Chapter 7
Heavy Metals and Metalloids as Micronutrients for Plants and Animals

Brian J. Alloway

Abstract Much of the emphasis of the chapters in this book is on heavy metal(loid)s as soil contaminants, their bioavailability and possible toxicity to plants, ecosystems, animals and humans. However, many of the heavy metal(loid)s are actually micronutrients, that is they are essential (in small quantities) for the normal growth of plants and/or animals. Copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni) and zinc (Zn) are the heavy metals that are essential for higher plants. For animals and humans, chromium (Cr), Cu, cobalt (Co), Mn, Mo, selenium (Se), vanadium (V) and Zn are the micronutrient heavy metal(loid)s. Iron (Fe), not usually considered a heavy metal is essential for both plants and animals. Several other elements, including arsenic (As), cadmium (Cd), lead (Pb) and tin (Sn) may possibly have an essential role at very low concentrations. This chapter briefly covers the essential functions of these heavy metal(loid)s in plants and/or animals and the significance of relatively low and high available concentrations in soils. Deficiencies and toxicities of micronutrients adversely affect plant and animal health, cause reductions in growth rate (and yield), overt symptoms of physiological stress and, in extreme cases, the death of the plant or animal. In many parts of the world, the adverse effects of deficiencies of essential heavy metal(loid)s are more important economically than toxicities arising from soil contamination.

Keywords Micronutrients • Essentiality • Hidden deficiency • Toxicity • Symptoms • Enzymes • Plant nutrition • Human nutrition • Homeostasis

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7.1 Introduction

'Micronutrients' are the trace elements required in small, but critical, quantities for the normal healthy growth of plants and animals. There are eight micronutrients required by higher plants and these are: boron (B), chlorine (Cl), Cu, iron (Fe), Mn, Mo, Ni and Zn. In addition, Co is essential for the bacterial fixation of nitrogen (N) in nodules on the roots of legumes [5, 8, 9]. With the exception of B and Cl, these elements are all classed as heavy metals. In higher animals and humans, the proven micronutrients are: chromium Cr, Cu, Fe, iodine (I), Mn, Mo, Se, V and Zn. Other elements which are being investigated for possible essential functions in animals and humans include: B, silicon (Si), As, fluorine (F), lithium (Li) and Sn. There is even some evidence that Cd, Pb and Sn may be essential at very low concentrations [12, 28, 31]. However, the micronutrients which have been conclusively proven to be essential in animal and/or human nutrition and whose concentrations in diets are critical are Co (ruminants only), Cr, Cu, Fe, I, Mn, Mo, Se and Zn.

An element can be considered 'essential' for plants if they cannot complete their life cycles without it, it cannot be replaced by other elements and it is directly involved in plant metabolism [8]**.** Essential trace elements are also known as 'micronutrients'. For animals and humans, Reilly [28] quotes the definition of essential elements used by many nutritionists as: "The trace element must: (1) be present in healthy tissue, (2) its concentration must be relatively constant between different organisms, (3) deficiency induces specific biochemical changes, (4) the changes are accompanied by equivalent abnormalities in different species, and (5) supplementation with the element corrects the abnormalities."

All micronutrient heavy metal(loid)s have homeostatic mechanisms in plants and/or animals which regulate the bioavailable concentrations of the elements. It is when these mechanisms break down and are unable to maintain the optimal range of supply of a particular micronutrient that either deficiencies or toxicities can occur.

7.2 Heavy Metal Micronutrients in Plant Nutrition

It is very important that the micronutrient requirements of crops are met as well as their macronutrient needs (e.g., N, P and K) if they are to yield satisfactorily and bear products, such as grains, fruits, vegetable leaves or storage roots, of acceptable quality. In comparison with macronutrients, which are often present in thousands of mg kg^{-1}, micronutrients are only required in relatively small amounts (5–100 mg kg^{-1} DM). The dose response curves for all micronutrients show that yields can be affected by both deficiencies and toxicities. Typical dose-response graphs for micronutrients and non-essential elements are shown in Fig. 7.1. Although these are primarily based on generalised plant data, dose response graphs for animals show similar trends.

