible with herbicides and fungicides in tank mixes for foliar application. Where genetically modified crops, which are resistant to glyphosate, are grown, there will be a need for additional micronutrients, especially Mn, to compensate for any deficiencies induced by this herbicide (Brown, Chap. 11).

Climate change and increasing economic pressures on water resources will affect crop production in many parts of the world, especially subtropical and semi-arid regions. Heat, drought and high light intensity stresses can all affect crop requirements for Zn and possibly other micronutrients (Moraghan and Mascagni, 1991). In China and other rice-growing countries, there will be a trend to growing aerobic and upland rice instead of paddy rice and this has important implications for Zn and possibly other deficiencies (Zou et al., Chap. 5).

As discussed in Chaps. 2 and 12, in addition to optimising crop yields, there will be increasing emphasis on fortifying food crops with micronutrients which are important in human diets, including Fe, Zn, I and Se. It is estimated that 60–80% of the world's population have diets which are deficient in Fe and about 50% deficient in Zn. However, biofortification with micronutrient fertilisers will have to be carefully planned in order to avoid the build up of excessive concentrations in soils. It may be increasingly necessary to use foliar applications to supply the necessary micronutrients without causing significant increases in the total concentrations in soils and hence avoiding possible toxic effects in plants or soil biota.

In conclusion, micronutrients are vitally important for maintaining and increasing food crop production for a growing world population. The micronutrient composition of these crops is also important in providing adequate intakes of these elements for human and animal nutrition. The following chapters in this volume identify the main micronutrient deficiency problems in different countries and continents around the world, the ways in which they are being ameliorated and the challenges posed by changes in crop production brought about by economic pressures and global climate change.

References

Alloway, B.J. (1976). Field studies on the magnesium, copper and zinc nutrition of maize. Journal of Agricultural Science, Cambridge, 86: 93–101.

Alloway, B.J., Tills, A.R. (1984) Copper deficiency in world crops. Outlook on Agriculture, 13: 32–42.

Alloway, B.J., Jewell, A.W., Murray, B.N. (1985) Pollen development in copper deficient cereals. Project 345, International Copper Research Association, New York.
Alloway, B.J. (1995a) Soil processes and the behaviour of metals. In Alloway, B.J (Ed.), Heavy Metals in Soils (2nd Edn.), Blackie, Chapman & Hall, London, pp. 11–37.
Alloway, B.J. (1995b) Origins of heavy metals in soils. In Alloway, B.J (Ed.), Heavy Metals in Soils (2nd Edn.), Blackie, Chapman & Hall, London, pp. 38–57.
Alloway, B.J. (2004) Zinc in Soils and Crop Nutrition. International Zinc Association, Brussels, 130 pp. Available at www.zinc-crops.org.
Alloway, B.J. (2005) Copper Deficient Soils in Europe. International Copper Association, New York, 129 pp.
Arnon, D.I., Stout, P.R. (1939) The essentiality of certain elements in minute quantity for plants with special reference to copper. Plant Physiology, 14: 371–375.
Asher, C.J. (1991) Beneficial elements, functional nutrients and possible new essential elements. In Mortvedt, J.J., Cox, F., Shuman, L.M., Welch, R.M. (Eds.), Micronutrients in Agriculture (2nd Edn.), Soil Science Society of America Book Series No. 4, Madison, WI, pp. 703–724.
Barker, A.V., Pilbeam, D.J. (2007) Introduction. In Barker, A.V., Pilbeam, D.J. (Eds.), Handbook of Plant Nutrition, CRC, Taylor & Francis, Boca Raton, FL, pp. 3–18.
Barrow, N.J. (1993) Mechanisms of reaction of zinc with soil and soil components. In Robson, A.D. (Ed.), Zinc in Soils and Plants, Kluwer, Dordrecht, The Netherlands, pp. 15–32.
Bernards, M., Thelen, K., Penner, D. (2002) The manganese fertilizer antagonism of glyphosate story for 2002. Available at http://www.msu.edu/varietytrials/corn/Cropping%20Systems/mngly.pdf
Brown, P.H., Welch, R.M., Cary, E.E. (1987) Nickel: A micronutrient essential for higher plants. Plant Physiology, 85: 801–803.
Brown, P.H. (2007a) Nickel. In Barker, A.V., Pilbeam, D.J. (Eds.), Handbook of Plant Nutrition, CRC, Taylor & Francis, Boca Raton, FL, pp. 395–410.
Dobermann, A., Fairhurst, T. (2000) Rice: Nutrient Disorders and Nutrient Management. Potash and Phosphate Institute, Potash Institute of Canada, International Rice Research Institute, Los Baños, Philippines, 192 pp.
Eker, S., Ozturk, L., Yazici, A., Erenoglu, B., Romheld, V., Cakmak, I. (2006) Foliar-applied Glyposate substantiallu reduced uptake and transport of iron and manganese in Sunflower (*Helianthus annuus* L.) plants. Journal of Agricultural and Food Chemistry, 54 (26): 10019–10025.
Epstein, E. (1965) Mineral metabolism. In Bonner, J., Varner, J.E. (Eds.), Plant Biochemistry, Academic, London, pp. 438–486.
FAO-UNESCO (1974) Soil Map of the World, Volume 1: Legend, UNESCO, Paris.
Follet, R.H., Murphy, L.S., Donohue, R.L. (1981) Fertilizers and Soil Amendments. Prentice-Hall, Englewood Cliffs, NJ.
Gao, X.P., Kuyper, T.M., Zou, C.Q., Zhang, F.S., Hoffland, E. (2007) Mycorrhizal responsiveness of aerobic rice genotypes is negatively correlated with their zinc uptake when nonmycorrhizal. Plant Soil, 290: 283–291.
Graham, R.D., Nambiar, E.K.S. (1981) Advances in research on copper deficiency in cereals. Australian Journal of Agricultural Research, 32: 1009–10037.
Graham, R.D. (1984) Breeding for nutritional characteristics in cereals. In Tinker, P.B., Läuchli, A. (Eds.), Advances in Plant Nutrition, Volume 1, Praeger, New York, pp. 57–102.
Graham, R.D., Rengel, Z. (1993) Genotypic variation in zinc uptake and utilization by plants. Chap. 8. In Robson, A.D. (Ed.), Zinc in Soils and Plants, Kluwer, Dordrecht, The Netherlands, pp. 107–118.
Grewal, H.S., Graham, R.D., Rengel, Z. (1996) Genotypic variation in zinc efficiency and resistance to crown rot disease (*Fusarium graminaearum* Schw. Group1) in wheat. Plant Soil, 186: 219–226.
Györi, D., Palkovics, M. (1983) The effect of borax applications on the boron uptake and yield of vines. Agrokémica és Talajtan, 32 (1–2): 88–96.

