

Trace elements in soil: status and management

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Introduction

There is an increasing awareness of the need to pay greater attention to the role of trace elements in plant and animal nutrition as we seek to explain the adverse effects of deficiencies and toxicities, and avoid suboptimal concentrations that limit the attainment of optimum economic yields of crops and animal productivity and welfare. The term trace element is useful but imprecise because it can refer to any element in the soil-plant-animal system regardless of its role. Originally the term was applied to the many elements found in plants at concentrations that were so small that the then available methods of analysis could only report them as “a trace”, and often before any role could be assigned to them. Now with modern analytical techniques, concentrations as little as ng g^{-1} can be determined but there is still uncertainty about the optimum concentration of many trace elements in plant tissue and even less information on adequate levels of plant available trace elements in soil.

Some trace elements are essential nutrients for plant growth and often also for food and feed quality because the primary route for their intake by humans and animals is plants. These trace elements might better be called micronutrients. Included in this group are boron, chlorine, copper, iron, manganese, molybdenum and zinc. The importance of other trace elements found in plants but, as yet without any recognised function, relates to their role in animal nutrition. Their presence in plants would appear to have allowed animals to use them in their metabolic processes, often in enzyme systems. Among such elements are cobalt, chromium, fluorine, iodine, nickel and selenium. Animals having developed a dependency on these trace elements they too could be described as micronutrients. More elements have been shown to be essential for animals than for plants. Thus it is essential that micronutrients, whether required by plants or animals, are present in sufficient plant-available concentrations in the soil to ensure optimum productivity.

A problem with the term trace element is that it might suggest that, even if an element is not essential for plants or animals, it has no adverse effect on either. But some elements can accumulate even as traces to concentrations that are toxic to the plant or to the animal feeding on it. For example, plant growth is adversely affected by excess manganese (Mn) and aluminium (Al) in many soils if they are allowed to become acid, or by nickel (Ni), cobalt (Co) or chromium (Cr) in acid soils derived from minerals in which there is a natural abundance of these elements. In other soils, concentrations of trace elements have increased as a consequence of human activity and such pollution often results in increased plant uptake with adverse effects on humans, as for example with cadmium (Cd). In these cases it is essential to ensure that the concentration of the element in the soil solution does not exceed an agreed critical value.

The microelements that are required in trace amounts by plants and animals and the range of concentrations of each element found in soil are in Table 1. For a general review see Adriano (1986) and Mertz (1981).

Table 1. Essential micronutrients for plants and animals. (Adapted from Wild, 1988)

Element	Plants	Animals	Typical range of soil content ¹
Boron	Y	*	0.9 - 1000
Chlorine	Y	Y	18 - 806
Cobalt	*	Y	0.3 - 200
Chromium	*	Y	0.9 - 1500
Copper	Y	Y	2.5 - 60
Fluorine	*	Y	6 - 7070
Iodine	*	Y	<0.09 - 80
Iron	Y	Y	0.01 - 21%
Manganese	Y	Y	<1 - 18300
Molybdenum	Y	Y	0.07 - 5
Nickel	*	Y	0.1 - 1523
Silicon (as dioxide)	*	Y	50 - 70%
Selenium	*	Y	0.03 - 2
Zinc	Y	Y	1.5 - 2000

Y, essential; * essentiality not yet established

¹ Units of measurement mg kg⁻¹ except where % is used

Sources of trace elements in soils

The trace element content of a soil depends initially on the parent material from which it was formed (Mason and Moore, 1982) but subsequent leaching and nutrient cycling through plants and animal excreta creates both depletion and enrichment often in specific soil horizons. The soil profile can also gain elements through deposited dust, important in areas prone to dust storms, by adsorption from water draining into a soil from elsewhere and by pollution due to human activity.