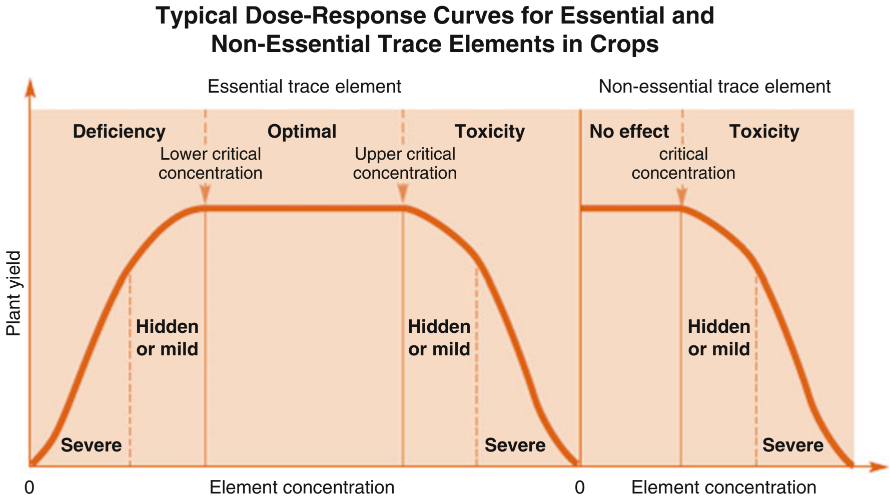

Fig. 7.1 Typical dose-response curves for essential and non-essential trace elements (Reproduced from Alloway [3] (Copyright (2008) with permission from International Zinc Association and International Fertiliser Industry Association))

Micronutrient deficiency problems in crops have only been widely recognised and treated in the field over the last 70 years. These deficiencies became apparent with the intensification of arable farming in many parts of the world and also with the cultivation of virgin and/or reclaimed land. Intensification involves the increased use of N, P and K fertilisers, growing new and higher yielding crop cultivars, increased use of pesticides and, where necessary, liming to optimise soil pH and/or increased use of irrigation. Prior to this intensification, much lower crop yields were usually accepted as the norm in many parts of the world, but the crop cultivars grown were generally well adapted to local soil and climatic conditions [2]. A similar situation has arisen with intensively managed livestock, but in the case of humans, trace element malnutrition is often related to poverty and restricted diets with either a shortage of foods containing adequate concentrations of micronutrients, or foods, such as grains containing relatively high levels of antinutrients such as phytates, which reduce the availability of some micronutrients [31, 33].

The functions of the plant micronutrients are briefly summarised in Table 7.1. All of these essential heavy metals have roles as constituents or activators of enzymes in physiological pathways. Although Fe is not normally considered to be a 'heavy metal' it is included in Tables 7.1 and 7.2 because of its very important functions and the fact that it interacts with several heavy metals such as Mn, Cu and Zn and macronutrients such as Ca.

Critical deficiency concentrations of these micronutrient heavy metals in most crop plant species are generally in the range (in mg kg^{-1} DM): Cu 1.0–5.0, Fe 50–150, Mn 10–20, Mo 0.015–0.05, Ni 0.01–10 and Zn 15–20 [6, 7]. Critical concentrations in soils vary with the soil test procedure used, the crop and the type of soil. For Cu extracted with ethylenediamine tetraacetic acid (EDTA) deficiencies are highly likely <0.5 mg EDTA Cu kg^{-1} and still possible 0.5–08.

Table 7.1 Brief summary of the essential functions of metal micronutrients and beneficial elements in plants

