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Trace Elements as Fertilizer Micronutrients

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15.1 Introduction

The occurrence of trace elements is ubiquitous – they can be found in soils, plants, waters, air, and humans (animals). The division of trace elements according to the groups in the periodic table is: trace elements of group 1: lithium (Li), rubidium (Rb), cesium (Cs); of group 2: beryllium (Be), strontium (Sr), barium (Ba), radium (Ra); of group 3: scandium (Sc), yttrium (Y), lanthanides, actinides; of group 4: titanium (Ti), zirconium (Zr), hafnium (Hf); of group 5: vanadium (V), niobium (Nb), tantalum (Ta); of group 6: chromium (Cr), molybdenum (Mo), tungsten (W); of group 7: manganese (Mn), technetium (Tc), rhenium (Re); of group 8: iron (Fe), ruthenium (Ru), osmium (Os); of group 9: cobalt (Co), rhodium (Rh), iridium (Ir), of group 10: nickel (Ni), palladium (Pd), platinum (Pt); of group 11: copper (Cu), silver (Ag), gold (Au); of group 12: zinc (Zn), cadmium (Cd), mercury (Hg); of group 13: boron (B), aluminum (Al), gallium (Ga), indium (In), thallium (Tl); of group 14: silicon (Si), germanium (Ge), tin (Sn), lead (Pb); of group 15: arsenic (As), antimony (Sb), bismuth (Bi); of group 16: selenium (Se), tellurium (Te), polonium (Po); of group 17: fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) [1]. In programs of agricultural development, the role of micronutrients is very important due to their role in increasing of crop yield and quality [2]. In agroecosystems, trace elements are present at low concentrations (mg/kg or less) [3]. However, their deficiencies in plants can affect animals and humans because they are their consumers.

The micronutrients that are known to be required by plants are boron, chlorine, cobalt, copper, iron, manganese, molybdenum, nickel, and zinc [4]. Aller *et al.* [5] indicated that some elements such as titanium, vanadium, cobalt, nickel, aluminum, silicon, arsenic, selenium, fluorine, and iodine have been shown to have some beneficial effects on the growth of only a few plant species. These plants use the listed trace elements in small quantities. Some of the trace elements, such as cobalt and selenium are not essential to plant growth but are required by animals and humans [3]. Some of the listed trace elements (e.g., cadmium, lead, chromium, mercury, and arsenic) are introduced to the

soil and then to plants by the use of fertilizers, animal manures, biosolids (sewage sludge), and compost [6]. They have no function in plant nutrition and have toxic effects on living organisms. They are considered as contaminants [3].

This chapter describes the effect of trace elements essential for plants (their deficiency and excess) on plant growth and development.

15.2 Fertilizers as a Source of Trace Elements – The Positive and Negative Aspects

The application of fertilizers aims to ensure guaranteed amounts of plant nutrients [7] and is effective in correcting micronutrient deficiencies in crop production [3]. However, in the agroecosystems there are different sources of trace elements, as well as toxic metals, not only fertilizers. Trace elements can originate from soil parent materials or inputs caused by human activities [3]. The main contributors to the trace element burden (especially the content of toxic metals) of cultivated soils are fertilizers and atmospheric dry and wet deposition [8]. He *et al.* [3] showed that the repeated use of metal-enriched chemicals, fertilizers and organic amendments such as sewage sludge, and wastewater may cause contamination on a large scale.

15.3 Effect of Trace Elements on Plant Growth and Development

Plants require adequate amounts of trace elements for proper growth [9]. These elements, essential to plant growth, must be in an available form in soils at the moment the plants need them for growth and development. If the soil is not able to supply trace elements to plants in the quantity and at the time the plants need them, they will present deficiency symptoms [8]. On the other hand, trace elements can also be toxic to plants at higher concentrations [9]. Both deficiency and toxicity of trace elements occur in agroecosystems [3]. If trace elements are present in soil in excess and in the available form, they can be taken up by plants and accumulated in plant biomass, which may consequently be hazardous for the plants as well as for animals and humans. Accumulated trace elements in organisms can cause several health problems, depending on the element [8]. Fertilizing agricultural soils in well-balanced manner, considering the status of trace elements in the soil solution, seems to be very difficult. This is not only because they are present at the trace level, but also because of the very narrow range of doses that give positive effects (Figure 15.1). Frequently, trace elements are overloaded or under-supplied [10, 11, 12, 13]. Low recommended supplement doses combined with simultaneously low bioavailability of supplemented forms of trace elements can contribute to serious symptoms of excess or deficiency that are described in the following sections.

15.3.1 Trace Elements

15.3.1.1 Boron

Boron found in soils is mostly inaccessible to plants [14]. Soil minerals contain insoluble boron in the form of tourmaline, as well as very soluble hydrated B minerals (e.g., boric

