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MICRONUTRIENTS IN TROPICAL FOOD CROP PRODUCTION

PAUL L.G. VLEK
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Foreword

The mission of the International Fertilizer Development Center is to increase food production through the improvement of fertilizers and fertilizer practices for the developing countries with special emphasis on tropical and subtropical agriculture. The principal aim is to ensure that fertilizer technology is not a limiting factor to food production in those regions. Although the full extent to which deficiency of micronutrients hampers food production is yet unknown, there is ample evidence that problem areas exist and more will be identified as crop production is intensified and marginal lands are exploited. Therefore, it seems fully appropriate at this time that IFDC, as an international organization, take a leadership role in developing micronutrient fertilizer technology appropriate for the tropics and subtropics.

The gravity of micronutrient deficiency as a limiting factor to crop production varies from crop to crop and from soil to soil. The effects may range from slight yield reductions to complete crop failure. While the economic impact of omitting micronutrients in seriously affected areas (e.g., Zn in Brazilian Cerrado) is convincing, it is difficult to estimate the yearly loss in crop production due to unsuspected micronutrient deficiency. Active soil and crop testing programs in regions with advanced agricultural systems are aimed at recognizing micronutrients as a limiting plant nutrient in time to allow corrective measures and prevent yield loss. Successful micronutrient monitoring systems are generally limited to developed economies or to developing economies producing export cash crops.

The extent to which micronutrient fertilizers are used on food crops in the tropics and subtropics is very limited and is no indication of the extent to which micronutrient deficiencies occur. On the other hand, the increased number of published papers on micronutrients in some countries should not be interpreted as an index of the problem. In India alone, as many as 800 papers appeared during the seventies. With such conflicting indicators it is difficult to assess the future role of micronutrient fertilizers in the tropics and subtropics, the mandate area of IFDC. For this reason IFDC conducted a survey of micronutrient problems in its mandate region. The results of this survey and related contributions from invited authors have been collected in this monograph entitled: "Micronutrients in Tropical Food Crop Production."

The University of Florida cosponsored the effort by making available Dr. J.J. Street, Associate Professor, Soils, as a micronutrient expert. In addition to his survey involvement, several authors benefitted from his careful reading of their manuscripts. Other chapters were reviewed by Dr. R. Howeler (CIAT), Dr. E. Bornemisza (University of Costa Rica), Dr. P.D. Tanner (Soil Productivity Research Laboratories, Zimbabwe), Dr. G.W. Cooke (England), Dr. R. Menon (FAO), Dr. B.H. Janssen (Agricultural University, Wageningen,

The Netherlands). Special mention is due to the able help provided by IFDC staff, Ernest Frederick and Mrs. Beth Roth for general editing, and the Word Processing Center of IFDC for many hours of typing.

It is our sincere hope that the compilation of the information provided in this monograph will spur renewed interest in research and development of micronutrient fertilizers. It will form the basis for future activities of IFDC in this important area.

June 1984

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1. The chemistry of micronutrients in soil

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Introduction

Of the 17 elements known to be essential for plants, 7 are required in such small amounts as to be called micronutrients. Micronutrient elements include boron (B), manganese (Mn), iron (Fe), copper (Cu), Zinc (Zn), molybdenum (Mo), and chlorine (Cl). This text will be limited to B, Mn, Fe, Cu, Zn, and Mo since natural deficiencies of Cl are essentially nonexistent.

The term micronutrients does not imply that all of these elements would occur in minute quantities in the lithosphere or in soils. In fact, 2 of the micronutrient elements, Fe and Mn, are among the 12 most abundant elements in the lithosphere. The remaining micronutrients occur at concentrations of less than 0.1% in the lithosphre and may be referred to as minor or trace elements.

The occurrence of micronutrients in soils generally reflects the influence of type and age of the parent materials, climatic conditions during weathering and soil formation, vegetation, and other soil-forming factors. Locally, micronutrient contents of soils may be affected by mining or industrial activities. In agricultural lands, micronutrient contents may be influenced by the application of fertilizers, such as phosphates, containing traces of micronutrients. In the tropics, where levels of fertilizer application are generally low, fertilization is not presently considered a major contributor to micronutrient contents of soils.

The relationships between total and plant-available micronutrient contents of soils are rather complex, and they differ among the micronutrient elements. Total contents of micronutrients, which reflect the influence of parent materials and soil formation, are quite stable in time. Available micronutrient contents in soils are more dynamic; they depend on soil and climatic conditions during the growing season and may change with time and depth in the soil profile.

In the present chapter, some aspects of the chemistry and natural abundance of micronutrient elements and some of the factors and processes that determine the availability of these elements in soils will be discussed. No

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attempt is made to compile an exhaustive review of the chemistry and occurrence of micronutrients in soils. References to selected textbooks and scientific publications are given in the text. For the interested reader, the publication *Micronutrients in Agriculture* [31] would serve as an excellent introduction to the subject.

Natural abundance

About 95% of the earth's crust is made up of igneous rocks and the remainder of sedimentary rocks. The surface of the earth shows a greater proportion of sediments, which tend to form a relatively thin layer overlaying igneous rocks. About 80% of the rocks of sedimentary origin are shales, about 15% sandstones, and 5% limestones.

Twelve elements constitute more than 99% (by weight) of the earth's crust [27]: O (46.6%), Si (27.7%), Al (8.1%), Fe (5.0%), Ca (3.6%), Na (2.8%), K (2.6%), Mg (2.1%), Ti (0.44%), H (0.14%), P (0.12%), and Mn (0.10%). The remainder consists of some 70 elements, which include 4 of the 6 micronutrient elements considered in this chapter. In abundance, the six micronutrient elements range from the fourth most abundant element in the earth's crust, Fe, to the very scarce metal Mo (Table 1). Additional information regarding the occurrence of micronutrients in various geological environments is provided in Chapter 10.

The distribution of the micronutrient elements in igneous and sedimentary rocks is not uniform (Table 1). The selected averages for soils are close to the average contents in the earth's crust, which indicates that soils are formed in parent materials derived from all rocks.

Igneous rocks

Igneous rocks may be classified as ultrabasic (less than 45% SiO_2), basic (45%–52% SiO_2), intermediate (52%–65% SiO_2), and acid rocks (65%–75% SiO_2). The chemical composition of these rock types is quite different as can be seen from Table 2. Ultrabasic and basic rocks are richer in Mg, Fe, and Mn but poorer in Si, Al, and K than are the more acid rock types. From Table 1 it follows that contents of Cu and Zn also tend to be higher in basic rocks such as basalt than in acid rocks such as granite. The distribution of B and Mo in igneous rocks is less well established, but acid rocks are probably richer in these elements than are basic rocks. These trends are further illustrated in Figure 1.

In Goldschmidt's geochemical classification of the elements, the six micronutrient elements have been classified as lithophile (B and Mn), chalcophile (Cu and Zn), and siderophile (Fe and Mn). Most of the micronutrients, however, have properties of more than one group: B and Mn occur mainly in silicate minerals (lithophile), Zn in silicates and sulfides (lithophile and chalcophile), Cu and Mo in sulfides or as the native elements with iron

Table 1. Abundance of micronutrient elements in the earth's crust [12], igneous and sedimentary rocks [21], soils [42], and seawater [6]. Selected averages for soils are given in parentheses [26]

Element	Unit	Earth's crust	Igneous rocks		Sedimentary rocks			Soil	Seawater (ppm)
			Granite	Basalt	Limestone	Sandstone	Shale		
Fe	%	5.00	2.70	8.60	0.38	0.98	4.70	1.0–10.0 (3.8)	2×10^{-3}
Mn	ppm	1000	400	1500	1100	10–100	800	20–3000 (600)	2×10^{-4}
Zn	ppm	80	40	100	20	16	95	10–300 (50)	1×10^{-6}
Cu	ppm	70	10	100	4	30	45	2–100 (30)	5×10^{-4}
B	ppm	10	15	5	20	35	100	2–100 (10)	4.4
Mo	ppm	2.3	2	1	0.4	0.2	2.6	0.2–5 (2)	0.01

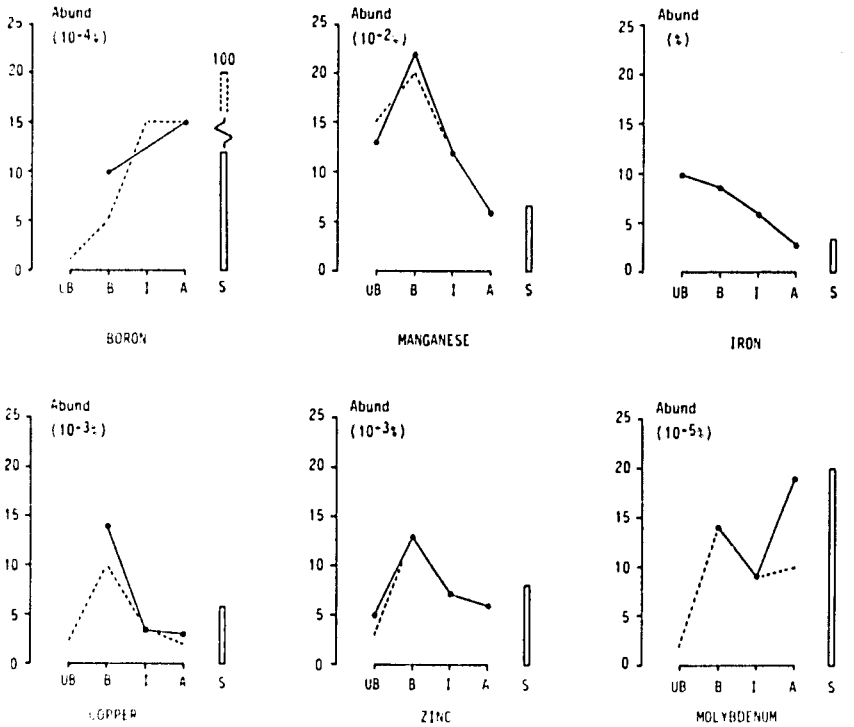


Figure 1. Abundance of micronutrient elements in ultrabasic (UB), basic (B), intermediate (I) and acid (A) rocks, and sediments (S), according to Vinogradov [43] (solid lines) and Milovsky [28] (broken lines)

(chalcophile and siderophile), and Fe in silicates, sulfides and as the native metal (all three groups) [22].