Element	Functions
Cobalt	Not a plant micronutrient, but is essential for the symbiotic fixation of N_2 in the root nodules of legumes and some non-legumes by *Rhizobium* and other N_2- fixing microorganisms in which three enzymes are known to be Co-dependent. It may also have beneficial roles in some higher plant families.
Copper	Plays important structural and functional roles in oxidative enzymes (including: super oxide dismutase (SOD), cytochrome oxidase, ascorbate oxidase, polyphenols oxidase and electron-transfer proteins (e.g., plastocyanin in chloroplasts)). The physiological processes involving these Cu-dependent enzymes and proteins affect photosynthesis, carbohydrate metabolism, respiration, protein metabolism, lignification of cell walls (and water transport) and pollen formation. It is also required for N-fixation in root nodules of legumes.
Iron	Constituent of cytochromes (electron-transfer proteins) and metalloenzymes and is essential for many biochemical and physiological processes in plants. These include: photosynthesis, utilization of N and S, production of the plant hormone ethylene and biosynthesis of chlorophyll. Iron is generally incorporated into heme and non-heme proteins, such as cytochromes. Heme proteins are involved with the formation of lignin and suberin and in catalase enzymes which breakdown hydrogen peroxide in cells. In legumes, Fe-containing heme proteins called leghemoglobins, regulate the supply of O_2 to N_2-fixing bacteria in root nodules.
Manganese	Activates a large number of enzymes which catalyse oxidation-reduction, decarboxylation and hydrolytic reactions and affects the production of lignin, flavonoids, fatty acids, the growth hormone indole acetic acid (IAA) and N metabolism. In C4 plants, such as maize and sugar cane and plants which fix their C at night, Mn is required for CO_2 assimilation. Only two enzymes contain Mn: the Mn protein in photosystem II, which catalyses the photolysis of water in photosynthesis and a superoxide dismutase (MnSOD) which protects tissues from damage caused by the oxygen free radical (O_2^-).
Molybdenum	Required for the functioning of several enzymes involved in redox reactions including nitrate reductase which is essential for the reduction of NO_3 to allow it to be assimilated into plants and aldehyde oxidase which is involved in the synthesis of growth hormones. Molybdenum is also a component of the bacterial enzyme nitrogenase involved the fixation of N_2 in legume root nodules.
Nickel	Constituent of the enzyme urease and therefore essential for the few plant species that produce this enzyme and other plants supplied with urea as the sole source of N. It is required for healthy embryo and seedling vigour in cereals and is also important in plant disease resistance. Nickel is also a component of the enzyme hydrogenase involved in N fixation by bacteria.
Zinc	Constituent of several enzymes with roles in carbohydrate and protein synthesis, gene regulation, structure and integrity of biomembranes, protection of cells from damage due to free radicals, regulation of auxin synthesis and pollen formation. Meristematic tissues have a high Zn requirement and the Zn-containing enzyme carbonic anhydrase is required for photosynthesis. Plants with C4 –type CO_2 fixation in photosynthesis have a higher requirement for carbonic anhydrase, than C3 plants and are therefore more sensitive to Zn deficiency, but Zn deficiency reduces net photosynthesis in all plants. As a result of its role in maintenance of biomembranes, roots of Zn-deficient plants tend to 'leak' amino acids and phenolics. Classic symptoms of Zn deficiency, such as stunting and 'little leaf' are due to the oxidative degradation of auxin (growth hormone).

Adapted from: Marschner [19], Bell and Dell [6], Srivastava and Gupta [30], Fageria et al. [9], Brown [7], Humphries et al. [14] and Asher [4]

Table 7.2 Some common visible symptoms of micronutrient deficiencies in crops

Element	Symptoms	Sensitive crops
Copper	Wilting, melanism, white twisted tips, reduction in panicle formation, disturbance of lignification and of the 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 turgour. 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	Brassicae and legumes
Nickel	Leaf tip necrosis (legumes), chlorosis and patchy necrosis (*Graminae*)	Pecan, wheat, potato, bean, soya bean
Zinc	Interveinal chlorosis (mainly in monocotyledons), stunted growth, "little leaf", rosetting of trees and violet-red points on leaves	Cereals (especially maize and rice), grasses, flax/linseed and fruit trees (citrus)

Adapted from Kabata-Pendias [15] and Fageria et al. [9]

Mg EDTA Cu kg^{-1} [1]. For Zn extracted with diethylenediamine pentaacetic acid (DTPA) typical threshold concentrations are 0.1–1.0 mg DTPA Zn kg^{-1} [21] (see Sect. 17.5.1), but around the world the critical range can extend up to 2.0 mg DTPA Zn kg^{-1} [3].

When the supply of a micronutrient to plants is either deficient or excessive, in addition to crop yields and quality being affected, visible symptoms of physiological stress are often observed, especially in cases of severe deficiency or toxicity [5]. Although plant species differ in the nature of the symptoms of micronutrient deficiencies and toxicities 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 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, or even white, but they can also turn brown. Deficiency symptoms can also include smaller or twisted leaves, and loss of turgour. 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 in terminal buds with B deficiency. Green veins (on chlorotic leaf laminas) are seen on new leaves with Fe and Mn deficiency and yellow veins with Cu deficiency [27]. A summary of the main types of deficiency symptoms associated with each of the plant micronutrients is given in Table 7.2. Less severe deficiencies may not manifest themselves until later stages in the development of the plant. Visible symptoms can provide a convenient and low-cost means of identifying micronutrient deficiency problems, but can sometimes be confused with deficiencies of other macro or micronutrients, toxicities of metal(loid)s or symptoms of disease, drought, heat stress, or damage by agrichemicals [5].