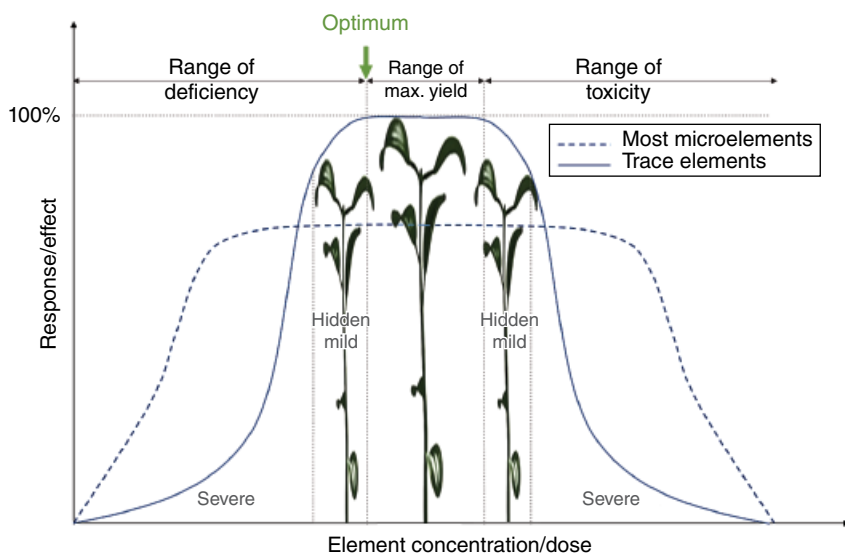


Figure 15.1 Plant growth dependent on the nutrient supply of soil. (See insert for color representation of the figure.)

acid $B(OH)_3$). For soil pH 4–8, boric acid is in a non-dissociated form, therefore boron can be easily leached from the soil [14]. This form of boric acid (potentially permeable to plant cells) is taken up by roots from the soil solution [14].

Boron plays a role in the processes that preserve cell wall structure, maintain membrane function, support metabolic activities, and pollination [15, 16]. It is also suggested that boron plays an important role in the legume–*Rhizobium* symbiosis, maintaining the cell wall structure of N_2 -fixing legume root nodules [15].

In the case of boron, there is a small window between deficiency and toxicity to plants [17]. Boron is immobile in plants, therefore deficiency symptoms appear in younger tissues [18]. The main symptoms of boron deficiency in soil solutions are the slowing down or ceasing growth of plants. Boron deficiency inhibits root elongation through limiting cell enlargement and cell division in the growing zone of root tips. Severe B deficiency can lead to the death of root tips. Additionally, leaf expansion is inhibited, that indirectly decreases the photosynthetic capacity of plants [19]. Boron deficiency can be solved by the application of boron-enriched fertilizers [17]. Borax (11% B) and sodium tetraborate (14 and 20% B) are the most commonly used boron fertilizers. Solubor (20% B), sodium pentaborate (18% B) and boric acid (17% B) are used occasionally for direct soil application or as a foliar spray [18].

The content of available boron in soil greater than 5 mg/kg can be toxic to many agronomic crops [18]. The symptoms of B toxicity involve marginal leaf burn, tip die back in young shoots, profuse gumming in the leaf axil, and the appearance of brown corky lesions along stems and petioles [16].

Further details concerning the role of boron in plants are available in the review papers and book chapters of Mengel and Kirkby [14], Brown *et al.* [20], Brown and Shelp [16], Dell and Huang [19], and Bolaños *et al.* [15].

15.3.1.2 Cobalt

The effect of cobalt on plant growth (absorption, transport and accumulation, biochemical functions, deficiency, as well as toxicity) is described in review papers and book chapters by Aller *et al.* [5], Mengel and Kirkby [14], and Palit *et al.* [21].

The main sources of cobalt in the soil are mining and smelting activities, the spreading of sewage sludge, and the use of fertilizers. Cobalt occurs in minerals such as cobaltite (CoAsS), smaltite ((Co,Fe,Ni)As₂) and erythrite (Co₃(AsO₄)₂·8H₂O) [22, 23]. Plants can accumulate small amounts of Co from the soil. Cobalt is absorbed by roots and involves active transport [21, 24]. Its uptake is limited by the presence of humus and high content of manganese in the soil [24]. Cobalt can be strongly adsorbed to oxide surfaces, particularly to Mn oxides [14], when is not then available to plants [21]. Cobalt is more available to plants as pH decreases [21].

Cobalt has been identified as an essential element for some but not all species of higher plants. Cobalt is crucial for symbiotic N₂ fixation in root nodules of leguminous plants which possess vitamin B₁₂ (cobalamin) and cobamide coenzymes and in the non-legumes (e.g., *Alnus glutinosa* and *Casuarina cunninghamiana*), as well as for rhizobial growth [14, 21]. Cobalt compounds (e.g., CoCl₂, CoSO₄) influence photoperiodism, heme biosynthesis, morphology, cell walls and cell membranes, germination, nitrogen fixation, growth, and yield and so on [21].

Vitamin B₁₂ is synthesized by organisms that are able to fix atmospheric nitrogen. Therefore, deficiency of cobalt in plants may result in symptoms similar to nitrogen deficiency (it can delay the onset of N₂ fixation because of the lower degree of *Rhizobium* infection) [14], as well as in reduced seed germination in dry conditions and reduced plant growth [21].

Toxic effects of excess amount of Co are related to the displacing by Co of other toxic metals in physiologically important centers. The symptoms of Co toxicity involve chlorosis, necrosis, and leaf fall. High concentration of cobalt in plants may result in iron deficiency. Therefore, symptoms are often characteristic of iron deficiency [14, 21].

15.3.1.3 Copper

The concentration of copper in soil solutions is usually very low (from $1 \cdot 10^{-5}$ to $6 \cdot 10^{-4}$ mol/m³) and decreases with increasing pH. Copper, under normal growth conditions, is taken up by the plant in only very small quantities since copper concentrations in most plant species is low and in the range of 5–20 µg/g dry matter [14, 25]. Both the lack and excess of copper in biotic systems is a potential hazard for plants. When copper concentrations in the leaves is below 5 µg/g dry weight, the signs of copper shortage become evident; at a concentration >20 µg/g, the signs of toxic effect of the metal are observed [26].