Boron occurs in complex borosilicates, such as tourmaline (about 3% B), and as a trace constituent in micas. Manganese occurs in silicate minerals such as rhodonite, $MnSiO_3$, or as a trace constituent of ferromagnesian silicates. The most abundant zinc mineral is sphalerite, ZnS, but zinc also occurs in silicate minerals. Copper occurs mainly in sulfides, with Fe or other elements. The most abundant copper mineral is chalcopyrite, $CuFeS_2$, and copper may substitute for Mg^{2+} or Fe^{2+} in ferromagnesian silicates. Molybdenum occurs mainly as the simple sulfide molybdenite, MoS_2, although it can probably substitute for Ti, Fe, and Al in silicates such as biotites and feldspars. Molybdenum is also found in trace quantities in olivines, probably substituting for Si. Iron forms stable compounds with both S and O plus Si. The common sulfides include pyrite, FeS_2, and pyrrhotite, $Fe_{1-x}S$. Silicates include olivines, $(Fe,Mg)_2SiO_4$. Other common iron minerals are magnetite, $FeFe_2O_4$, and ilmenite, $FeTiO_3$.

Weathering

Rock materials that are exposed to the atmosphere are subject to physical and chemical weathering. Water is the most important agent in the chemical weathering of rocks, both because water itself is an active agent in weathering and because several substances that react with rock materials dissolve in water. When carbon dioxide dissolves in water it forms carbonic acid, H_2CO_3, which is a weak acid. The predominant ionic species in water at equilibrium with the atmosphere (which contains 0.03% CO_2 by volume) would be HCO_3^-, and the resulting pH would be about 5.7. The solution of inorganic acids, such as HNO_2 or HNO_3, would further lower the pH of rainwater. Therefore, natural waters are usually slightly acidic, which helps to speed up weathering processes such as dissolution and dissociation of minerals.

Most of the rock-forming minerals were formed in reducing environments, that is, under conditions of high electron activities (low redox potential). Therefore, many of the elements are present in these minerals in one of their lower oxidation states (e.g., Fe^{2+}, Cu^+, Mo^{4+}, S^{2-}) that are unstable in an oxidizing environment. As a result, oxidation reactions are of importance in the geochemistry of micronutrient elements.

Oxidation reactions involving metals in their lower oxidation states may decrease the pH of the aqueous medium, which in turn speeds up the dissolution and dissociation of more resistant minerals. The lowering of the pH of aqueous solutions in the oxidation zone of sulfidic minerals may also be caused by the oxidation of sulfides, such as in $Fe(II)S_2$ (pyrite):

$$2S^{-}\ (\text{or: } S^{2-}S^0) + 7O + H_2O \rightleftharpoons 2SO_4^{2-} + 2H^+$$

The lowering of the pH and the slightly reducing conditions that develop upon the oxidation of Fe^{2+} and Mn^{2+} and the precipitation of the (hydrous) oxides increase the mobility of elements such as Cu and Zn. Some of the Fe and Mn may remain in solution, either as Fe^{2+} and Mn^{2+}, as hydrolysis products, or as complexes (e.g., $FeSO_4^0$), and be transported over considerable distances with subsurface waters. Upon exposure to the atmosphere, most of the Fe^{2+} and Mn^{2+} would precipitate as the hydrous oxides and thereby lower the solubility of Cu^{2+} and Zn^{2+} as well, through coprecipitation, occlusion, or adsorption [19]. The mobility of Mo and B is less affected by pH than is the mobility of Mn, Fe, Cu, and Zn, because Mo and B occur in solution as the weak acids $H_2MoO_4^0$ and $H_3BO_3^0$ or their dissociation products. The crystalline forms of these acids and oxides formed by Mo and B are quite soluble in aqueous environments; therefore, these elements tend to be rather mobile.

The decrease in the pH upon the oxidation of metal sulfides also creates conditions favorable for the dissolution of silicates. For example, the dissolution of $(Mg,Fe)_2SiO_4$ (olivine) may be written as:

$$(Mg,Fe)_2SiO_4 + 4H^+ \rightleftharpoons 2(Mg,Fe)^{2+} + H_4SiO_4^0$$

Table 2. Average chemical composition of igneous rocks, adapted from Milovsky [28] (% w/w)

	Rock Type	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O
Acid	Granite	72.54	0.32	12.98	1.97	1.68	0.07	0.34	0.68	3.68	4.96
	Granodiorite	66.88	0.57	15.66	1.33	2.59	0.07	1.57	3.56	3.84	3.07
Intermediate	Syenite	58.79	0.88	15.39	2.92	4.01	0.14	2.72	4.17	4.67	5.37
	Andesite	54.20	1.31	17.17	3.48	5.49	0.15	4.36	7.92	3.67	1.11
Basic	Gabbro	48.36	1.32	16.84	2.55	7.92	0.18	8.06	11.07	2.26	0.56
	Basalt	47.71	1.75	13.70	3.15	8.43	0.16	10.38	10.35	2.22	0.81
Ultrabasic	Peridotite	43.54	0.81	3.99	2.51	9.84	0.21	34.02	3.46	0.56	0.25
	Dunite	40.16	0.20	0.84	1.88	11.87	0.21	43.16	0.75	0.31	0.14

Table 3 shows that many of the micronutrients are present in easily weatherable minerals. Part of the Fe and Mn will oxidize to relatively insoluble oxides and remain with the weathered materials instead of being carried off in solution. The precipitation of the oxides is enhanced by the increase in pH resulting from the hydrolysis of primary silicate minerals. Hence, part of the Fe and Mn and traces of Cu and Zn tend to precipitate in the proximity of the partly decomposed Al-Si-O frameworks of the original silicate minerals and thus create an environment favorable for the formation of complex alumino silicates, such as clay minerals.

Table 3. Relative stability of selected minerals of igneous rocks and their associated trace elements

Degree of stability	Mineral	Major constituents (except Si, O)	Minor constituents
Stable	Tourmaline	Ca, Mg, Fe, B, Al	–
	Magnetite	Fe	Zn
	Ilmenite	Fe, Ti	–
	Muscovite	K, Al	(B)
	Orthoclase	K, Al	Cu
	Garnet	Ca, Mg, Fe, Al	Mn
	Albite	Na, Al	Cu
	Oligoclase	Na, Ca, Al	Cu
	Andesine	Ca, Na, Al	Cu, Mn
	Anorthite	Ca, Al	Cu, Mn
	Biotite	K, Mg, Fe, Al	Mn, Zn, Cu, (B, Mo)
	Augite	Ca, Mg, Al	Mn, Zn, Cu
	Hornblende	Mg, Fe, Ca, Al	Mn, Zn, Cu
Easily weathered	Olivine	Mg, Fe	Mn, Zn, Cu, Mo

Source: Adapted from Mitchell [29].

Micronutrient elements form part of a range of secondary minerals, including oxides, carbonates, silicates, borates, and molybdates. In surface environments, Fe and Mn mainly occur as the oxides in which the elements may be present in more than one oxidation state. In aqueous environments, Fe and Mn tend to form hydroxides or hydrated oxides rather than well-defined crystalline oxides. Upon dehydration these amorphous precipitates may recrystallize and form thermodynamically stable minerals, such as Fe_3O_4 (magnetite), Fe_2O_3 (hematite), FeOOH (goethite), Mn_3O_4 (hausmannite), MnOOH (manganite), and MnO_2 (pyrolusite). Both Fe and Mn also form silicates and carbonates, the latter being particularly important for Mn.

Copper occurs in weathered rocks or soils as oxides, silicates, and carbonates, including the complex carbonates, $Cu_2(OH)_2CO_3$ (malachite) and $Cu_3(OH)_2(CO_3)_2$ (azurite). Zinc forms oxides, carbonates, and several silicates, such as Zn_2SiO_4 (willemite) and $Zn_4(OH)_2Si_2O_7 \cdot H_2O$ (hemimorphite). Both Cu and Zn occur as trace constituents of hydrous oxides of Fe and Mn. Solubilities of a number of common oxides, carbonates, silicates, and sulfates of Fe, Mn, Cu, and Zn are discussed in the section on Solubility Relationships.

Boron and molybdenum do form oxides, but these are quite soluble. The minerals of major importance are borates and molybdates. Among the many anhydrous and hydrous borates known, $Na_2B_4O_7 \cdot 10H_2O$ (borax) is probably the most widespread. Among the molybdates, $PbMoO_4$ (wulfenite) and $CaMoO_4$ (powellite) predominate, although molybdates are formed with many metals including Mn, Fe, Cu, and Zn. Because of the high mobility of B and Mo, their contents in seawater are relatively high as compared to those of other micronutrient elements (Table 1).