Symptoms of severe toxicity in plants vary with the metal(loid) involved (including non-essential and micronutrient elements), but certain symptoms tend to be commonly found. These include: chlorosis (Co, Cr, Cu, Hg, Mn, Mo, Ni, Se, Tl and Zn); stunted or deformed roots (As, Cd, Cr, Cu, Co, Hg, Mn, Mo, Ni, Pb, Ni and Zn); dark green leaves (Cu, Fe and Pb); grey green leaves (Ni); brown necrotic spots on leaves (As); brown leaf margins (Cd); white or necrotic leaf tips (Zn) and general stunting (Cd, Hg and Zn) [15]. Upper critical concentrations (in mg kg^{-1} DM) causing a 10% depression in yield (due to toxicity) are in the range: As 1–20, Cd 10–20, Cr 1–10, Cu 10–30, Hg 1–8, Ni 10–30 and Zn 100–500 [18].

In cases of marginal deficiency or toxicity, the manifestation of symptoms is often less distinct and more difficult to recognize in the field. The yields of many crops, especially cereals, can be significantly reduced (sometimes by 20% or more) and the quality of crop products impaired, without the manifestation of distinct visible symptoms due to marginal deficiencies of micronutrients such as Cu and Zn. These are usually referred to as hidden deficiencies, 'hidden hunger', latent, and/or sub-clinical deficiencies. In many parts of the world, this type of deficiency is more widespread and has a greater economic impact than acute micronutrient deficiencies. The apparent absence of deficiency or toxicity symptoms in a crop does not necessarily imply that the supply of micronutrients is optimal. More than one element may be deficient or causing phytotoxicity at a particular site (multi-micronutrient deficiencies or toxicities). 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.

From Table 7.3 it can be seen that crop species vary considerably in their susceptibility to deficiencies of different micronutrients. Maize, rice, citrus and fruit trees are particularly susceptible to Zn deficiency, which is the most ubiquitous micronutrient deficiency disorder in crops. Small grain cereals, such as wheat, barley and oats as well as citrus and alfalfa are highly susceptible to Cu deficiency. However, although wheat is considered reasonably tolerant of Zn deficiency, in many countries, especially those with calcareous soils, Zn deficiency in wheat is a major problem (due to low availability) (see Chap. 17, Sect. 17.5) [21]. Intra-specific variations (between varieties or cultivars) can sometimes be even greater than differences in susceptibility between species, but all crops will be affected by a severe deficiency of any of the 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 (cultivars).

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 and those which are unable to tolerate such low levels of this micronutrient are 'inefficient'. Genotypic variations in efficiency have been reported for: B, Cu, Fe, Mn and Zn in crop plants [11]. Differences in micronutrient efficiency are probably due to genotypic variations in the volume and length of roots, root-induced changes in rhizosphere, increased absorption through vesicular

Table 7.3 The relative susceptibility of crops to deficiencies of micronutrients

	Micronutrient					
Crop	B	Cu	Fe	Mn	Mo	Zn
Alfalfa	High	High	Med[a]	Med	Med	Low
Apple tree	High	Med	Low	High	Low	High
Barley	Low	High/Med	Med	Med	Low	Med
Bean	Low	Low	High/Med	High	Med	High
Cabbage	Med	Med	Med	Med	High/Med	–
Citrus	Low	High	High	High	Med	High
Cotton	High	Med	High/Med	Med/Low	Low	High/Med
Flax	Med	–	High	Low	–	High
Grapevine	High/Med	Med	High	High	Low	Low
Maize	Med/Low	Med	Med	Med/Low	Low	High
Oats	Low	High	Med	High	Med/Low	Low
Pea	Low	Med/Low	Med	High	Med	Low
Peanut[b]	High/Med	–	High	–	High	Low
Potato	Low	Low	–	High/Med	Low	Med
Rapeseed[c]	High	Low	–	Med	–	Med
Rice	Med/Low	Low	High/Med	Med	Low	High/Med
Rye	Low	Low	Low	Low	Low	Low
Sorghum	Low	Med	High/Med	High/Med	Low	High
Soya bean	Low	Low	High/Med	High	High/Med	Med
Spinach	Med	High	High	High	High	Med
Sugarbeet	High	Med	High/Low	High/Med	Med	Med
Sunflower	High	High	–	–	–	Med
Tomato	High/Med	Med	High	Med	Med	Med
Wheat	Low	High	Med/Low	High	Med/Low	Low