Depending on their valence and ionic radius, trace elements can become incorporated in silicate crystals and one ion can substitute for another. For substitution to occur, the ionic radius of the two ions must not differ by more than 15%. For example, the ionic radius of magnesium (Mg) is 66 pm (pm = 10⁻¹² m) and it can be replaced by cobalt (II) (72 pm), chromium (III) (63 pm), nickel (69pm) and zinc (74pm). Consequently, soils derived from basic rocks are usually not deficient in micronutrients and crop deficiencies occur rarely. Indeed, toxicities may sometimes be a problem on such soils, for example soils derived from serpentine can contain large amounts of plant available chromium (Cr) and nickel (Ni), and on these soils a flora tolerant of the large concentrations of these two elements can be found. In contrast, acid igneous soils are generally poor in some micronutrients so that deficiency adversely affects plants and animals. For example, Co deficiencies are common on soils derived from granite or rhyolite. There is a complicating factor in relation to the forms of metallic micronutrients. If sulphur (S) is present then metal ions are preferentially bound to S atoms rather than oxygen (O) atoms. Such sulphide ore minerals when they occur in rocks near the surface of the Earth, weather and release the metals, especially copper (Cu), lead (Pb) and zinc (Zn), and they then accumulate in soil. As with the presence of large amounts of Cr and Ni, this has led to the development of specialised, metal-tolerant flora. The ability to develop tolerance and accumulate such metals, has led to a search for plants that will remove metals from metal-contaminated soils.

Agriculturally, the main sources of trace elements are the sedimentary rocks that cover about 75 percent of the earth's surface. As the primary minerals weather, the alkaline earth elements and alkali metals tend to remain in solution and some of the metallic micronutrients pass into the lattices of the secondary or clay minerals, while others are adsorbed onto clay-

sized particles or become incorporated into humified organic matter. Where the composition of a soil is closely similar to that of the parent material i.e. for young soils, it is possible to make some generalisations about their trace element content. For example, soils derived from shales often have a satisfactory trace element composition.

In contrast to the very broad generalisations that can be made about the likely trace element content of young soils, little general guidance can be given about the trace element composition of old soils rich in Fe, Mn and Al oxides. This is because old soils have undergone very variable degrees of weathering.

Trace elements are released into the soil solution as weathering decomposes silicate minerals and a number of factors then come into play. 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). Elements with ratios above 95 form oxyanions and they include B, Cr (VI), Mo (VI) and silicon (Si). Elements like Cd, Co, Cu, Mn (II), Ni and Zn have IP values below 30 and form soluble cations. These soluble cations may become “trapped” in precipitates of compounds derived from elements with IP values between 30 and 95. Elements in this group include Cr (III), Fe (III), Mn (III), Mn (IV) and Mo (IV). They tend to accumulate as precipitated hydrous oxides in the residues from weathered silicate minerals and are found as discrete particles or as a coating on soil crumbs and the soil around voids within soil. The chemical control that these hydrous oxides exert on the action of other ions far exceeds what might be expected from their concentrations (Jenne, 1986). As the hydrous oxides are formed, other trace elements can be occluded in the precipitate (Taylor and Giles, 1970). For example, both Ni and Co are associated with Mn oxides and Cu and Zn with both Mn and Fe oxides. As pH increases, the hydrous oxides have strong adsorption affinities at their surfaces for trace cations and after adsorption the ions can migrate by solid state diffusion into the clay lattice on which the oxide is held. Hydrous oxides can also dissolve and then precipitate again in response to changes in soil pH and redox potential and this can cause changes in the plant availability of the trace elements. The plant availability of many micronutrients depends on soil pH. Boron, Cu and Zn are plant available over a soil pH range of 5 to 7 but Fe and Mn have greater availability below pH 6 whilst Ca and Mg are more available above pH 6.5.

Under undisturbed vegetation, especially on light textured soils, the distribution of trace elements in the soil profile is strongly influenced by their uptake by plants from a large volume of soil and their subsequent return to the surface in leaf fall. Under these conditions, trace elements are retained initially in association with organic matter (Swain and Mitchell, 1960), but as the humus decomposes the trace elements can move down through the soil profile in drainage water and be lost or they can be retained in clay rich horizons lower down the profile. When such light textured soils are reclaimed for agricultural use micronutrient deficiencies can occur because soil cultivation increases the rate at which humus decomposes and the biogeochemical cycling of the elements is disrupted when they are removed in the harvested produce.