Clay minerals

Clay minerals may be formed upon the weathering of primary silicates in surface or near-surface environments. Most of the clay minerals belong to the phyllosilicates, consisting of alternating sheets of Al^{3+} in octahedral coordination with O^{2-} or OH^-, and of Si^{4+} in tetrahedral coordination with O^{2-} or OH^-. The structure of the octahedral or gibbsite sheet (O-sheet) is similar to the structure of the mineral gibbsite, $Al_2(OH)_6$, and the tetrahedral or silica sheet (T-sheet) is structurally related to the mineral tridymite, a high-temperature polymorph of SiO_2.

An important characteristic of clay minerals is the replacement of Al^{3+} ions in the O-sheet and of Si^{4+} ions in the T-sheet by other cations of approximately the same size. This phenomenon is referred to as isomorphous substitution. In the T-sheet, Si^{4+} may be replaced by Al^{3+} because these ions have similar ionic radii in tetrahedral coordination with oxygen. In the O-sheet, Al^{3+} may be replaced by a variety of cations, such as Fe^{3+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, and Fe^{2+}. Ions with a higher charge would be preferred, but these ions are usually not present in sufficient amounts in aqueous solution. Therefore, higher charged cations are often replaced by lower charged cations, and the process of isomorphous substitution usually results in an excess of negative charge in the clay mineral, which may be balanced by substitution of OH^- for O^{2-}, by introduction of excess cations in the O-sheet, or by adsorption of cations on the surface of the mineral. Some of the excess negative charge of clay minerals is always compensated for by adsorption of cations, so that an important characteristic of most clay minerals is their capacity to adsorb cations from solution.

The surface charge densities of the different clay minerals are of the order of 0.1 (montmorillonite), 0.2 (kaolinite), and 0.3 Coulomb m^{-2} (illite). The specific surface areas range from 1–40 $m^2\ g^{-1}$ for kaolinite and 50–200 $m^2\ g^{-1}$ for illite to about 600–800 $m^2\ g^{-1}$ for montmorillonite [5]. The effective charge densities per unit weight, or cation-exchange capacities (CEC), are usually expressed in milligramequivalents (meq) per 100 g of clay. The electric charge of 1 gramequivalent is 96487 C (Faraday's constant). Hence, the CEC would range from about 0.2–8.0 for kaolinite and 15–60 for illite to about 60–80 meq/100 g for montmorillonite.

The importance of clay minerals for the micronutrient elements is twofold. First, clay minerals contain elements such as Fe, Zn, and Cu that have become part of structure of the minerals through isomorphous substitution. These elements may be released when clay minerals decompose or transform, and hence become available to the plant. Second, micronutrient elements may be adsorbed by clay minerals, which would prevent them from being leached with infiltrating rainwater. Reversibly adsorbed ions form a very important pool of available nutrients for plants.

Cations captured between layers of clay minerals are relatively unavailable to plants, but ions adsorbed onto the surface of units of layers are more readily available, depending on soil conditions and composition of the soil solution. Anions, such as molybdates, and uncharged compounds, such as undissociated boric acid, may be adsorbed on the edges of clay minerals where the Al-OH and Si-OH groups are exposed. The mechanism of anion adsorption on these groups is rather complicated, and the reaction is not truly reversible. The process is important, however, because it prevents the anions from being leached, and the adsorbed anions constitute a source of nutrients for the plant.

Sediments and soils

The micronutrient contents of shales are generally close to the average contents in the earth's crust, which reflects the fact that shales are formed of debris from all other rocks (Table 1). Boron contents of shales are exceptionally high, which suggests that dissolved borates have been present in relatively high concentrations in seawater from earliest times on [21]. Boron is also a rather volatile element and may be transported as the acid vapor from the sea to the land through the atmosphere.

Micronutrient contents are lower in sandstones than in shales. The relatively high levels of B may be due to the occurrence of B in stable minerals, such as tourmaline (Table 3). Micronutrient contents of limestones are generally low, except for Mn which tends to concentrate in limestone. The high Mn contents of limestone are probably due to substitution of Mn^{2+} for Ca^{2+} in carbonates. The ionic radii of Ca^{2+} and Mn^{2+} are in the same range, and they are larger than those of Fe^{2+}, Cu^{2+}, and Zn^{2+}.

The micronutrient contents of soils vary widely reflecting differences in parent materials; age of the soils; and climatic, topographic, and biological conditions.

The abundance of micronutrients in parent materials is one of the major factors determining micronutrient contents in soils, particularly, in younger soils. Soils formed in acid rock materials, such as granites, may be expected to be lower in elements such as Cu and Zn than are soils formed in basic materials, such as basalts. These differences are even more pronounced among soils formed from different sedimentary rocks. Soils formed from sandstones would be inherently low in elements such as Mo, Cu, Zn, and Mn.

The fact that many of the micronutrients in these sediments occur in resistant minerals, and the generally high permeability and low adsorption capacity of these materials mean that micronutrient deficiencies can easily develop in soils formed from sands or sandstones. Soils formed from limestones could be deficient in Fe, Zn, or Cu, also because the generally high pH in these soils would tend to decrease the availability of these elements to the plant.

The age of the materials in which the soils are formed and the climatic conditions during weathering and soil formation are also important factors in determining micronutrient contents in soils. In general, the ratio of secondary to primary minerals will increase with time. Processes of weathering and soil formation proceed faster in warm, humid climates than under cooler or drier conditions.

Soils formed from recent volcanic deposits in the humid tropics may be rich in Mn, Zn, and Cu and may be very fertile. Soils formed from old basaltic materials in the humid tropics may be low in fertility because all mobile elements have been leached with the percolating rainwater and only insoluble oxides of elements such as Fe, Al, and Si are left in the soils.

If weathering and soil formation occur under climatic conditions in which clay minerals are the stable endproducts of weathering of primary minerals, the fertility of soils does not necessarily decline with time. Under humid conditions, the more mobile elements will be leached from soils, and this will result in changes in the composition of the soil solution and cause the further transformation of secondary minerals formed.

Mobile elements such as Mo and B are likely to be leached first among the micronutrients. In humid climates they may be carried off with the percolating rainwater, whereas in semiarid and arid climates they are likely to accumulate in soils owing to capillary rise and evaporation of soil moisture.

Topographic conditions are of importance in weathering and soil formation. Water may collect in depressions in the landscape, and this may result in the deposition of salts, including molybdates or borates, or in the development of peat soils.

Micronutrient contents of peat soils are directly related not to the composition of inorganic rock materials but rather to the composition of the aqueous medium in which the peat develops. The development of peat soils is generally associated with reducing conditions, and thus metal ions in solution may precipitate as the sulfides. The generally low availability of copper in peat soils may be due to low aqueous concentrations of Cu or to the strong bonds that are formed between Cu and organic materials.

Biological factors play an important role in the occurrence and distribution of micronutrients in soils. Trees and deep-rooting crops may extract micronutrients from deeper layers and deposit them on the soil surface in organic form (biological enrichment). The decomposition of organic materials may result in the release of micronutrients but also of organic acids and chelating agents that form soluble complexes with elements such as Fe, Mn,

Cu, and Zn. These elements may then leach down and accumulate in a B-horizon or leach down to deeper layers and be carried away with natural waters.

General chemistry

The six micronutrients form a rather diverse group of elements. According to Mendeleev's Periodic System of the Elements, they would be classified as a light nonmetal (B); three metals of the first transition group (Mn, Fe, and Cu); one metal that follows on the first transition group (Zn); and one metal of the second transition group (Mo) (Table 4). Although Zn is generally not classified as a transition metal, there are similarities between Zn and the elements of the first transition series, in particular the ability of Zn to form complexes [8]. Metals with a specific gravity greater than 5 are sometimes referred to as 'heavy' metals. It follows from Table 4 that all micronutrient elements, except for B, could be classified as heavy metals.

Table 4. Classification of micronutrient elements in the periodic system of the elements (Mendeleev) and some physical data. Atomic weights ($g\,mol^{-1}$) are based on $^{12}C = 12.000$. Specific gravities ($g\,cm^{-3}$) were calculated from Robie et al. [37] for the elements in their most stable form at 1 bar (0.987 atm) pressure and 298.15 K. Atomic radius (10^{-10} m)

Element	Atomic number	Periodic system Group	Period	Atomic weight	Specific gravity	Atomic radius
B	5	IIIb	2	10.81	2.46	0.80
Mn	25	VIIa	4	54.94	7.47	1.17
Fe	26	VIII	4	55.84	7.87	1.17
Cu	29	Ib	4	63.54	8.93	1.17
Zn	30	IIb	4	65.38	7.14	1.25
Mo	42	VIa	5	95.9	10.22	1.29

The atomic radii listed in Table 4 provide a qualitative basis for comparison [34]. Within one group in the Periodic System, atomic radii tend to increase from the first to the higher periods. The electronic configuration of the micronutrient elements is such that most elements can occur in more than one oxidation state. Elements tend to assume the electronic configuration of noble gases. This would be the case for B^{3+} (helium), Mn^{7+} (argon), and Mo^{6+} (krypton). These oxidation states play a role in the chemistry of these elements, but they do not occur as the simple aquo ions in these high oxidation states. This is because there is considerable energy required to reach these oxidation states, more than would be compensated for by hydration energies of these ions in aqueous solution.

The amount of energy required to remove one electron from an element in the gaseous state is called the (first) ionization potential:

$$M(g) \rightarrow M^{+}(g) + e^{-}$$

It follows from Table 5 that for every element the ionization potentials increase with the number of electrons removed. The oxidation state in which an element occurs in a natural system is determined by a number of factors, such as (1) the ionization potential of the atom, (2) the electronic structure, (3) the ionic radius, (4) the nature of the anions or ligands involved with respect to their polarizability and bonding capacities, (5) the stereochemistry either in a complex compound or a crystalline lattice, and (6) the nature of solvents or other media. In addition, the conditions of the natural medium, such as the pH and the free electron activity (redox conditions), play a role.