Copper is an essential micronutrient for plants, which belongs to the 3d transition elements along with iron, zinc, and so on. In living cells, divalent copper (Cu²⁺) is readily reduced to monovalent (Cu⁺) copper, which is unstable and gets oxidized back unless it is stabilized by strong ligands [27]. Copper is a vital micronutrient in organisms, most notably because it participates in the physiological processes of plants including photosynthesis, respiration, protein synthesis, carbohydrate distribution, nitrogen reduction and fixation, protein metabolism, and cell wall metabolism [28]. By binding to the cell wall copper supports processes of lignification, increasing cell wall strength. Copper is a cofactor for some enzymes, such as nitrate reductase and certain proteases. A wide

range of copper dependent processes largely depend on the activity of this metal as a cofactor of numerous enzymes: Cu/Zn superoxide dismutase (SOD), cytochrome oxidase, polyphenol- and monophenol oxidase, ascorbate oxidase, amino oxidase, laccase, urease, and so on [29].

However, despite being an important micronutrient, copper can be a potential toxicant at high concentrations due to its ability to catalyze the formation of harmful free radicals or to initiate lipid peroxidation [30], it may cause morphological, anatomic and physiological changes in plants, decreasing both food productivity and quality [31]. Copper is often applied to soil and crops as fertilizer to ameliorate micronutrient deficiencies caused by prolonged, intensive agriculture. It is also often used as a fungicide, especially in viticulture [28]. Continuous use of fungicides has caused copper accumulation in soils, which represent a major environmental and toxicological concern.

Copper is a trace element necessary for many different processes of plant life. Many of the symptoms of its deficiency in plants are associated with the deterioration of the cell wall structure. Lack of this element can be determined by some characteristic external appearances of a plant; for example, it can cause impaired lignification and enhanced risk of lodging, twisting flag leaves, dried out leaf tips, melanism, a dark pigmentation on the stem, peduncle, spike and grains, reduced intensity of leaf color, bent stems, and increased abortions of seeds [29].

Interactions between copper and other nutrients occur when plants are exposed to stresses that enhance low concentration of copper in the soil. High concentrations of copper in the soil have been reported to aggravate Zn deficiency in wheat by increasing growth and by depressing Zn absorption; Zn^{2+} and Cu^{2+} are antagonistic for absorption [32].

When soils are limited in copper, either copper must be added to correct the deficiency or plants which can tolerate low soil copper levels may be grown. Several Cu-based compounds have been used to amend Cu-deficient soils. Copper sulfate ($CuSO_4 \cdot 5H_2O$), copper oxychloride ($CuCl_2 \cdot 2CuO \cdot 4H_2O$), copper oxide (Cu_2O), and copper chelates ($Na_2CuEDTA$, $NaCuHEDTA$) have been used on different Cu-deficient soils worldwide.

15.3.1.4 Iodine

Although iodine is essential for animals, there has been no direct evidence of its essentiality in plant growth [5, 33]. Iodine has a stimulating effect on plant growth at low content in the soil – in the order of 0.1 $\mu g/g$. The uptake of iodine by plant roots from soil is difficult because most of this element is adsorbed with Fe and Al sesquioxides and the process of iodine desorption to soil solution is slow [34]. A method to improve iodine uptake by plants can be fertigation with iodine solution (e.g., KIO_3 , KI) [34] or cultivation of plants in the hydroponic systems [33]. Soluble inorganic iodine is readily available to plants [5]. Smoleń and Sady [34] showed that fertigation with iodine can be more effective in obtaining plants biofortified with this element than soil fertilization with iodine. Zhu *et al.* [33] found that the increased iodine concentrations (0, 1, 10, 50, and 100 μM of iodate – IO_3^- and iodide – I^-) in the growth solution (hydroponic cultivation) significantly enhanced iodine content in spinach plant tissues (*Spinacia oleracea* L.). Leyva *et al.* [35] also found that the application of iodine as iodate improved the antioxidant response (boosted the activity of antioxidant enzymes) of lettuce plants grown under salinity stress (100 mM of NaCl).

Iodine deficiency is rather better known in humans than in plants. However, its deficiency in soil and, consequently, in consumable plants can directly cause the limited supply of iodine in the human diet [33, 34]. It has been shown that the content of iodine in plants correlates positively to its concentration in soil solution [5]. In humans, iodine deficiency can cause inadequate synthesis of the thyroid hormone. About 80% of iodine in the human body comes from edible vegetable food [36].

The toxic effects of iodine on plants are observed at higher concentrations in soil and nutrient solution – in the range 0.5–1.0 µg/g [14]. The degree of phytotoxicity is dependent on the form of iodine that exists in the soil solution. Typically, I^- is more phytotoxic than IO_3^- , due to the greater ability of plant roots to absorb the reduced form [37]. The toxic effects of high iodine content begins in the older leaves [14]. The main symptoms of iodine toxicity involve chlorosis in older leaves, whereas in the younger leaves a very dark green color is observed. The growth of plants is severely limited. Moreover, the leaves curl back and necrosis occurs at the tip and edges. In severe cases the plant dies [5, 14].

Details concerning the effect of iodine on plant cultivation can be found in the review papers of Aller *et al.* [5] and Mengel and Kirkby [14].

15.3.1.5 Iron

Despite the high abundance of iron in most soils, iron is the major limiting factor for plant growth and development due to its low bioavailability [38, 39]. The soluble amount of iron in the soil is much less than the total iron concentration. The reason is that the solubility of hydrous Fe(III) oxides is extremely low [14, 25]. Because of that the plant can use only soluble forms of metal ions. Two main strategies for acquiring iron from soils are developed in plants: reduction of Fe^{+3} , because only Fe^{+2} can cross the plasma membrane [41]; production of phytosiderophores, small chelating compounds with high selectivity toward Fe^{3+} [14, 25, 40]. Both these strategies are systemically induced by iron deficiency.