Derived from: Martens and Chesterman [20], Prasad and Power [25], Rashid and Ryan [26] and Loué [17]

[a]Med = medium susceptibility, – = no information

[b]Peanut (*Arachis hypogea* L.) also called groundnut

[c]Rapeseed (*Brassica napus* L) also called oil seed rape or canola

mycorrhizae, release of root exudates to facilitate uptake, efficiency of utilization of the micronutrients once absorbed into plants, recycling of elements within the tissues of the growing plant, or tolerance of factors, which inhibit uptake, such as HCO_3^- and Zn in rice [10, 13, 19].

In a large-scale programme of field experiments at 190 sites in 28 developing countries plus Finland, Silanpää [29] found that Zn deficiency occurred in 49% of the experimental sites, B deficiency in 31%, Mo deficiency in 15%, Cu deficiency in 14%, and Mn deficiency in 10%. However, for all elements except Zn, much higher percentages of these deficiencies were of the latent or hidden type (e.g., Cu 4% acute and 10% latent; Mo 3% acute and 12% latent), but in the case of Zn, there were almost equal percentages (25% acute and 24% latent) for the two types of deficiency.

7.3 Heavy Metal(loid) Micronutrients in Animal and Human Nutrition

Just as in plants, the heavy metal(loid)s essential for higher animals and humans are constituents and/or activators of enzymes. Their essential functions are given in Table 7.4.

In grazing livestock, Mn deficiency is rare, but when it does occur it often results in lameness. Zinc concentrations in herbage need to be above 20 mg kg^{-1} in order to avoid Zn deficiency whose effects include, loss of appetite, poor growth and reduced fertility. With more severe deficiency (intakes <5 mg Zn kg^{-1}) symptoms include loss of hair and wool, reduced immunity to disease and thickening and cracking of the skin. Copper deficiency can be associated with low Cu contents in herbage, but also to elevated Mo contents (see Sect. 18.4). Mild Cu deficiency symptoms, like those of Zn, tend to be non-specific and include poor growth and/or roughness and loss of pigmentation in coat. More severe Cu deficiency is accompanied by symptoms including diarrhoea, anaemia, and lameness. In sheep, Cu deficient lambs can develop a neurological condition called ‘swayback’ (or enzootic ataxia) [32].

The US Recommended Dietary Allowances (RDAs) [23] for Cu, Mn, Fe, Zn and Se for humans are shown in Table 7.5.

Apart from the proven essential trace elements, some other heavy metal(loid) s are being investigated to see whether they are also essential for animal and human nutrition. Several of these, such as As, Cd and Pb have only been considered as potentially toxic elements until recently, but there is some evidence that very small amounts of these elements may be essential. In most cases, the experimentation has involved using diets depleted of the elements of interest and some responses in growth rate and other parameters have been observed. This work is likely to be most relevant in medicine where patients may have to be maintained on total parenteral nutrition (TPN) [28]. However, it is highly unlikely that cases of deficiency of these elements will be found in humans consuming mixed diets or in livestock under normal agricultural conditions. The possible functions of the metal(loid)s currently under investigation are shown in Table 7.6.

7.4 Soil Types Commonly Associated with Micronutrient Deficiencies

The effects of soil type and soil conditions on the bioavailable concentrations of heavy metalloids are covered in detail in Chaps. 3, 6 and 9–18. However, Table 7.7 summarises the most typical soil conditions leading to either deficiencies in crops, or low concentrations of micronutrients required by animals in herbage and crop products. Boron and Fe are also included because of the agronomic importance of them being deficient.