Table 5. Ionization potentials of the micronutrient elements in the gaseous state (eV atom^{-1})

	Oxidation state						
Element	I	II	III	IV	V	VI	VII
B	8.3	25.1	37.9[b]	259.3			
Mn	7.4	15.6[a,b]	33.7[b]	52[b]	76		119[b]
Fe	7.9	16.2[a]	30.6[a,b]	56.8			
Cu	7.7[a]	20.3[a,b]	36.8				
Zn	9.4	18.0[a,b]	39.7				
Mo	7.1	16.2	27.1	46.4[b]	61.2	68[b]	126

a. Common oxidation states of ions in aqueous solution.
b. Common oxidation states of ions in oxides or oxo complexes.
Source: Weast [45].

Redox relationships

In reduction and oxidation (redox) reactions, electrons are transferred from an electron donor (e.g., Fe^{2+}) to an electron acceptor (e.g., O). The electron donor itself is oxidized in this process (Fe^{3+}), and the electron acceptor is reduced (O^{2-}). The (relative) activity of the (free) electrons is a measure for the redox conditions of a medium. The electron activity is usually expressed as pe, the negative logarithm of the electron activity. The redox limits of aqueous systems are set by the reduction of water to hydrogen gas on the reduced side:

$$H_2O + e^- \rightleftharpoons \tfrac{1}{2}H_2\ (g) + OH^-$$

and by the oxidation of water to oxygen gas on the oxidized side:

$$H_2O \rightleftharpoons 2H^+ + 2e^- + \tfrac{1}{2}O_2\ (g)$$

Hence, reduction of water would increase the pH, and oxidation of water would decrease the pH. It follows that there is a relation between pe and pH, and the parameter pe + pH has been proposed as a single-term expression for defining the redox status of aqueous systems. This parameter would range from zero on the reduced side to 20.78 on the oxidized side [26]. The relation between pe and the redox potential, Eh (in Volts), at 298.15 K is given by:

$$Eh = 0.059\ pe$$

The oxidation states in which the micronutrient elements are most likely to occur in aqueous systems can be calculated from thermodynamic data. The relation between the equilibrium constant for a chemical reaction, K^o, and the standard free energy change of the reaction, ΔG_r^o, at 298.15 K is given by:

$$\text{Log } K^o = \frac{-\Delta G_r^o}{1.364}$$

where ΔG_r^o is in kcal mol^{-1} (1 kcal = 4.184 kJ). The standard free energy change of a chemical reaction can be calculated from the free energies of formation, ΔG_f^o, of products and reactants in their standard states:

$$\Delta G_r^o = \Sigma \Delta G_f^o \text{ (products)} - \Sigma \Delta G_f^o \text{ (reactants)}$$

For example, for the redox reaction:

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

the log K^o is calculated as -13.04. Hence, the ratio of the activities of Fe^{3+} and Fe^{2+} in aqueous solution is given by:

$$\log Fe^{3+} - \log Fe^{2+} = -13.04 + pe$$

It follows that even under mildly oxidizing conditions Fe^{2+} would be the predominant ion in aqueous solution (Figure 2). However, the solubility of Fe^{3+} in aqueous solution is strongly increased through hydrolysis and complex formation.

The free energies of formation (kcal mol^{-1}) of the divalent metal ions decrease in the following order:

$$Cu^{2+}\ (15.67) > Fe^{2+}\ (-21.80) > Zn^{2+}\ (-35.19)$$
$$> Mn^{2+}\ (-55.11)$$

Hence, Cu is the most noble metal in this series and the most resistant to oxidation. Copper can exist in solid form, Cu(c), in reducing aqueous environments, in equilibrium with Cu^+ and Cu^{2+} (Figure 2), but Fe(c), Zn(c), and Mn(c) would be unstable and dissolve as Fe^{2+} (Fe^{3+}), Zn^{2+} and Mn^{2+} ions. The trivalent form of manganese, Mn^{3+}, is generally unstable in aqueous solutions, either because it is reduced to Mn^{2+} or because it disproportionates:

$$2Mn^{3+} + 2H_2O \rightleftharpoons Mn^{2+} + MnO_2\ (s) + 4H^+$$

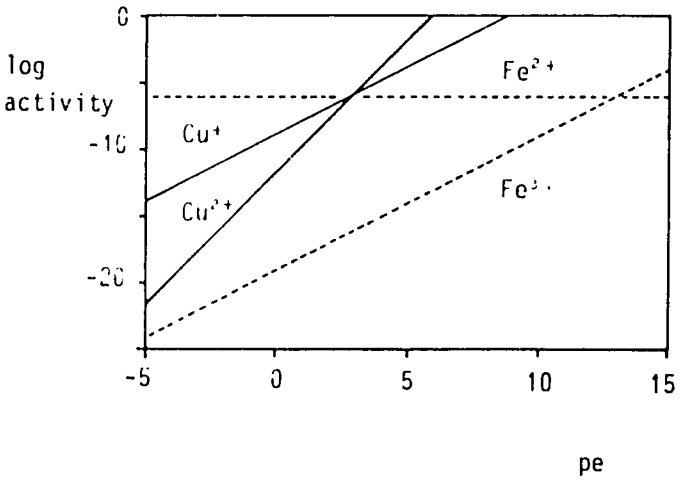


Figure 2. Activities of Cu^{2+} and Cu^{+} in equilibrium with solid Cu(c) in aqueous solution, as a function of pe (solid lines). Activity of Fe^{3+} in aqueous solution, when the activity of Fe^{2+} is fixed at 10^{-6} (broken lines)

Higher oxidation states of Fe and Mn may be stable in oxides or hydroxides under conditions where Fe^{2+} and Mn^{2+} are the predominant ionic species in solution. For example, $Mn(IV)O_2$ (pyrolusite) can exist in equilibrium with aqueous Mn^{2+} over a wide range of redox conditions, whereas in mildly reducing environments $Fe(II)Fe(III)_2O_4$ (magnetite) can exist in equilibrium with aqueous Fe^{2+}. The highest oxidation state of manganese, Mn(VII), only occurs in oxo compounds, such as MnO_4^-. In aqueous environments, however, MnO_4^- is unstable and acts as an oxidizing agent.

Boron always occurs in the trivalent oxidation state, but the total energy required to produce B^{3+} ions is far more than would be compensated for by lattice energies of ionic compounds or by hydration of such ions in solution. Consequently, covalent bond formation is of major importance, and boron compounds usually resemble those of other nonmetals, notably silicon (Si), in their properties and reactions. Oxygen compounds of boron are among the most important, comprising nearly all the naturally occurring forms of the element [8]. In aqueous systems, H_3BO_3 or $B(OH)_3$ is the stable form under all redox conditions.

Molybdenum occurs in aqueous solutions in the Mo(VI) oxidation state in the form of oxo compounds, such as the dissociation products of molybdic acid, H_2MoO_4. In concentrated, acidic solutions polynuclear oxo anions may be formed. Under reducing conditions the Mo(IV) oxide would be stable, and under oxidizing conditions the Mo(VI) oxide (molybdite).

Coordination compounds and crystal structures

In crystal structures and aqueous solutions, atoms or ions are surrounded by a set (usually between 2 and 9) of other atoms, ions, or small molecules (ligands). Charged or uncharged compounds, in which a central atom or ion is surrounded by a set of ligands, are referred to as coordination compounds or complexes. Important properties of coordination compounds are the coordination number, i.e. the number of ligands bonded to the central atom or ion, and the geometric arrangement of these ligand atoms.

Coordination compounds will generally adopt the geometric arrangement that provides the greatest stability, that is, the lowest energy. The optimum arrangement of ions in a crystal (or complex) is the one allowing the greatest number of oppositely charged ions to touch the central ion (attractive Coulomb forces) without any squeezing together of ions with the same charge (repulsive Coulomb forces). Therefore the crystal ionic radii of the elements are of importance in determining which geometric configuration is most likely to be achieved. Ionic radii for an octahedral configuration of ligands around the central ion (6-coordination) have been presented by Goldschmidt [12] and Pauling [35]. The ionic radii listed in Table 6 were taken from Weast [45]. Most micronutrient elements (except for B) occur in 6-coordination with oxygen, e.g., octahedral MnO_2 and Fe_2O_3, and in 4-coordination with sulfur, e.g., tetrahedral ZnS. At a given coordination number, more than one crystal ionic structure may be formed. For example, tetrahedral ZnS may occur as hexagonal (wurtzite, β-ZnS) or as cubic crystals (sphalerite or zinc blende, α-ZnS).

Table 6. Ionic radii (10^{-10} m), ionic potentials, and electronegativities

Element	Charge	Ionic radius	Ionic potential	Oxidation state	Electronegativity
B	3 +	0.23	13.0	III	2.04
Mn	2 +	0.80	2.5	II	1.55
	3 +	0.66	4.5		
	4 +	0.60	6.7		
	7 +	0.46	15.2		
Fe	2 +	0.74	2.7	II	1.83
	3 +	0.64	4.7		
Cu	1 +	0.96	1.0	II	1.90
	2 +	0.72	2.8		
Zn	2 +	0.74	2.7	II	1.65
Mo	4 +	0.70	5.7	II	2.16
	6 +	0.62	9.7		

The concept of ionic potential, defined as the quotient of the positive charge of a simple cation divided by its radius [22], has been used in geochemistry to explain the behavior of elements in aqueous environments.