Although iron is essential for plants and other organisms, it is potentially toxic and excess may also cause yield loss in crop plants. Therefore, iron homeostasis in plants is tightly regulated [42]. Iron is required as a cofactor for the activity of many proteins involved in essential cellular processes, such as the electron transfer chain in respiration, photosynthesis, DNA synthesis, and detoxification of reactive oxygen species (ROS) [43].

Iron is usually applied as a foliar spray in the form of chelates such as Fe-EDA (9% Fe) or Fe-EDDHA (6% Fe) [11]. The low mobility of iron in calcareous soils reduces the photosynthetic rate and alters chloroplast structure, leading to symptoms in young leaves generally described as chlorosis. Under these conditions plants show limited growth and yields, and the quality of fruit is poor [38, 44]. Some of these iron deficiency stress responses (enhanced ferric reducing capacity and acidification) are also induced by Cu-deficiency but not by the deficiency of other nutrients such as K, Ca, Mg, Mn, or Zn [46].

Plant iron nutrition does not rely only on iron availability but it is significantly affected by the changing availability of other essential nutrients in the rhizosphere. Previous studies suggest a reciprocal influence between sulfur and iron, in which the deficiency of one of the two nutrients induces physiological modifications allowing an adequate and balanced assimilation of the other element. In particular, plant capability to take up and accumulate iron is strongly dependent on S availability in the growth medium and, on the other hand, iron deficiency adaptation requires the adjustment of S uptake and assimilation rate [40].

15.3.1.6 Molybdenum

The role of molybdenum in agricultural plant production has been described in review papers and book chapters by Zimmer and Mendel [47], Kaiser *et al.* [48], and Mengel and Kirkby [14]. The source of molybdenum in agricultural soils is weathering from solid minerals such as molybdenite (MoS_2), wulfenite (PbMoO_4), and ferrimolybdenite [$\text{Fe}_2(\text{MoO}_4)$] [49].

Molybdenum is required by selected enzymes to carry out redox reaction activity. These enzymes participate in nitrogen metabolism (e.g., nitrate reductase and nitrogenase), purine catabolism (e.g., xanthine oxidase), hormone biosynthesis (e.g., aldehyde oxidase), and sulfur metabolism (e.g., sulfite oxidase). The molybdenum cofactor (Moco), in which molybdenum is an integral part, binds to molybdenum-requiring enzymes (molybdoenzymes) found in most biological systems (e.g., humans, microbes, animals, and plants) [47, 48]. Similar to cobalt, molybdenum is a structural constituent of enzymes related to N metabolism (*Rhizobium* bacteria in root nodules of legumes require molybdenum to fix atmospheric or molecular nitrogen), Vieira *et al.* [50] proposed the use of foliar application of molybdenum in the cultivation of legume plants (e.g., common bean crop). This approach can minimize the amounts of nitrogen applied in fertilizers which, in excess, can cause negative environmental effects. It was shown that Mo increased greatly the nitroge-nase activity and extended the period of high nitrate reductase activity.

The availability of molybdenum for plant growth strongly depends on the soil pH – in alkaline soils, molybdenum becomes more soluble and is accessible to plants mainly as anion MoO_4^{2-} . In acidic soils (pH lower than 5.5), molybdenum availability decreases [49].

Molybdenum is required by plants in very small amounts and has a narrow deficiency and toxicity range [48, 51]. Deficiency of molybdenum in plants is usually under 0.2 mg/kg in dry matter [14]. The occurrence of this deficiency is often associated with acidic soils [52]. Molybdenum is readily retranslocated within the plant. Its deficiency frequently begins in the middle and older leaves. Symptoms of Mo deficiency usually involve interveinal mottling, marginal chlorosis of the older leaves, upward curling of the leaf margins, and finally necrotic spots at leaf tips [14, 48].

A key factor controlling molybdenum toxicity is the strength of binding anionic species of molybdenum to positively charged soil components such as amorphous Fe and Al oxides and clays. This reduces the bioavailability and uptake of Mo by soil organisms such as higher plants [14, 51]. Molybdenum toxicity in plants cultivated under most agricultural conditions is rare [48]. High molybdenum content in soil can cause the accumulation of anthocyanins in tomato and cauliflower leaves, changing the color to purple. In legumes, the color changes to yellow [52].

Commonly used molybdenum fertilizers are: molybdenum fortified superphosphate applied that supplies phosphorus, sulfur, and molybdenum simultaneously in legume-based pastures; molybdenum trioxide used as a seed dressing for grass and/or legume seeds when establishing or over-sowing pasture; sodium molybdate or ammonium molybdate applied in solution, either as foliar sprays or through a boom-spray to the soil (Incitec Pivot Limited, Melbourne, Australia).

15.3.1.7 Manganese

Manganese (Mn) occurs in various primary rocks and particularly in ferromagnesian materials. The most important Mn soil fraction is Mn^{2+} , which can be dissolved in the soil solution or adsorbed to clay and humates [14]. Soils with higher Mn sorption

capacity have lower potential for plant absorption of Mn [53]. The level of Mn^{2+} in the soil depends on oxidation-reduction reactions and pH [2, 14]. As pH decreases, the amount of exchangeable manganese – mainly the Mn^{2+} form – increases in the soil solution [54].