Heckman, J.R. (2007) Chlorine. In Barker, A.V., Pilbeam, D.J. (Eds.), Handbook of Plant Nutrition, CRC Press, Taylor & Francis, Boca Raton, FL, pp. 279–291.

Hotz, C., Brown K.H. (2004) Assessment of the risk of zinc deficiency in populations and options for its control. UNU Food and Nutrition Bulletin, 25(Suppl. 2): S91–S203.

Humphries, J.M., Stangoulis, J.C.R., Graham, R.D. (2007) Manganese. In Barker, A.V., Pilbeam, D.J. (Eds.), Handbook of Plant Nutrition, CRC, Taylor & Francis, Boca Raton, FL, pp. 351–374.

ISSS Working Group R.B. (1998a) World Reference Base for Soil Resources: Introduction (1st Edn.) Deckers, J.A., Nachtergaele, F.O., Spaargaren, O.C. (Eds.), ISRIC-FAO-ISSS, Acco, Leuven.

ISSS Working Group R.B. (1998b) World Reference Base for Soil Resources: Atlas, Bridges, E.M., Batjes, N.H., Nachtergaele, F.O. (Eds.), ISRIC-FAO-ISSS, Acco, Leuven.

Jewell, A.W., Murray, B.G., Alloway, B.J. (1988) Light and electron microscope studies on pollen development in barley (*Hordeum vulgare* L.) grown under copper-sufficient and deficient conditions. Plant, Cell and Environment, 11: 273–281.

Kabata-Pendias, A. (2001) Trace Elements in Soils and Plants (3rd Edn.), CRC Press, Boca Raton, FL.

Loneragan, J.F., Webb, M.J. (1993) Interactions between zinc and other nutrients affecting the growth of plants. Chap. 9. In Robson, A.D. (Ed.), Zinc in Soils and Plants, Kluwer, Dordrecht, The Netherlands, pp. 119–134.

Loué, L. (1986) Les Oligo-Elements en Agriculture. SCPA, Agri Nathan International, Paris, p. 339.

Marschner, H. (1995) Mineral Nutrition of Higher Plants (2nd Edn.), Academic, London, p. 889.