Cations with ionic potentials less than 2.5 tend to remain in aqueous solution as aquo ions, whereas cations with ionic potentials between 2.5 and 9.5 tend to precipitate as hydroxides and at values greater than 9.5 form stable oxo compounds and remain in solution as complex ions. It follows from Table 6 that Cu^+ would tend to remain in solution as the simple aquo ion, whereas B(III) and Mo(VI) would remain in solution as the oxo compounds $B(OH)_3$ and MoO_4^{2-}. Most of the ionic potentials listed in Table 6 are between 2.5 and 9.5, and therefore these elements tend to precipitate as the hydroxides in the oxidation states listed. Ionic potentials of divalent cations of Mn, Fe, Cu, and Zn are between 2.5 and 2.8; therefore, these cations would be relatively mobile as compared with Fe^{3+}, Mn^{3+}, or Mn^{4+}.

Ions with a high ionic potential, such as B^{3+} and Mo^{6+} tend to form stable oxo compounds. The bonding energies in these compounds arise from electron pair sharing (covalent bonds) rather than from electron transfers and Coulombic attraction (ionic bonds). Most covalent bonds are polar, the electronic charge being unequally distributed over the atoms in a molecule or complex compound. The power of an atom in a molecule to attract electrons to itself is referred to as the electronegativity of an atom [35]. If two atoms in a molecule have different electronegativities, the electronic charge will be concentrated on the more electronegative atom and the resulting bond will be partly ionic in character. Bonds between micronutrient elements and oxygen are generally more ionic in character than bonds with sulfur, which are largely covalent in character. This may partly explain why the sulfides of these elements are generally less soluble than the oxides. The B(III)-O and Mo(II)-O bonds are more covalent in character, and oxides of these elements are quite soluble. This is because these elements dissolve as the oxo compounds, rather than the aquo ions.

Chemical equilibria

Micronutrient elements in soils and natural waters occur in aqueous solution or associated with one or more solid phases. Most chemical reactions and plant uptake occur through the solution phase, involving hydrated ions or aqueous complexes. Aqueous complex formation and the solubility of mineral phases can be described by chemical thermodynamics, provided equilibrium exists between different phases and the elements occur in well-defined states in the system. The latter conditions, however, are rarely met in soils. Soil temperature, O_2 and CO_2 levels, redox conditions, moisture contents, and the composition of the soil solution are continuously changing because of changing conditions at the soil surface, transport processes, and biological activity in the soil.

In addition to changing conditions, the mechanisms and kinetics of chemical reactions have to be considered. Rates of dissolution, in particular of primary minerals, are generally slow. Precipitation often occurs via

adsorption onto charged surfaces; many solid phases thus occur as (amorphous, hydrated) surface coatings rather than as discrete crystalline phases. Therefore, most natural systems cannot be considered true equilibrium systems, but rather transient systems, approaching equilibrium. The principles, however, of hydrolysis and complex formation and the solubility of mineral phases do apply to soil systems and provide a guide to the nature and direction of processes occurring in soils.

Hydration

The concept of the ionic potential is based on the Coulombic attraction between the positively charged cation and the negative charge on the water molecules surrounding the central cation in aqueous solutions. Water has a relatively large dipole moment, 1.87 D (1 Debye unit = 10^{-18} e.s.u. cm), and water molecules interact with positively charged ions through ion-dipole and other electrostatic interactions.[1] The energy of solvation of an ion is a measure for the energy involved in the electrostatic interactions between an ion and the solvent. The hydration energy is the energy change accompanying the solution of a gaseous ion in excess water at 1 atmosphere pressure and 298.15 K. The change in enthalpy (or: Helmholtz free energy) accompanying a chemical reaction, ΔH, is related to the change in free energy (or: Gibbs free energy), ΔG, through the thermodynamic relation:

$$\Delta G = \Delta H - T\,\Delta S$$

where T is the absolute temperature (K) and ΔS the change in entropy ($J\,mol^{-1}\,K^{-1}$). In any chemical reaction the system tries to minimize H and to maximize S, and equilibrium is reached when G is at minimum. For an ion like Na^+, the energy of hydration is about 400 $kJ\,mol^{-1}$, which is relatively small. Ions with a low ionic potential, such as Na^+, tend to remain free in solution, surrounding themselves with a loosely held layer of water molecules. In the case of the divalent ions of Mn, Fe, Cu, and Zn, the ion-dipole inter-

Table 7. Enthalpies of hydration ($kJ\,mol^{-1}$) and hydrolysis constants for zero ionic strength

Element	Charge	Enthalpy of hydration	Hydrolysis constants			
			K_1^0	K_2^0	K_3^0	K_4^0
Mn	2+	1841	−10.95		−34.00	−48.29
Fe	2+	1946	6.74	−16.04	−31.99	−46.38
	3+	4430	2.19	−5.69	−13.09	−21.59
Cu	2+	2100	7.70	−13.78	−26.75	−39.59
Zn	2+	2046	7.69	−16.80	−27.68	−38.29

Source: Cotton and Wilkinson [8], Lindsay [26].

[1] Ion-induced dipole and ion-quadrupole interactions [2].

actions are strong because of the small ionic radii and the high charge, and the energies of hydration are low. Absolute values for energies (enthalpies) of hydration (Table 7) are based on the assignment of $-1091 \pm 10\,kJ\,mol^{-1}$ to H^+ [8].

Divalent metals form well-defined aquo ions of the form $[M(H_2O)_6]^{2+}$ in aqueous solution. The six water molecules surround the central cation in an octahedral arrangement, thus creating an electrostatic field around the central ion, which may produce an additional bonding effect, the ligand field stabilization energy [7]. The six water molecules bonded to the metal ion cannot move freely in the solution, and the water molecules in the immediate vicinity of the metal ion are restricted in their translational motion because of ion-dipole interactions and the formation of hydrogen bonds. The number of water molecules bonded to a cation in aqueous solution probably ranges from 3 to 5 in the case of Na^+ and K^+, and from 10 to 12 in the case of Zn^{2+}, Cu^{2+}, and Fe^{2+} [2]. The water molecules bonded to a cation in aqueous solution increase the effective size of the ion and affect the reactivity of the cation in a number of chemical reactions, such as complex formation and adsorption onto charged surfaces.

Hydrolysis

The present-day use of the term hydrolysis is largely confined to the reaction between water and the ion of a weak acid or a weak base. In the present text, the term hydrolysis will be used to describe the reaction of metal ions with water. The reaction of anions of weak acids in water will be described in terms of acid dissociation reactions.

If a salt of a strong acid and a weak base, such as zinc chloride, $ZnCl_2$, is dissolved in water, the zinc ion reacts with water:

$$Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+$$

and as a result, the pH of the solution decreases. It may be more appropriate to write this hydrolysis reaction as follows:

$$[Zn(H_2O)_6]^{2+} \rightleftharpoons [Zn(H_2O)_5OH]^+ + H^+$$

that is, as the dissociation of the coordinated water molecules of the aquo ions. The hydrolysis of the aquo ions of Mn, Fe, Cu, and Zn may be written as:

$$M^{m+} + nH_2O \rightleftharpoons M(OH)_n^{m-n} + nH^+$$

where it has to be noted that the metal ions are present as aquo ions, rather than as unhydrated cations. The equilibrium constant for the above hydrolysis reaction may be written as:

$$\log K_n^0 = \log M(OH)_n^{m-n} - \log M^{m+} - npH$$

where the logarithms on the right-hand side refer to the activities of the aqueous species. Activity coefficients of ions in dilute solutions can be calculated from the extended Debye-Huckel equation. A detailed description of the thermodynamic calculation procedures used in this section, is provided by Lindsay [26].

From the hydrolysis constants listed in Table 7 it follows that Fe^{3+} hydrolyzes more strongly than any of the divalent metal ions. If the aquo ions are described as Lewis acids (electron pair acceptors), one would say that Fe^{3+} is the strongest acid and Mn^{2+} is the weakest.

The activity of Mn^{2+} in aqueous solution under oxidizing conditions, in equilibrium with β-Mn(IV)O_2, pyrolusite, is given by:

$$\beta\text{-}MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O \qquad \log K^0 = 41.89$$

It follows from Figure 3 that Mn^{2+} is the predominant aqueous species at all pH values. The Mn^{2+} aquo ion is stable and resistant to oxidation.

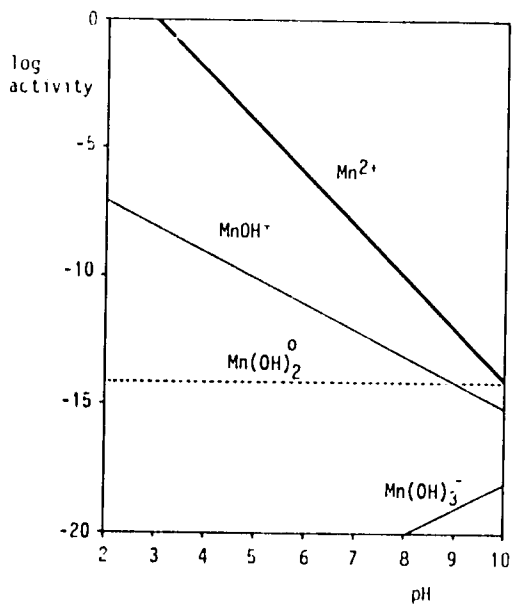


Figure 3. Aqueous species of Mn^{2+} in equilibrium with β-MnO_2 (pyrolusite) at pe + pH = 18. The activity of $Mn(OH)_2^0$ is estimated (dotted line)

Under less-oxidizing conditions (pe + pH < 16.6) γ-Mn(III)OOH manganite, would be the stable oxyhydroxide, whereas under mildly reducing conditions (pe + pH < 13.7 at 0.0003 atm CO_2 pressure) Mn(II)CO_3, rhodochrosite, would be the stable solid phase determining the solubility of aqueous Mn^{2+}.