In plants, manganese plays an important role in oxidation and reduction processes such as electron transport in photosynthesis, as well as in chlorophyll production and activation of enzymes (nitrate-reducing enzyme activity, enzymes in carbohydrate metabolism) [2, 54]. Manganese is an enzyme antioxidant-cofactor (superoxide dismutase) that protects plant cells by deactivating free radicals which can destroy plant tissue [2, 54]. Manganese shows the same properties as soil alkaline cations such as calcium and magnesium and other metals like zinc and iron. These metal ions influence the uptake and transport of manganese in plants [2].

Manganese deficiency in plants mainly occurs in soils with a high pH (mainly in arid and semi-arid areas of the world), in calcareous soils, and in soils with poor ventilation [2, 14]. In the case of Mn deficiency, photosynthesis efficiency is decreased and therefore also crop yield and quality. Typical symptoms of Mn deficiency are interveinal chlorosis, premature senescence of older leaves, and dark brown spots on leaves [2, 55]. Manganese deficiency is similar to magnesium deficiency [2]. In order to eliminate manganese deficiencies in plants, the application of fertilizers containing Mn is recommended. The most commonly used fertilizers containing manganese are: manganese sulfate ($MnSO_4 \cdot 3H_2O$, 26–28% Mn), manganese oxide (MnO, 41–68% Mn), manganese carbonate ($MnCO_3$, 31% Mn), manganese kalat (Mn-EDTA, 12% Mn), manganese chloride ($MnCl_2$, 17% Mn), and manganese dioxide (MnO_2 , 63% Mn) [2].

Manganese toxicity is a major factor that limits plant growth in acidic soils – high manganese content in the leaves reduces photosynthesis [2]. Toxicity of Mn is likely with plants that are fertilized with acid-forming fertilizers, high rates of superphosphate or nitrate (NO_3^-), being a source of nitrogen N, or plants that are low in silicon or deficient in calcium, iron, magnesium, or phosphorus [53]. Symptoms of Mn toxicity include reductions in biomass and photosynthesis, biochemical disorders such as oxidative stress, marginal chlorosis and necrosis of leaves, and plant roots turning brown. Brown spots (localized accumulations of oxidized Mn) on older leaves surrounded by chlorotic zones are typical indicators of Mn toxicity [53, 54].

Further information can be found in Campbell and Nable [55], El-Jaoual and Cox [53], Mengel and Kirkby [14], Millaleo *et al.* [54], and Mousavi *et al.* [2].

15.3.1.8 Selenium

Selenium (Se) is known to be an essential element for animals and humans, but has also been found to be beneficial to plants [56]. Selenium is present in soils in an organic form, as well as in inorganic anions such as selenide (Se^{2-}), selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}) [14]. Soluble species of selenium (SeO_3^{2-} and SeO_4^{2-}) are readily taken up by plant roots. Uptake of SeO_3^{2-} by plants is usually slower than SeO_4^{2-} [5]. Selenite (SeO_3^{2-}) binds strongly to Fe-oxides and clay minerals and is less mobile [57]. Therefore, selenate, which only occurs in aerated alkaline soils is the most important direct source for plant uptake [58]. In most soils, Se occurs in very low concentrations (0.01–2 mg/kg; world average is 0.4 mg/kg [57]) and often less than 0.2 $\mu g/g$ soil [14].

Selenium levels in plants are influenced by plant type and soil factors such as geology, soil type, and pH (the effect of pH on Se uptake decreases as the clay and organic-matter

concentrations in soils increases [59]). Other influential factors include the chemical form of selenium, soil water regime, concentration of sesquioxides, e.g., Fe_2O_3 and CaCO_3 , salinity, fertilizer treatment, rate of deposition of atmospheric selenium, climatic conditions, as well as temperature (the higher the temperature, the greater uptake) and rainfall (plants from high rainfall areas have a lower content of selenium than plants growing in areas with low rainfall) [5, 59].

There is a narrow range of concentration within which the effect of selenium on plants changes from beneficial to toxic [56]. In plants, selenium counteracts various abiotic stresses such as cold, drought, high light, water, salinity, and heavy metals (metalloids) [56]. Selenium often acts as an antioxidant in plants. The application of selenium can partially alleviate oxidative stress induced by high temperature and its negative impacts on physiology, growth, and grain yield from plants [60].

Selenium resembles sulfur in its chemical properties. Both elements have an affinity for the same uptake system and are therefore in competition in plant uptake [14]. Selenium toxicity is related to the incorporation of Se-cysteine (Se replaces S in this molecule) into proteins [14]. Plants can suffer selenium toxicity because it competes with essential metabolites for sites in the plant's biochemical structure and may replace essential ions – mainly iron, manganese, copper, and zinc. A negative correlation between higher concentrations of selenium in soil and plant growth (decreases in dry weight, root length, shoot height) has been observed [57].

Selenium is particularly important in animal nutrition and is required in very low concentrations [14]. Selenium can counteract the toxicity caused by toxic metals such as Cd, Hg (both inorganic and methyl-Hg), and Ag. Selenium is their antagonist and antioxidant [59]. Selenium deficiency in the diet is a common problem in many countries [56]. A source of selenium in a human diet can be the edible parts of crops. For this reason, fertilization of crops with Se is recommended in order to increase selenium content in animal and human food [14]. For example, Se can be added to commercial fertilizer in the form of sodium selenate [59].

Further details can be found in Aller *et al.* [5], Mengel and Kirkby [14], Fordyce [57], and Feng *et al.* [56].