Table 7.4 Functions of essential heavy metal(loid)s in higher animals and humans

Element	Functions
Chromium	Important in carbohydrate metabolism as a constituent of the 'glucose tolerance factor' (GTF) a dinicotinic acid-glutathione complex, which potentiates the action of insulin. Chromium participates in lipoprotein metabolism and there is some evidence that an improved Cr status has a beneficial effect on blood lipid levels in elderly persons. Improved Cr status may also reduce factors associated with cardiovascular disease as well as with diabetes.
Cobalt	Its only known function is as a constituent of Vitamin B12 which can only be synthesised by bacteria in the rumen or in the soil and plays a major part in animal cells where active division is taking place e.g., blood-forming tissues of bone marrow. Vitamin B12 cannot be absorbed on its own and has to combine first with a glycoprotein produced in the stomach lining, called the 'gastric intrinsic factor'. Vitamin B12 deficiency in humans causes pernicious anaemia and severe effects on the nervous system. In livestock it causes progressive loss of appetite and wasting leading to death. It is called 'bush sickness' in New Zealand and "Coast disease" in south Australia, but is found in many other countries.
Copper	Essential for the immune system, the nervous system, skeletal health, Fe metabolism and the formation of red blood cells. It is involved in redox systems and the scavenging of free radicals (Cu–SOD). It is a constituent of more than 12 metalloenzymes and a few genes which regulate Cu-dependent transcription factors. In sheep Cu deficiency can cause swayback disease (enzootic ataxia) in lambs and loss of crimp in wool. In cattle, deficiency causes depigmentation of the facial hair and sudden death. Subclinical Cu deficiency can cause reductions in liveweight gain and fertility and occurs much more widely than acute forms, especially in more intensively farmed livestock.
Iron	Although not considered a heavy metal, Fe is vitally important in animal physiology because it is a component of haemoglobin which carries oxygen in the red blood corpuscles. Iron requirements differ with species, gender, age and level of activity; shortage of Fe causes anaemia and can also result in increased absorption of potentially harmful elements such as Cd and Pb.
Manganese	Manganese is involved in bone formation and in the metabolism of amino acids, cholesterol and carbohydrates. It is a constituent of six key enzymes and affects the functioning of other enzymes such as glycosyltransferases and xylosyltransferases which are involved in bone formation and proteoglycan synthesis. Manganese activates a number of enzymes, but some can also be activated by other metals, especially Mg. The most common Mn deficiency symptoms in livestock are impaired reproduction, skeletal deformities and shortened tendons in the newborn, can also cause impaired insulin production, lipoprotein metabolism, oxidant defence and growth factor metabolism.
Molybdenum	In animals, Mo is required for the functioning of several enzymes involved in transformations of C, N and S. It is a co-factor in the enzymes sulphite oxidase, xanthine oxidase and aldehyde oxidase. Sulphite oxidase is very important in humans because it is involved in the metabolism of S-containing amino acids and bisulphite preservative in foods. In grazing livestock, a close connection between Mo, Cu and S is involved in the condition called "teart" (or molybdenosis) which is a Mo-induced Cu deficiency.
Selenium	Selenium has antioxidant and anti-inflammation functions and is involved in thyroid hormone metabolism. It also has roles in the prevention of certain infections, some forms of cancer and diabetes in humans. It appears to have valuable detoxification properties for As and Hg. Selenium deficiency is thought to affect 0.5–1.0 billion people worldwide. "Keshan disease" (a fatal cardiomyopathy) and "Kashin Beck's disease" (osteopathy) in humans can be prevented by dietary supplementation with Se. In livestock, muscular dystrophy

(continued)

Table 7.4 (continued)

Element	Functions
	("White muscle disease") in sheep and cattle and a myocardial disease in pigs can also be prevented with Se supplementation (often in combination with Vitamin E). Livestock require higher intakes of Se than humans. Excess Se causes various toxic (selenosis) conditions, including "alkali disease" lack of vitality, loss of weight, loss of hair, hoof deformation, dermatitis and lameness.
Zinc	Zinc is essential for DNA and protein synthesis, cell division and growth. It is required for male and female reproduction and neurological function and is also essential for immune function. In humans, the main consequences of Zn deficiency are: impaired immunocompetence, increased prevalence of childhood infections such as diarrhoea and pneumonia, impaired growth and development among infants, children and adolescents and impaired maternal health and pregnancy outcome. Animals cannot store Zn, so a continuous adequate supply is required. However, in general, few cases of Zn deficiency are reported in farm animals. Symptoms of deficiency disorders such as decreased growth, testicular atrophy, alopecia and dermal lesions are normally observed mainly in young animals. Hidden (or subclinical) deficiency is probably more important than acute deficiencies.