The aqueous activity of Fe^{3+} under oxidizing conditions in equilibrium with α-Fe_2O_3, hematite, is given by:

$$\alpha\text{-}Fe_2O_3 + 6H^+ \rightleftharpoons 2Fe^{3+} + 3H_2O \qquad \log K^0 = 0.18$$

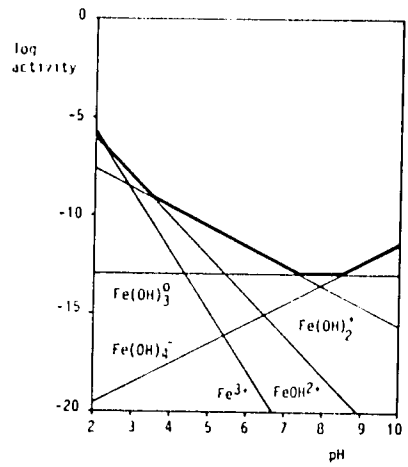


Figure 4. Aqueous species of Fe^{3+} in equilibrium with α-Fe_2O_3 (hematite) in an oxidizing environment.

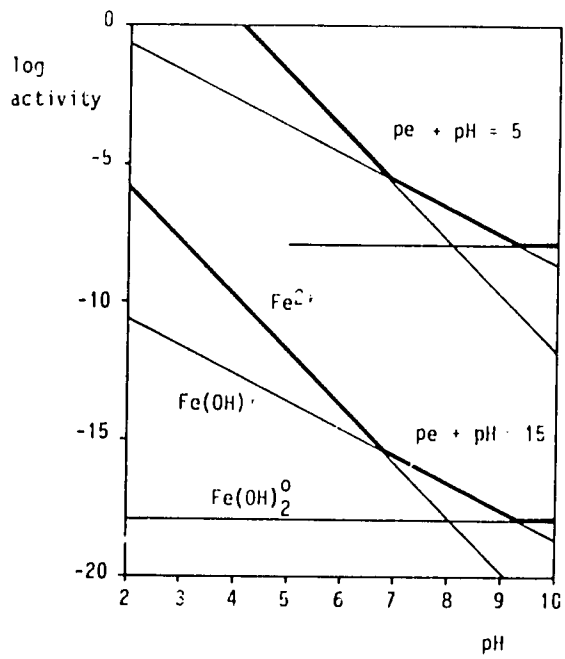


Figure 5. Aqueous species of Fe^{2+} in equilibrium with α-Fe_2O_3 (hematite) at two values of pe + pH: 5 (reducing) and 15 (oxidizing)

As is seen in Figure 4, even in slightly acidic solutions Fe^{3+} is strongly hydrolyzed, the predominant species being $Fe(OH)_2^+$. Hematite also controls the solubility of aqueous Fe^{2+} (Figure 5), according to:

$$\alpha\text{-}Fe_2O_3 + 6H^+ + 2e^- \rightleftharpoons 2Fe^{2+} + 3H_2O \qquad \log K^0 = 26.16$$

Thus, the ferrous ion predominates over the ferric ion except under highly oxidizing conditions (cf. Figure 2). The solubility of Fe^{3+} is strongly increased, however, through the formation of several hydrolysis products.

As in the case of Mn, the Fe(III) oxides are more resistant to reduction than the aqueous Fe^{3+} ions. At pe + pH = 3.7, hematite would be in equilibrium with magnetite, $Fe(II)Fe(III)_2O_4$. At lower values of pe + pH, magnetite or siderite, $FeCO_3$, would be the solid phase determining the solubility of aqueous Fe^{2+}.

Both Cu and Zn form mixed oxides with Fe(III): α-$CuFe_2O_4$ (cupric ferrite) and $ZnFe_2O_4$, which is a form of franklinite, a mixed oxide of the general form (Zn, Fe, Mn) $(Fe, Mn)_2O_4$. These oxides may play a role in determining the solubilities of Cu^{2+} and Zn^{2+} in natural media, where the solubility of Fe^{3+} would be determined by one of the Fe(III) oxides, such as hematite or goethite [26]. The solubility of Cu^{2+} in equilibrium with cupric ferrite and hematite (Figure 6) can be represented by:

$$\alpha\text{-}CuFe_2O_4 + 2H^+ \rightleftharpoons \alpha\text{-}Fe_2O_3 + Cu^{2+} + H_2O \qquad \log K^0 = 9.95$$

and the solubility of Zn^{2+} in equilibrium with franklinite and hematite (Figure 7) by:

$$ZnFe_2O_4 + 2H^+ \rightleftharpoons \alpha\text{-}Fe_2O_3 + Zn^{2+} + H_2O \qquad \log K^0 = 9.67$$

Hence, the solubilities of Cu^{2+} and Zn^{2+} under oxidizing, acidic conditions would be quite similar. In alkaline solutions, the solubility of Cu^{2+} would be higher because of the high solubility of $Cu(OH)_2^0$. Under slightly reducing conditions, Cu^+ would predominate over Cu^{2+} (Figure 2).

The elements Mn, Fe, Cu, and Zn behave similarly in that they all form well-defined aquo cations that hydrolyze in aqueous solutions, and they all form oxides or hydroxides that may control the solubility of the aqueous species in near-neutral or alkaline solutions. The solubility of the metal ions decreases with increasing pH, except under highly alkaline conditions, where anionic hydrolysis products increase the solubility. The elements B and Mo behave quite differently. Both elements form stable oxo anions that act as Lewis bases (electron pair donors) in aqueous solution, rather than as Lewis acids. The oxides are too soluble to persist in most aqueous environments,

and the solubility of B and Mo in aqueous solutions tends to increase with increasing pH. Both elements form polynuclear hydrolysis products in concentrated solutions.

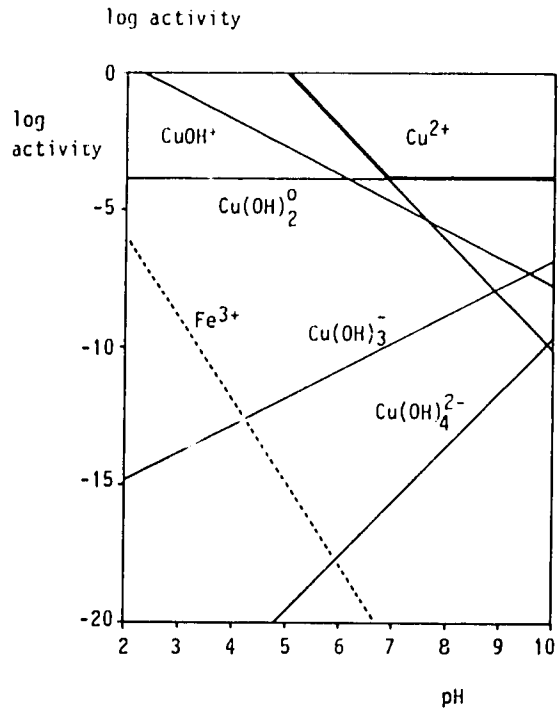


Figure 6. Aqueous species of Cu^{2+} in equilibrium with α-$CuFe_2O_4$ (cupric ferrite) and α-Fe_2O_3 (hematite) in an oxidizing environment, and the aqueous activity of Fe^{3+} in equilibrium with these minerals (dotted line)

Boron occurs in aqueous solutions mainly as the undissociated boric acid, H_3BO_3 or $B(OH)_3$, which may dissociate or react as a Lewis acid [8]:

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \qquad \log K \cong -9$$

The tetrahedral BO_4 units are important in the formation of polynuclear anions in solution. At low concentrations, essentially only the mononuclear species are present in solution (Figure 8). In concentrated solutions, polynuclear species may form, such as:

$$3B(OH)_3 \rightleftharpoons B_3O_3(OH)_4^- + H^+ + 2H_2O \qquad \log K \cong -6.8$$

which consists of trigonal BO_3 units only, and

$$4B(OH)_3 \rightleftharpoons B_4O_5(OH)_4^{2-} + 2H^+ + 3H_2O \qquad \log K \cong -15.0$$

which consists of two trigonal BO_3 units and two tetrahedral BO_4 units. Under conditions where concentrated boric acid solutions may occur, such as in depressions in arid regions, polynuclear borates may precipitate, usually in hydrated form, such as in borax, $Na_2B_4O_5(OH)_4 \cdot 8H_2O$.