15.3.1.9 Zinc

Zinc (Zn) is one of the most common elements in the earth's crust and the second most abundant transition metal in organisms after iron (Fe) [61].

The amount of zinc in unpolluted soils are typically lower than 125 mg/kg [62]. Insoluble zinc comprises >90% of soil zinc and is unavailable for plant uptake. Soil zinc occurs in three primary fractions: (i) water-soluble zinc (including Zn^{2+} and soluble organic fractions); (ii) adsorbed and exchangeable zinc in colloidal fraction (associated with clay particles, humic compounds, and aluminum and iron hydroxides); and (iii) insoluble zinc complexes and minerals [61].

Although it is recognized as a heavy metal, zinc plays a very important role in metabolic processes in plants [63]. As an essential micronutrient, it is necessary for normal plant growth as it is present in vital metabolic processes such as protein synthesis, maintenance of cell membrane integrity, and DNA transcription. Likewise, zinc plays important roles in starch synthesis and in ROS detoxification [64]. Of most significance is its activity as a cofactor in defining the structure and function of more than 300 enzymes, such as Cu/Zn superoxide dismutase (Cu/Zn-SOD), carbonic anhydrase, and

sorbitol dehydrogenase [65], and is the only metal represented in all six enzyme classes (oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases) [61]. Zinc plays a vital role in various processes such as plant photosynthesis, carbohydrate metabolism, and phytohormone regulation. Zinc directly participates in the biological synthesis of auxin and gibberellin [65].

Zinc concentrations in plants vary between 0.02–0.04 mg g⁻¹ dry weight while at concentrations above 0.2 mg g⁻¹ dry matter potential phytotoxicity develops. Beyond initiating negative interferences with the uptake of other nutrients and enzyme activities, excess Zn²⁺ elicits wilting [62], chlorosis, necrosis of old leaves, biomass decline and inhibition of cell elongation and division, decreased root number and length, and a sharp depression in the mitotic activity of root growth [66]. Other common zinc toxicity effects include decreases in tissue water content and changes in P and Mg concentrations in plant tissues [67].

Zinc deficiency is a major problem in agricultural crops of many world regions as it is estimated that approximately 30% of the agricultural soils in the world are zinc deficient which is a major threat to crops [26, 64]. Zinc deficiency causes significant disturbances in plant growth and development due to the large diversity of essential cellular functions and metabolic pathways directly influenced by zinc; a low zinc concentration induces accumulation of amino acids and reducing sugars in plant tissue [62]. Its deficiency results in depressed photosynthetic rates, and ultimately influences yield and quality [65]. Severe symptoms such as interveinal chlorosis in leaves, reddish-brown or bronze tints, epinasty, internode shortening, inward curling of leaf lamina, and reductions in leaf size have been associated with zinc deficiency [68]. Zinc is usually applied to deficient crops as foliar spray of zinc sulphate (e.g., 23% Zn) or zinc chelate (e.g., Zn-EDTA), for soil application a rate of 5–10 kg/ha zinc is recommended [11].

15.3.1.10 Silicon

The effect of silicon (Si) (deficiency and excess) on plant growth and development is described in Chapter 10 (*Fluorine and silicon as essential and toxic trace elements*). For further details see also review papers by Aller *et al.* [5], Tubaña and Heckman [69], Epstein [70], Sacała [71], Ma *et al.* [72], Guntzer *et al.* [73], Mengel and Kirkby [14], and Haynes [74].

15.3.1.11 Nickel

Nickel is one of many trace metals widely distributed in the environment, being released from both natural sources and anthropogenic activity [75]. Its content in soil varies across a wide range from 3–1000 mg/kg [76]. It can exist in soils in several forms: inorganic crystalline minerals or precipitates, complexed or adsorbed on organic cation surfaces or on inorganic cation exchange surfaces, water soluble, free-ion, or chelated metal complexes in soil solution [75, 76]. The Ni²⁺ ion is most likely to predominate in the soil solution to participate in sorption reactions and to be taken up by plants [77].

With decreasing pH, the solubility and mobility of nickel increases, hence, soil pH is a major factor controlling nickel solubility, mobility, and sorption [76]. Nickel from anthropogenic sources is more readily taken up by plants than that from naturally occurring sources [76]. Some fertilizers and soil amendments, which are used in agriculture, are important sources of nickel in soil. Phosphate rock, which is used as a raw material for phosphorus fertilizers, is known to contain nickel ranging between

16.8–50.4 mg/kg [78]. With increasing nickel pollution, an excess of nickel rather than deficiency, is more commonly found in plants [79].

Nickel is a functional constituent of seven enzymes. Among the seven, urease is extremely important to N metabolism in plants. Without the presence of nickel, conversion of urea into the ammonium ion which is used by plants as a source of N, is impossible. Nickel is accumulated in plant organs or tissues, such as leaves [80].

Nickel toxicity levels given in the literature varies widely between 25–246 mg/kg dry weight of plant tissue, depending on the plant species and cultivars [76]. The symptoms of nickel toxicity in plants includes: inhibition of mitotic activities, reductions in plant growth, adverse effects on fruit yield and quality [79, 86], chlorosis and inhibition of root system growth [77], and sometimes brown interval necrosis and symptoms specific to the plant species [78].

Although, visual symptoms of nickel deficiency are relatively rare in plants compared with other essential micronutrients, mostly because of the low levels needed by plants (about 1–100 ng/g dry weight) in relation to the relative abundance of nickel in the soils (>5 kg/ha) [79], scarcity of nickel can be severe enough to trigger both visual and non-visual signs that may be more common than generally supposed [81, 82]. The existence of nickel deficiency is becoming increasingly apparent in crops, especially for ureide-transporting woody perennials [79, 83].