Based on: WHO [33], Kabata-Pendias and Mukerjee [16], Reilly [28] and Bell and Dell [6]

Table 7.5 Recommended dietary allowances (RDAs) in humans of the US National Academy of Sciences for copper, manganese, zinc, iron and selenium

Gender and age	Cu (mg d^{-1})	Mn (mg d^{-1})	Zn (mg d^{-1})	Fe (mg d^{-1})	Se (μg d^{-1})
0–6 months	0.2	0.003	2	0.27	15
7–12 months	0.22	0.6	3	11	20
Children					
1–3 years	0.34	1.2	5	7	20
4–8 years	0.44	1.5	8	10	150
Males					
9–13 years	0.7	1.9	11	8	40
14–18 years	0.89	2.2	11	11	55
19–30 years	0.9	2.3	11	8	55
31–50 years	0.9	2.3	11	8	55
50–70 years	0.9	2.3	11	8	55
>70 years	0.9	2.3	11	8	55
Females					
9–13 years	0.7	1.6	8	8	40
14–18 years	0.89	1.6	9	15	55
19–30 years	0.9	1.8	8	18	55
31–50 years	0.9	1.8	8	18	55
50–70 years	0.9	1.8	8	8	55
>70 years	0.9	1.8	8	8	55
Pregnancy					
≤18 years	1.0	2.0	12	45	60
19–30 years	1.0	2.0	11	45	60
31–50 years	1.0	2.0	11	45	60
Lactation					
≤18 years	1.3	2.6	13	45	70
19–30 years	1.3	2.6	12	45	70
31–50 years	1.3	2.6	12	45	70

From US Food and Nutrition Board of the National Academy of Sciences [23] and Reilly [28]

Table 7.6 Possible functions of other heavy metal(loid)s in animals and humans

Element	Possible functions
Arsenic	Various adverse responses to As deprivation diets (<12 μg As kg^{-1} rats and chicks and <35 μg As kg^{-1} goats) have been reported, including: depressed growth, abnormal reproduction (impaired fertility and perinatal mortality); depressed serum triglyceride concentrations and myocardial damage during lactation in goats. Arsenic appears to be involved in the methylation of metabolically or genetically important molecules whose functions are associated with methyl incorporation. Abnormally low As intake in patients undergoing haemodialysis correlated with injuries to their central nervous system, vascular diseases and cancer. Some beneficial effects of supranutritional doses of As in treatment of acute promyelocyte leukaemia through apoptotic (programmed cell death) mechanisms. If humans are found to need As, the requirement would probably only be 12–25 μg d^{-1}.
Cadmium	Cadmium-deprived goats and rats have shown depressed growth which was improved by increasing their intake of Cd. However, Cd has a long body half-life so even slightly elevated intakes could result in harmful accumulations (WHO max safe intake 70 μg d^{-1} for 70 kg person), typical daily intake is 10–20 μg.
Lead	Low dietary intake of Pb has been found to cause adverse effects in pigs and rats (depressed growth, anaemia, elevated serum cholesterol, phospholipds and bile acids; disturbed Fe metabolism, decreased liver glucose). Lead supplementation improved growth and alleviated Fe deficiency in rats. Any requirement for Pb is only likely to be very small (5–50 μg d^{-1}). Toxicity from excessive Pb intakes is much more important and is not dependent upon the route of exposure and can be predicted by blood Pb concentrations. When blood Pb reaches 10–15 μg dL^{-1}, toxic effects can occur in bone development, mental development and blood pressure. Anaemia, nephrotoxicity and more overt neurological impairments occur when blood concentrations are above 30 μg Pb dL^{-1}.
Nickel	Not proven to be essential, but experiments with Ni-deprived animals show it to be a bioactive element with some beneficial functions. Deprivation affects reproductive function in goats and rats, changes carbohydrate and lipid metabolism – possibly through depressed activities of enzymes degrading glucose and enzymes involved in the citric acid cycle. Nickel has beneficial effects in bone and may also have a function affecting Vitamin B12 (Ni can alleviate Vit B12 deficiency). If proved essential, Ni intake should probably be <100 μg d^{-1}.
Tin	Dietary deficiency of Sn has been reported to cause hair loss, depressed growth, response to sound, feed efficiency, heart zinc, tibial Cu and Mn, muscle Fe and Mn, spleen Fe, kidney Fe and lung Mn (Typical intake 1–40 mg Sn).
Vanadium	A bioactive element, whose only proven essential role is in several types of marine algae where it controls bromoperoxidases and iodoperoxidases. In humans and animals, it appears to have insulin-like actions at the cellular level stimulating cellular proliferation and differentiation. Bone abnormalities have been reported in V-deprived goats and so it appears to play a role in the formation and function of bone and connective tissue. Requirement is probably only 1–2 μg d^{-1}.