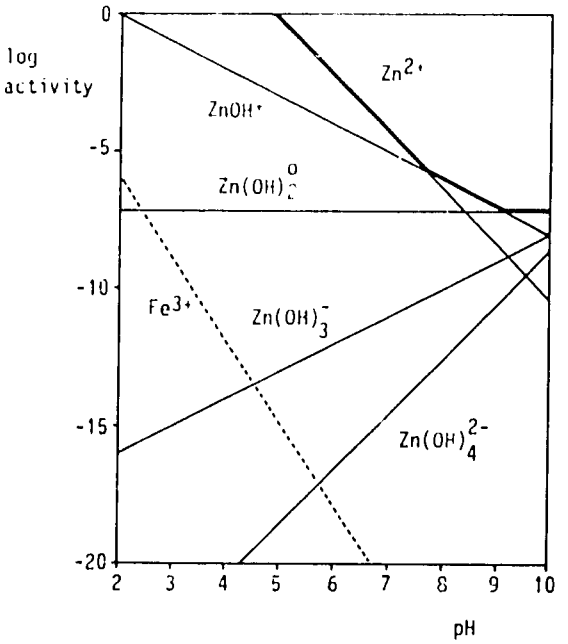


Figure 7. Aqueous species of Zn^{2+} in equilibrium with $ZnFe_2O_4$ (franklinite) and α-Fe_2O_3 (hematite), and the aqueous activity of Fe^{3+} in equilibrium with these minerals (dotted line)

Molybdenum occurs in aqueous solutions mainly as the molybdate ion, MoO_4^{2-}. Molybdates form salts with many metal ions, including Mn^{2+}, Fe^{2+}, Cu^{2+}, and Zn^{2+}. The solubility of crystalline molybdic acid increases with increasing pH (Figure 9) as follows from:

$$H_2MoO_4(c) \rightleftharpoons 2H^+ + MoO_4^{2-} \qquad \log K_{so} = -13.37$$

In dilute solutions, essentially only mononuclear molybdate species occur, but in concentrated solutions (Figure 9), or under acid conditions (Figure 10), isopoly anions such as $[Mo_7O_{24}]^{6-}$ (paramolybdate) or $[Mo_8O_{26}]^{4-}$ (octamolybdate) may be formed. Such conditions, however, are rarely encountered in nonsaline soils.

Complex formation

The displacement of water molecules in the inner coordination sphere of an aquo ion by one or more ligands is called complex formation. For divalent

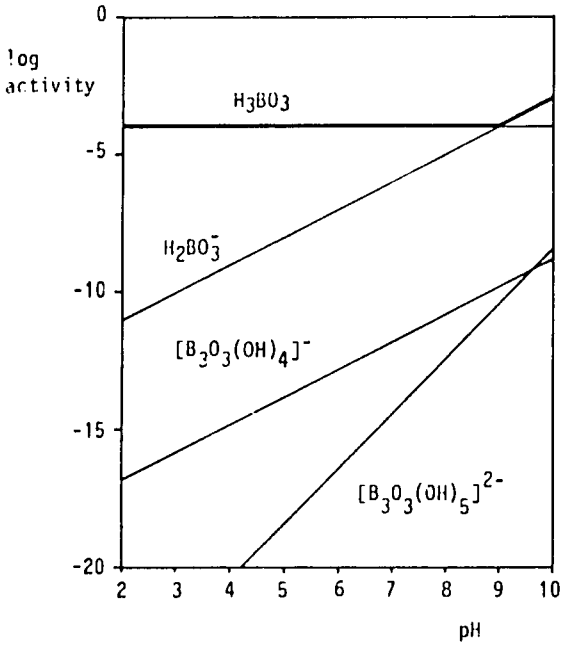


Figure 8. Aqueous species of $H_3BO_3^0$ (boric acid) at a fixed boric acid concentration of 10^{-4} mol l^{-1}. Log K-values at 298.15 K and I = 3.0 were taken from Smith and Martell [41]

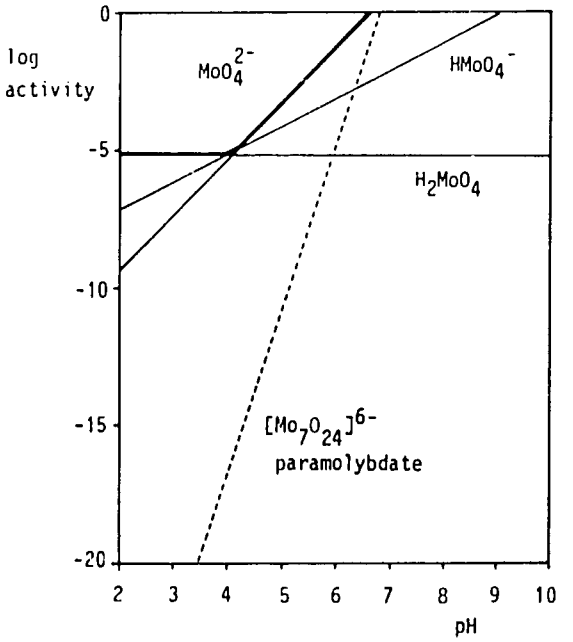


Figure 9. Aqueous molybdate species in equilibrium with crystalline molybdic acid, H_2MoO_4 (c). The log K-value for paramolybdate refers to an ionic strength of 1.0 [41]

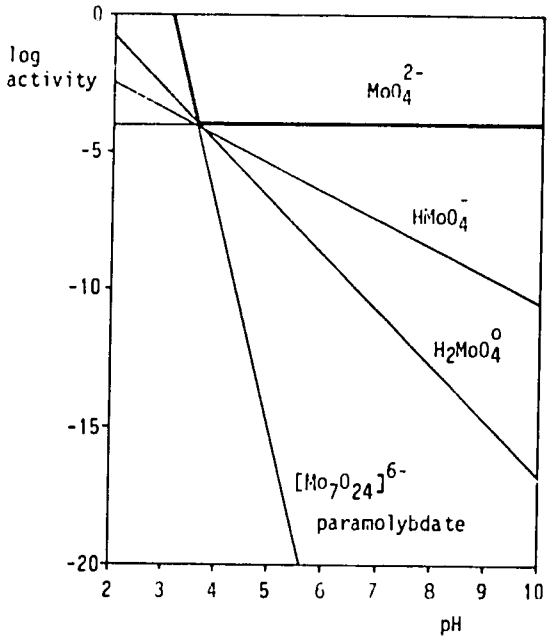


Figure 10. Aqueous molybdate species at a fixed molybdate activity of 10^{-4}. Log K-values are for 298.15 K and I = 1.0 [41]

metal ions, the complex formation with an uncharged ligand, L, can be represented as:

$$[M(H_2O)_n]^{2+} + L \rightleftharpoons [M(H_2O)_{n-1}L]^{2+} + H_2O$$

In principle, stepwise complex formation can proceed until all water molecules are displaced:

$$[M(H_2O)L_{n-1}]^{2+} + L \rightleftharpoons [ML_n]^{2+} + H_2O$$

where it is assumed that the coordination number of the metal ion does not change. Whether the coordination number changes depends on steric factors, such as the size of the ligands, and on ligand-metal ion interactions [8].

Metal ions in solution may coordinate with uncharged ligands, such as H_2O and NH_3, with monovalent anions, such as Cl^-, NO_3^-, $H_2PO_4^-$, and HCO_3^-, and with divalent anions such as SO_4^{2-}, HPO_4^{2-}, and CO_3^{2-}. Stability constants of metal-ion complexes have been tabulated by Sillen and Martell [39, 40]. A number of equilibrium constants for common ligands have been summarized in Table 8 for the chemical reactions given in the last column [41, 26].

Polydentate ligands are ligands that contain more than one donor group and that are structurally capable of permitting all the donors simultaneously to form bonds with the same metal atom or ion. Polydentate ligands are also called chelating ligands, from the greek "chela" meaning "claw", because in

metal chelates the chelates tend to form ring structures that incorporate the metal in the center of the structure. The stability of metal chelates is primarily determined by the number of rings formed by the chelating ligand, the size of the rings, the nature of the donor atoms, the effects of resonance stabilization, and steric relationships [24].

The stability of chelates of Mn^{2+}, Fe^{2+}, Cu^{2+}, and Zn^{2+} often follows the Irving-Williams order, $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$, which is related to the reciprocal of the ionic radii and the second ionization potentials of the metals concerned [17]. Inspection of Table 8 shows that the stabilities of complexes with acetate, oxalate, and EDTA are in the predicted order. The electronegativities of Mn, Fe, Cu, and Zn (Table 6) follow the same order. Acetate is a bidentate ligand: the two oxygen atoms of the carboxylate group form a four-ring ligand with the metal. Similarly, oxalate, with two carboxylate groups, is a quadridentate ligand. Ethylene diamine tetra acetate, or $EDTA^{4-}$, is a hexadentate ligand, with four carboxylate groups and two N atoms as the donor groups. $EDTA^{4-}$ forms stable complexes with Mn^{2+}, Fe^{2+}, Cu^{2+}, and Zn^{2+} (Table 8), and with other metal ions [33, 26].

Entropy considerations are important in the formation of complexes between metal ions and polydentate ligands. This is illustrated by the stability of complexes of metal ions with acetate ions (ac^-) and oxalate ions (ox^{2-}). For example, Cu^{2+} forms more stable complexes with ox^{2-} than with 2 ac^- (Table 8), even though in both cases the copper ions are coordinated with two carboxylate groups. The negative change in free energy in the reaction:

$$Cu(ac)_2 + ox^{2-} \rightleftharpoons Cu(ox) + 2ac^- \qquad \Delta G^0 = -3.55$$

is probably due to an increase in entropy, rather than to an enthalpy effect. This is because at equal activities of ox^{2-} and ac^- in solution, the probability that Cu^{2+} will coordinate with ac^- or with one carboxylate group of ox^{2-} is approximately the same for both ligands. The probability, however, that $Cu(ox^-)^+$ will coordinate with the second carboxylate group of ox^{2-} is much larger than that $Cu(ac)^+$ will coordinate with a second acetate ion. Hence, entropy increases when Cu(ox) is formed in equilibrium with $Cu(ac)_2$.