High levels of zinc, copper, iron [84], cobalt, cadmium, or magnesium in the growing medium can induce nickel deficiency. Crops that are most sensitive to nickel deficiency include legumes (beans and alfalfa), pecans, plum, peach, citrus, barley, wheat, and certain wetland plants. Minor nickel deficiency displays no visual symptoms, but can reduce growth and yield of plants. Significant nickel deficiency will display visual symptoms typically in the old leaves of the plants as nickel is a mobile element. Deficiency symptoms in legumes are exhibited as whole leaf chlorosis along with necrotic leaf tips (caused by the accumulation of toxic levels of urea) [80]. In woody ornamentals, symptoms occur in the spring in emerging new growth and may include shortened internodes, weak shoot growth, death of terminal buds, and the eventual death of shoots and branches. In pecans, the symptoms are similar to woody ornamentals, but also include decreased expansion of the leaf blade and necrosis of the leaf tips. The leaves develop a condition called “mouse-ear” in which the leaflets are small with rounded tips rather than long and pointed tips [79, 86].

15.3.1.12 Chlorine

Natural inputs of chlorine (Cl) to soils come mainly from rainwater, sea spray, dust, and air pollution. In addition, human practices, such as irrigation and fertilization, contribute significantly to chlorine deposition [85]. Chlorine occurs predominantly as Cl^- in soil and plants, and is mainly available to plants in this form [86]. Chlorine (in chloride form) plays a role in fungal degradation of lignin, humic substances, and phenolic organic matter that constitute important components of the soil environment [87]. Chlorine is a critical micronutrient in plants [88]. Because of its physicochemical properties its presence is one of the elements crucial in growth, photosynthesis, and activation of enzymes in plants [89]. Chlorine accumulates in certain tissues or single cells such as guard cells and plays an essential role in stomatal regulation [90]. The opening and closing of stomata is mediated by the flux of potassium and anions such as malate and chloride [86, 91].

Chlorine is vital to all plants, but for many plants high doses and concentrations are undesirable (e.g., potato, tobacco, hops, vegetables such as beans, cucumber, onion, lettuce, strawberries, and blueberries). Chlorine is considered as an essential micronutrient and plays an important role in the process of photosynthesis and transpiration. For many plants such as sugar beet, fodder beet, cabbage, celery, and spinach, chlorine promotes growth. Chloride is one of the main components responsible for salt stress [92]. Plants respond to salt stress by decreased growth rates, with corresponding formations of smaller and fewer leaves and reduced plant height. Consequently, changes in cell wall properties, cell water relations, and a reduction in photosynthetic rate, are observed. High accumulations of Na^+ and Cl^- lead to strong shoot reduction in plants [93].

The main chlorine-deficiency symptoms are as follows: reduction of leaf surface area, wilting of the plant, and restricted, highly branched root systems [91].

15.4 Forms of Trace Elements

Trace elements play many crucial functions in plant nutrition as has been described in this chapter. Micronutrients should be present in sufficient plant-available concentrations in the soil to ensure optimum productivity [94]. Agricultural fields have been fertilized with macronutrients for decades but fertilization with trace elements has been limited [95], since there was no need for their supplementation in the soil. Trace elements in the soil originate primarily from rocks subjected to geochemical and pedochemical weathering processes through which soil materials are formed. Secondary sources of trace elements include products formed by plant and animal decay, as well as from natural waters, materials from the atmosphere, fertilizers, insecticides, and fungicides [96]. But because of intensive agriculture, soils become deficient in many valuable trace elements, which creates a need for their supplementation in the soil [97].

Trace elements in soils may exist in the following forms: (i) in the soil solution; (ii) exchangeable ions bound by the electric charges of soil particles; (iii) complexes with organic material; (iv) precipitated; (v) occluded during the development of new solid phases in which they are not principal constituents, and (vi) constituents of soil minerals [96].

The total amounts of trace elements in soil naturally have a beneficial influence on the soluble or plant-available amounts [25]. The availability of different trace elements to plants, and the factors affecting it, varies considerably from one trace element and medium to another [98]. Several factors such as parent material, climate, texture, cropping intensity, pH, organic matter, clay minerals, moisture content, redox potential, and interrelations of trace elements and so on, influence solubility and the availability of trace elements to plants, which affects deficiency or toxicity [45, 96, 99]. Among trace elements, both cations and anions can be found, and factors affecting their availability are illustrated in Figure 15.2.

Trace elements are released into the soil solution as weathering decomposes silicate minerals, and a number of factors affects their chemical form, thus influencing their availability [100]. Trace elements may precipitate immediately or remain in solution depending on the ratio of ion charge to radius (in nm), often called the ionic potential (IP) [101]. Figure 15.3 shows the three main groups of trace elements divided according to the IP value, which determines the likelihood of specific chemical forms being

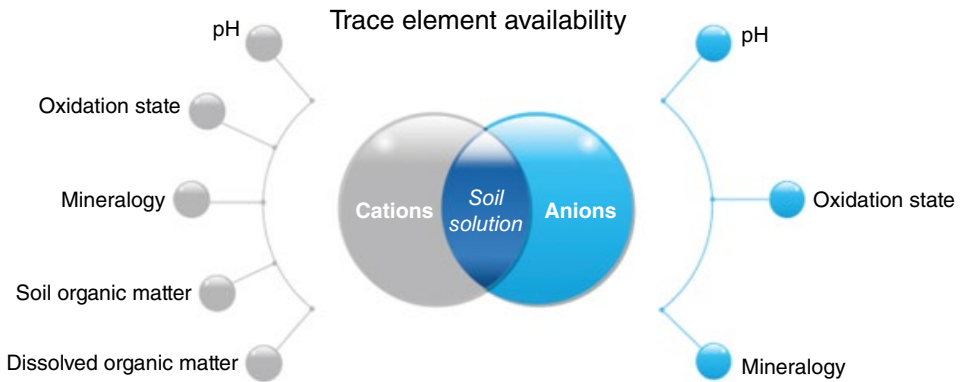


Figure 15.2 Factors affecting the availability of anions and cations of trace elements to plants. (See insert for color representation of the figure.)