Martens, D.C., Westerman, D.T. (1991) Fertilizer applications for correcting micronutrient deficiencies, In Mortvedt, J.J., Cox, F., Shuman, L.M., Welch, R.M. (Eds.), Micronutrients in Agriculture (2nd Edn.), Soil Science Society of America Book Series No. 4, Madison, WI, pp. 549–582.

Moraghan, J.T., Mascagni, H.J. Jr. (1991) Environmental and soil factors affecting micronutrient deficiencies and toxicities. In Mortvedt, J.J., Cox, F., Shuman, L.M., Welch, R.M. (Eds.), Micronutrients in Agriculture (2nd Edn.), Soil Science Society of America Book Series No. 4, Madison, WI, pp. 371–425.

Neumann, G., Kohls, S., Landsberg, E., Stock-Oliveira Souza, K., Yamada, T., Römheld, V. (2006) Relevance of glyphosate transfer to non-target plants via the rhizosphere. Journal of Plant Diseases and Protection, 20: 963–969.

Prasad, R., Power, J.E. (1997) Soil Fertility Management for Sustainable Agriculture. CRC Lewis Publishers, Boca Raton, FL, 356 pp.

Reddy, T.Y., Reddi, G.H.S. (1997) Mineral nutrition, manures and fertilizers. In Principles of Agronomy, Kalyani Publishers, Ludhiana, India, pp. 204–256. Available at www.plantstress.com/Articles/min_deficiency_i/impact.htm.

Reith, J.M. (1968) Copper deficiency in plants and effects of copper on crops and herbage. Paper in Symposium on Copper in Farming. Copper Development Association, Potters Bar, UK.

Rerkasem, B., Jamjod, S. (2004) Boron deficiency in wheat: A review. Field Crops Research, 89: 173–186.

Scharpenseel, H.W., Eichwald, E., Hauptenthal, Ch., Neue, H.U. (1983) Zinc deficiency in a soil toposequence grown to rice at Tiaong, Quezon Province, Philippines. Catena, 10: 115–132.

Shorrocks, V.M., Alloway, B.J. (1985) Copper in plant, animal and human nutrition. Copper Development Association, TN 35, Copper Development Association, Potters Bar, UK, p. 84.

Shorrocks, V.M. (1997) The occurrence and correction of boron deficiency. Plant and Soil, 193: 121–148.

Sillanpää, M. (1982) Micronutrients and the nutrient status of soils: A global study. FAO Soils Bulletin No. 48, FAO, Rome.

Sillanpää, M. (1990) Micronutrient assessment at the country level: An international study. FAO Soils Bulletin No. 63, FAO, Rome.

Sinclair, A.H., Withers, P.J.A. (1995) Copper deficiency in UK cereal crops: Occurrence, significance and treatment. HGCA Research Review No. 31, Home Grown Cereals Authority, London.

Soil Survey Staff (1999) Soil Taxonomy: A basic system of soil classification for making and interpreting soil surveys (2nd ed.). Agricultural Handbook 436, Natural Resources Conservation, USDA, Washington DC. USA, pp. 869.

Srivistava, P.C., Gupta, U.C. (1996) Trace Elements in Crop Nutrition. Science Publishers, Lebanon, NH, 356 pp.

Tills, A. (1981) Causes and Detection of Copper Deficiency in Arable Crops. Unpublished Ph.D. thesis, University of London.

Tills, A.R., Alloway, B.J. (1981) Subclinical copper deficiency in crops on the Breckland in East Anglia. Journal of Agricultural Science, Cambridge, 97: 473–476.

United States Environmental Protection Agency (USEPA) (1993) Standards for the use or disposal of sewage sludge. Federal Register, 58: 47210–47238.

Vetter, H., Grummer, H.J., Brosch, K.I. (1985) Magnesium, manganese and copper for soil, plants and animals. Booklet 333, West German Ministry of Agriculture, AID, Oldenburg, 30 pp.

Walter, K.H. (1988) Manganese fertilizers. In Graham, R.D., Hannam, R.J., Uren, N.C. (Eds.,) Manganese in Soils and Plants, Kluwer, Dordrecht, The Netherlands.

Wild, A., Jones, L.H.P. (1988) Mineral nutrition of crop plants. In Wild, A. (Ed.), Russell's Soil Conditions and Plant Growth (11th Edn.), Longman, Harlow, UK.

Xu, G., Magen, H., Tarchitzky, J., Kafkaf, U. (2000) Advances in chloride nutrition of plants. Advances in Agronomy, 28: 97–150.