Availability of micronutrients to plants

In general, the total content of a micronutrient in soil is only a very broad guide to its plant availability. In consequence, many chemical solutions have been tested as extractants for removing from soil amounts of micronutrients that relate to their availability to plants, and from the data indices of their plant availability have been developed. The data can be used in three ways. (i) To identify soils where a response to an application of the element in question might be expected or to identify or confirm a micronutrient deficiency following an observation that lack of an element might be the cause of poor growth. (ii) To identify soils, especially contaminated soils, where crop uptake of an element could lead to problems of

food/feed quality, e.g. soils with too large concentrations of Cd, Pb or arsenic (As). (iii) To identify the major soil pools of micronutrients (and toxic metals) by a chemical fractionation of the soil.

The same extractants can be used for all three purposes. Although no extractant is based on any firm theoretical foundation, all have proved of practical assistance in both advisory work and laboratory studies. Some of the more commonly used reagents are listed in Table 2 in the order in which they are used for sequential extraction and this relates to their increasing ability to extract more firmly bonded micronutrients and those in less soluble forms.

Table 2. Some common soil extractants used to extract micronutrients from soil and the chemical forms they are thought to extract. (Adapted from Wild, 1998)

Soil fraction	Common extractant
Soil solution	H ₂ O; 0.01 M CaCl ₂
Readily exchangeable	0.5 M CH ₃ COONH ₄ ; 0.2 M MgSO ₄ 0.1 M NH ₄ Cl; 1 M NH ₄ NO ₃
Specifically sorbed	0.5 M CH ₃ COOH; 0.1 M HCl; 0.1 M HNO ₃
Organically bound	0.05 M EDTA ¹ ; 0.05 M EDDHA ² ; 0.005 M DTPA + 0.1 M TEA + 0.01 M CaCl ₂ ³
Hydrous oxide bound	1 M CH ₃ COONH ₄ + 0.002 M C ₆ H ₆ O ₂ ⁴ 0.2 M (COO) ₂ (NH ₄) ₂ + 0.15 M (COOH) ₂ at pH 3.3
Residual	HF; Mixtures of hot concentrated acids

¹ Ethylene diamine tetraacetic acid, disodium or diammonium salt.

² Ethylene diamine di-(*o*-hydroxyphenyl acetic acid).

³ Diethylene triaminopentaacetic acid and triethanolamine with calcium chloride at pH 7.3.

⁴ Hydroquinone (1:4 dihydroxybenzene).

The concentration of micronutrients in the soil solution, from which plant roots take them up, is usually at the micromolar level. But micronutrient ions rarely exist in the soil solution in simple forms; they are usually complexed with both inorganic and organic ligands. Thus there has been much work on chemical speciation of micronutrients and complex computer programmes have been written to predict the main species in very dilute solutions. Table 3 lists the principal chemical species for some elements in aerobic soils in acid and alkaline conditions and the order from left to right is approximately that of decreasing concentration.

Table 3. Principal chemical species of trace metals in acid and alkaline soil solutions in aerobic soil conditions.

Metal	Principal species	
	Acid soils	Alkaline soils
Mn(II)	Mn ²⁺ , MnSO ₄ , Org*	Mn ²⁺ , MnSO ₄ , MnCO ₃ , MnHCO ₃ ⁺
Fe(II)	Fe ²⁺ , FeSO ₄ , FeH ₂ PO ₄ ⁺	FeCO ₃ , Fe ²⁺ , FeHCO ₃ ⁺ , FeSO ₄
Ni(II)	Ni ²⁺ , NiSO ₄ , NiHCO ₃ ⁺ , Org	NiCO ₃ , NiHCO ₃ ⁺ , Ni ²⁺
Cu(II)	Org, Cu ²⁺	CuCO ₃ , Org
Zn(II)	Zn ²⁺ , ZnSO ₄	ZnHCO ₃ ⁺ , ZnCO ₃ , Zn ²⁺ , ZnSO ₄

Nutrient uptake and root characteristics

As plant roots take up nutrients from the soil solution they are replenished by mass flow or by diffusion in response to the concentration gradient caused by depletion at the root surface (Davies, 1980). The processes that regulate nutrient uptake characteristics are not well understood and are specific for each ion. In general, for a given external concentration, the inflow is greater when the concentration within the plant is small than when it is large. To determine the effect of the nutrient composition of the plant on uptake characteristics requires very carefully conducted experiments (Junk, 1970) and will not be discussed further here.