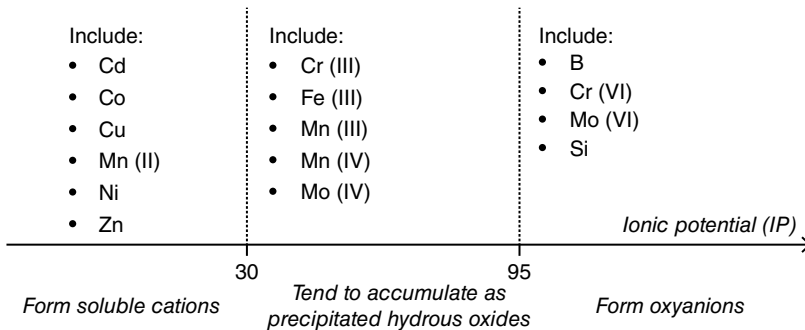


Figure 15.3 A graph that represents how ionic potential (IP) influences the chemical form of trace elements in the soil.

present. Cations, even those soluble with $IP < 30$, may become “trapped” in precipitates of compounds derived from elements with IP values between 30–95 [101].

Trace elements are usually added in the fertilizer production processes as dry salts, either as oxides or sulfates [102, 103]. Trace elements in solid forms can be mixed with the fertilizer blend and applied to the soil at the same time (if the soil pH is suitable) [104]. Trace elements in liquid forms can be used either as a foliar application to the leaves, or drip fed through fertigation/irrigation systems [105]. If the soil pH is above 8.0 (in water), foliar application of trace elements is the only suitable method of application [106]. Chelates are also used, but mainly in the liquid form [107]. Sulfates are regarded as being more soluble (and more available) than oxide formulations. However, in the soil environment both formulations react with soil constituents and become immobile in the months after application [108].

It is difficult to find any improved effect of, for example, nitrates, carbonates, or chelates compared to traditional and cheaper sulfates [109] because of very low concentrations of these compounds in soil solutions. The sulfates are water-soluble and readily available to plants, while the oxides are citrate soluble [110]. Trace elements can also be processed as water-soluble chelates where the cations are tied up to chelating agents. Chelates can be

added directly to the process and will act efficiently with high water-solubility. However, chelates are more expensive than oxides or salts, and are less frequently used in fertilizer technologies. The amount of cations may typically vary in the range 0.01–0.2% by weight in compound fertilizers [111]. Agronomically, a product which incorporates sulfates, oxides, and oxy-sulfate forms is considered best management for trace element applications [111].

Stability aspects are of crucial importance when designing and using products based on chelate chemistry, and factors like pH and heterogenic interactions must be taken into consideration [95, 112]. For example, some chelates are stable as long as the pH is kept on the acidic/base side, but as soon as a critical pH is exceeded, precipitated forms of trace elements can be observed because the competing equilibrium of chelate formation will “pump” trace elements out of the complex [95, 113]. Recently, some attempts have been made to introduce micronutrients to nitrogen fertilizers by applying the chelating properties of EDTA, with both ion-exchange properties of zeolites. Grupa Azoty ZAK SA (Poland), which is the second largest producer of fertilizers in Europe, led two implementation projects on nitrogen fertilizer with microelements that could solve the problem of the shortage of trace elements in agricultural soils.

Besides inorganic or chelate forms of trace elements, animal manure is also an important source of trace elements because most of the trace elements in animal feed are excreted by animals in manure and can then be incorporated in plant biomass when delivered in an available form [114].

However, more important than the form of nutrient used in fertilization is distribution through the soil and the time of delivery. The more sites available for plant roots to intercept nutrients, the less chance there is of deficiencies. The time of supplementation seems to be the most important factor when mitigating symptoms of deficiency, since the plant requirements for nutrients changes during the vegetation period. Therefore, it is important to deliver nutrients at a specific time, so that the root of the plant will be able to take up nutrients from the soil solution before it becomes unavailable to plants.

15.5 Conclusions

The trace element content of agricultural soils shows large regional and local variations, nonetheless, the decreasing pool of trace elements requires attention. Well-balanced fertilization of agricultural soils is a critical component in successful crop production. Very low levels of trace elements in soils need to be recognized regarding both the sufficiency for crops and for human diets. Since the concentrations of trace elements in crops are lower than the requirements for livestock nutrition, these elements are supplemented as mineral salts into animal feed to fulfil recommendations. Inorganic forms of trace elements are less available than biological forms. Reductions in trace element concentrations may result in unhealthily low intakes by domestic animals and humans and increased risks of deficiency-related symptoms and diseases. Fertilization seems to be one possible method for achieving suitable concentration levels of essential trace elements in agricultural crops. But, to achieve this it is necessary to use the best possible forms available to plants and efficient methods of delivery. These are the main issues that need to be solved in the future in sustainable agriculture.

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