Based on: WHO [33], Kabata-Pendias and Mukherjee [16], Reilly [28], Neilsen [24] and Asher [4]

Low total concentrations of micronutrients (and most non-essential trace elements) are often found on sandy textured soils (e.g., Podzols) and/or on heavily weathered tropical soils (e.g., Ferralsols) and can give rise single and/or multi-element deficiencies. High soil pH values (>7.0) such as are found on calcareous, heavily limed or saline soils are likely to cause deficiencies of B, Cu, Fe, Mn, Ni and Zn. Multi-element deficiencies are also highly likely on these soils. In contrast, Mo

Table 7.7 Soil factors associated with micronutrient deficiencies

Soil Factor	Micronutrients likely to be deficient or low uptake
Sandy texture (low total concentrations)	B, Co, Cu, Fe, Mn, Mo, Ni, Se, Zn
Heavily weathered tropical soil (low total concentrations)	B, Co, Cu, Fe, Mn, Mo, Ni, Se, Zn
High organic matter content	B, Co, Cu, Fe (calcareous), Mn, Se
Low organic matter content	B, Cu, Zn
Free $CaCO_3$	B, Co, Cu, Fe, Mn, Ni, Zn
High Fe, Mn, Al oxides	Co, Fe, Mo, Se, Zn
Clay-rich soils (liable to waterlogging)	Cu, Mn, Zn
High pH	Co, Cu, Fe, Mn, Ni, Zn
Low pH	Cu, Mn, Mo, Se, Zn
High salt content	Cu, Fe, Mn and Zn
High HCO_3^-	Fe, Zn
Gleying/flooded soil	B, Co, Cu, Se, Zn (especially paddy soils)
Free drainage	Mo
High P status	Cu, Fe, Zn
High N Status	Cu, Zn
High concentrations of other nutrients	Co (Fe & Mn), Cu (Zn), Mn (Fe), Se (S/SO_4^-)

Based largely on Kabata-Pendias [15], Fageria et al. [9] and Alloway [2]

is likely to be highly available in high pH soils, but can be deficient in acid soils. Organic matter-rich soils, such as peats (Histosols), muck soils and heavily manured mineral soils are likely to have low available concentrations of B, Cu, Mn, Se and Zn [2]. However, as shown in Table 7.7, low organic matter contents can also predispose to deficiencies of B, Cu and Zn.

Clay-rich soils which usually have relatively high adsorptive capacities and tend to be imperfectly to poorly drained (gleyed) can be deficient in Cu, Mn and Zn. Paddy soils used for wetland rice production are prone to Zn deficiency, but can have toxic Fe concentrations due to the reduction of insoluble Fe oxides. In general, micronutrient deficiencies in crops and herbage, tend to be reflected in low intakes in animal and human diets. However, in the case of grazing livestock the soil-plant-animal pathway may be bypassed by direct (usually accidental) ingestion of soil and so the amount of metal(loid)s ingested by the animals may not be affected by soil-plant barriers. However, the presence of adsorbent minerals and antagonistic elements in the animal GI tract can modify the availability of the micronutrient to the animal.

7.5 Plant Factors Associated with Micronutrient Deficiencies

The plant factors associated with the onset of deficiencies in crop plants are covered in detail in Chap. 6, but one or more of the following factors are often found to be involved:

- 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,
- Agrochemicals (e.g., glyphosate-induced deficiencies of Mn & Zn),
- Antagonistic effects of other micronutrients (e.g., Cu–Zn, Fe–Cu, Fe–Mn, Cu–Mn etc.),
- Previous crop species – there is some evidence that the mineralization products of some plant species can render certain micronutrients less available in the soil. An example of this is Cu deficiency in wheat following oil seed rape (canola).

Based on: [2, 7, 9, 12, 13, 19, 22]

7.6 Concluding Comments

This short chapter has been included in this latest edition of 'Heavy Metals in Soils' to draw attention to the importance of many heavy metals such as Cu and Zn which are micronutrients in both plants and animals and the metalloid Se, a vitally important micronutrient in animals and humans (see Chap. 16, Sect. 16.4). More details are given in Chaps. 9–17 and 21 dealing with the respective heavy metal(loid)s, but it is useful to see them dealt with as a group, to allow comparisons to be made between them. Ongoing and future research may increase the number of heavy metal(loid) s classed as micronutrients.

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