Root exudation and the rhizosphere

The immediate vicinity of a plant root, the rhizosphere, is important for nutrient uptake although it extends only 1-2 mm from the root surface. Within the rhizosphere are numerous microorganisms whose existence depends on the release of organic and inorganic material from the root. Whether organic compounds such as acids and chelates produced by rhizosphere organisms have any major influence on nutrient availability by dissolving compounds within the soil or by chelation of some elements making others more available is still an open question. It has been postulated that elements like Fe, Cu and Zn that readily form chelates could be made more available to higher plants.

The pH of the rhizosphere will affect nutrient availability and the form in which nitrogen (N) is supplied to the plant affects rhizosphere pH. Compared to the bulk soil outside the rhizosphere, the pH of the rhizosphere can be increased by one pH unit when nitrate N is applied and it can be decreased by one pH unit when ammonium N is applied. These pH changes are important for phosphorus (P) supply and may be for micronutrient supply also. There is evidence that rhizosphere pH is decreased when plants are suffering from a shortage of Fe (Marschner, 1983), the decrease in rhizosphere pH increases its availability.

Organic acids exuded by roots have been shown to increase the availability of some micronutrients. For example exuded malate ions appear to be important in the solubilization of MnO₂. Jauregui and Reisenauer (1982) have suggested that MnO₂ is reduced by exuded malate and chelation of the Mn²⁺ produced prevents its re-oxidation and increases its mobility in the rhizosphere.

Sites of localised low pH can occur in the rhizosphere. Within the root clusters (proteoid roots) of certain plants there can be an intensive extraction of nutrients from a limited soil volume because the exudates do not diffuse into a large volume of soil. Citric acid is the dominant compound in the proteoid root exudates of white lupin, *Lupinus albus*, (Gardner *et al.*, 1983) and is effective in mobilising Fe, Mn and Zn in the rhizosphere and this is an efficient way of increasing the uptake rate of these elements and their content in the plant. (Marschner, 1995).

Mycorrhizae and the mineral nutrition of their host plant

For micronutrients that occur in very small concentrations in the soil solution and frequently tend to be immobile, there is evidence that mycorrhizal fungi can play an important role in the uptake of some elements as judged by distinct improvements in growth often seen in plants with mycorrhizal associations. Mycorrhizal fungi occur in soils in close association with plant roots and are divided into two groups, ectotrophic and endotrophic mycorrhizae. Ectotrophic mycorrhizae (ECM) cover roots and rootlets with a thick mantle of hyphae that spread between the cortical cells of the roots ensuring close contact with the root. These fungi are mainly found on the roots of trees and shrubs and are of economic importance for the growth of forest trees.

Many plant species, including most agricultural crops, have endotrophic mycorrhizae of which vesicular arbuscular mycorrhiza (VAM) is the predominant type of fungal infection. The fungus has mycelium that actually penetrates cells in the root cortex and these are connected to an external mycelium in the root rhizosphere and soil. Both in the cortex and the

rhizosphere the hyphae branch extensively and the fine hyphae can enter pores within the soil that are too small for root hairs to enter. Thus they can access nutrients that would otherwise be unavailable to the plant.

For both ecto- and endo-mycorrhiza, the symbiotic association of host and fungus is such that only living roots are infected and the infection does not damage the root. The host provides the fungus with life-sustaining organic compounds while the fungus assists the roots in exploiting the soil for water and inorganic nutrients. These beneficial effects have been extensively studied in relation to the phosphorus (P) nutrition of crops (Tinker, 1980). However, VAM appear to be of particular importance for leguminous species because their presence enhances N fixation, perhaps because the fungi increase the uptake of Co, Mo, Cu and Fe, elements known to be involved in N fixation. Besides pasture and forage legumes, most crop species, including onions, maize, wheat, barley and many vegetables, have VAM associations, the most notable exceptions are brassicas and sugar beet.

The benefits of mycorrhizal associations in the uptake of micronutrients have been studied less than those for P. The uptake of Zn and Cu are usually larger in plants with VAM than in those without (Kothari *et al.*, 1990a,b). The uptake of these two elements by the external hyphae of VAM can account for about 50-60% of their total uptake in white clover and 25% in maize; and there is evidence that the plant regulates the uptake of P and Cu separately (Kothari *et al.*, 1990a,b; Li *et al.*, 1991). As a consequence of the greater uptake of Zn and Cu by VAM plants, the shoot contents are larger than those of non-mycorrhizal plants. It has also been observed that VAM may enhance Zn toxicity in the host plant when there is a large external supply of Zn (Schuepp *et al.*, 1987).

In contrast to the benefit bestowed by VAM in increasing the uptake of Zn and Cu, the shoot content of Mn is often much less in VAM plants. In red clover there is a distinct negative correlation between percent root colonisation with VAM and the Mn content of roots and shoots (Arines *et al.*, 1989). There are two possible mechanisms for this, a lack of sufficient uptake and transport of Mn in the external hyphae and/or possible VAM-induced changes in rhizosphere microorganisms in general and a decrease in the population of Mn reducers in particular.

Role of mycorrhizae in heavy metal tolerance

The term heavy metal is not rigorously defined but is usually applied to those elements having a density greater than 6000 kg per cubic metre. Using this definition, the following elements, important as micronutrients or as pollutants in agriculture, could be classed as heavy metals: Cd, Cr, Co, Cu, Fe, Mn, Pb, Mo, Ni and Zn. Some clearly are plant nutrients but when present in excess, these metals and others are considered as pollutants because they adversely affect crop growth or the health of animals that feed on the plants. Research shows that many ectotrophic mycorrhizal (ECM) fungi are effective in enhancing heavy metal tolerance of the host plant (Wilkins, 1991; Colpaert and van Assche, 1993) provided that the concentration is not so large as to be directly harmful to the fungus. The mechanisms by which protection may be achieved are interesting. Preferential binding of heavy metals may occur in the mucilage on the hyphal surface, in the fungal cell walls and/or in the cell vacuoles. See Marschner (1995) for a full discussion because much of the work on ECM fungi is applicable to trees and shrubs rather than to agricultural crops.

In contrast to ECM, there are only a few reports of the effect of VAM on heavy metal tolerance of the host plant. In view of the morphological differences between ECM and VAM and the possible mechanisms involved in heavy metal tolerance by ECM, corresponding direct ameliorating effects of VAM would not be expected, although the alleviation of Mn toxicity by VAM has been referred to above. Vesicular arbuscular mycorrhizae may have indirect effects by improving growth through increased P supply, and thereby any metal taken

up would be diluted through a larger mass of tissue to levels at which no adverse effects would occur.

Concluding remarks

There is an increasing awareness of the need to assess plant micronutrient requirements and their availabilities in soil as deficiencies of macronutrients are corrected. The quantity of a micronutrient that is available for plant uptake is invariably very much less than the total amount in soil and the availability of each micronutrient depends on the form – mineral or organic complex – in which it can be taken up by plant roots. A complicating factor of great importance is the fact that the relative proportions of the forms in which micronutrients occur in soil can change with soil pH and redox potential and the amount of soil organic matter. Thus the availability of micronutrients changes with soil conditions and this makes generalisations extremely difficult. Improvements in analytical techniques for determining micronutrients in plant tissue and available forms in soil in recent years suggest that refinements in estimating critical concentrations in plants and soils should be possible. With such information, correcting deficiencies, recognising toxicities and defining suboptimal micronutrient levels in soils and plants should ensure that no nutrient limits the attainment of optimum economic yields of crops and performance of animals. But to achieve this will also require that the best forms and ways of delivering micronutrients, i.e. by foliar application or by addition to the soil, are adequately researched. This paper attempts to summarise very briefly a paper by Johnston (2004) which, in turn, was dependant on material taken from the general bibliography and the references given below.

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