In soils, there are many naturally occurring chelating agents ranging from simple organic acids and amino acids to complex fulvic and humic acids. The common donor atoms in fulvic and humic acids are oxygen in carboxyl, hydroxyl and carbonyl groups; nitrogen in amino and azo groups; and sulfur in sulfonic acid and sulfhydryl groups. The stability of divalent metal-fulvic acid complexes has been shown to decrease in the order Cu > Zn > Mn [38].

Naturally occurring chelates play an important role in the chemistry of micronutrients in soils. Elements such as Mn, Fe, Cu, and Zn, in aqueous

Table 8. Equilibrium constants of aqueous complex formation, at 298.15 K and zero ionic strength (log K^m). The equilibrium constants for EDTA are expressed in concentrations of reactants and products, except for H^+, OH^-, and e^-, which are expressed in activities, at an ionic strength of 0.01 (K^m 0.01)

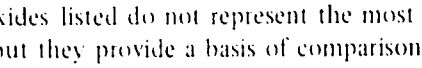
Ligand	Ionic species				Reaction
	Mn^{2+}	Fe^{2+}	Cu^{2+}	Zn^{2+}	
NH_3	1.00[a]		4.24[b]	2.38[b]	$M^{2+} + NH_3 \rightleftharpoons MNH_3^{2+}$
Cl^-	0.61		0.40	0.43	$M^{2+} + Cl^- \rightleftharpoons MCl^+$
	0.04	−0.07	−0.12	0.00	$M^{2+} + 2Cl^- \rightleftharpoons MCl_2$
NO_3^-			0.50	0.40	$M^{2+} + NO_3^- \rightleftharpoons MNO_3^+$
$H_2PO_4^-$		2.70	1.59	1.60	$M^{2+} + H_2PO_4^- \rightleftharpoons MH_2PO_4^+$
HCO_3^-	−6.02		−5.73		$M^{2+} + CO_2(g) + H_2O \rightleftharpoons MHCO_3^+ + H^+$
$C_2H_3O_2^-$	1.40	1.40	2.22	1.57	$M^{2+} + C_2H_3O_2^- \rightleftharpoons MC_2H_3O_2^+$
			3.63	1.9[c]	$M^{2+} + 2C_2H_3O_2^- \rightleftharpoons M(C_2H_3O_2)_2^0$
SO_4^{2-}	2.26	2.20	2.36	2.33	$M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4$
HPO_4^{2-}		−3.60	−4.00	−3.90	$M^{2+} + H_2PO_4^- \rightleftharpoons MHPO_4 + H^+$
CO_3^{2-}	−18.87		−11.43		$M^{2+} + CO_2(g) + H_2O \rightleftharpoons MCO_3 + 2H^+$
$C_2O_4^{2-}$	3.95	3.05[d]	6.23	4.87	$M^{2+} + C_2O_4^{2-} \rightleftharpoons MC_2O_4$
$EDTA^{4-}$	14.81	15.27	19.70	17.44	$M^{2+} + EDTA^{4-} \rightleftharpoons MEDTA^{2-}$

a. T = 20 °C, I = 2.0
b. I = 2.0
c. I = 0.1
d. I = 1.0

solution, are probably to a large extent associated with organic ligands, in particular under oxidizing and slightly alkaline conditions. For example, Hodgson et al. [16] found that 98% - 99% of the copper in soil solutions of calcareous soils was present as organic complexes. Hence, chelation of micronutrients in soils plays an important role in determining the availability of Mn, Fe, Cu, and Zn to plants [25].

Solubility relationships

All of the micronutrient elements form oxides or hydroxides. In the case of B and Mo, the oxides are too soluble to persist in most natural systems. The solubility constants for the metal (II) oxides listed in Table 9 refer to the dissolution reaction:

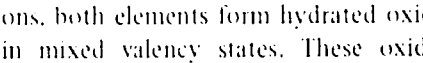


$$M(II)O + 2H^+ \rightleftharpoons M^{2+} + H_2O$$

The oxides listed do not represent the most stable metal oxides in oxidized soils, but they provide a basis of comparison among the elements. It can be seen from Table 9 that the solubilities of the metal (II) oxides follow the order of the electronegativities of the elements (cf. Table 6) in that Cu (II) forms the least soluble oxides and Mn (II) oxides are quite soluble. A similar trend can be observed for the solubilities of the metal (II) sulfides.

Stable oxides of Fe and Mn include α-Fe_2O_3 (hematite), α-FeOOH (goethite), β-MnO_2 (pyrolusite), and γ-MnOOH (manganite). Under soil conditions, both elements form hydrated oxides, in which the elements may occur in mixed valency states. These oxides may be present as surface coatings on minerals, such as phyllosilicates, and they play an important role in determining the solubilities of aqueous Fe and Mn, as well as other micronutrient elements, through surface adsorption, coprecipitation, or occlusion. Copper and zinc form stable oxides with Fe(III), $CuFe_2O_4$ (cupric ferrite), and $ZnFe_2O_4$ (franklinite) that may play an important role in determining the solubility of these elements in soils [26].

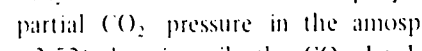
The partial CO_2 pressure in the amosphere is about 0.0003 atm (log CO_2 = -3.52), but in soils the CO_2 levels are usually higher because of respiratory processes and slow exchange of CO_2 with the atmosphere. In flooded soils, where rates of diffusion of CO_2 are even lower, CO_2 levels may go up to 0.1 atm or higher. Atmospheric carbon dioxide dissolves in water according to:



$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3 \qquad \log K^\circ = -1.46$$

Carbonic acid is a weak acid, the predominant aqueous species between pH 6.4 and 10.3 being HCO_3^-.

Under slightly alkaline conditions, and high levels of CO_2, the precipitation of metal (II) carbonates may become important. The equilibrium constants for carbonates, listed in Table 9, refer to the reaction:



$$M(II)CO_3 + 2H^+ \rightleftharpoons M^{2+} + CO_2(g) + H_2O$$

Table 9. Solubilities (log K°) of oxides, carbonates, silicates, phosphates, sulfates, and sulfides of divalent metals, at 298.15 K and zero ionic strength, and names of some minerals

	Mn (II)	Fe (II)	Cu (II)	Zn (II)
Oxides	18.39	13.48	7.66	11.16
MO	Manganosite		Tenorite	Zincite
Carbonates	8.08	7.92	8.52[a]	7.91
MCO_3	Rhodochrosite	Siderite		Smithsonite
Silicates	24.45	19.76		13.15
M_2SiO_4	Tephroite	Fayalite		Willemite
Phosphates	11.78 (n = 0)	3.11 (n = 8)	2.24 (n = 0)	3.80 (n = 4)
$M_3(PO_4)_2 \cdot nH_2O$		Vivianite	0.34 (n = 2)	Hopeite
Sulfates	3.43 (n = 0)	2.65 (n = 0)	3.72 (n = 0)[b]	3.41 (n = 0)[c]
$MSO_4 \cdot nH_2O$	0.47 (n = 1)	− 2.46 (n = 7)	Chalcocyanite	Zinkosite
			− 2.61 (n = 5)	
Sulfides	− 12.84[d]	− 16.21[e]	− 36.10[f]	− 24.70
MS	Alabanite	Trolite	Covellite	Sphalerite
	− 11.67			− 22.50
	(Green)			Wurtzite

a. $Cu_2(OH)_2CO_3$ (malachite), $Cu_3(OH)_2(CO_3)_2$ (azurite)
b. $Cu_4(OH)_6SO_4$ (bronchantite), $CuO \cdot CuSO_4$ (c)
c. $Zn(OH)_2 \cdot ZnSO_4$ (c), $ZnO \cdot 2ZnSO_4$ (c)
d. MnS_2 (hauerite)
e. FeS_2 (pyrite, markasite), $Fe(II)_{0.85}Fe(III)_{0.10}S$ (pyrrhotite)
f. Cu_2S (chalcocite)

Source: Lindsay [26]

and show that the solubilities of metal (II) carbonates are quite similar. The most important carbonates in soils are calcite, $CaCO_3$ (log $K^\circ = 9.74$); magnesite, $MgCO_3$ (log $K^\circ = 10.69$); and mixed Ca, Mg carbonates, such as dolomite, $CaMg(CO_3)_2$. Many Ca and Mg carbonates contain traces of other metals, in particular Mn (II). In nonsaline soils where calcite is present, the pH is usully in the range of 7 to 8. The pH in such soils follows from:

$$2pH = 9.74 \quad \log CO_2 \quad \log Ca^{2+}$$

For CO_2 levels from 0.0003 to 0.01 atm and Ca^{2+} activities from 10^{-3} to 10^{-2}, pH would be between 6.9 and 8.1. Calcium activities in soil solution are buffered through ion exchange and adsorption. Thus, in calcareous soils calcite may affect the solubilities of Mn, Cu, and Zn directly through surface adsorption, coprecipitation or occlusion, or indirectly through determining the pH.

Silicon is the second most abundant element in the earth's crust (after oxygen) and occurs in soils in primary silicate minerals, secondary alumino silicates, and various forms of SiO_2. The solubility of silica, according to the reaction:

$$SiO_2(s) + 2H_2O \rightleftharpoons H_4SiO_4$$

ranges from log $K^\circ = -2.7$ for amorphous silica, to log $K^\circ = -4.0$ for quartz (α-SiO_2). Silicic acid dissociates according to:

$$H_4SiO_4 \rightleftharpoons H^+ + H_3SiO_4^- \qquad \log K^\circ = -9.71$$

Hence, the predominant aqueous species below pH 9.7 is H_4SiO_4. In more concentrated solutions, or at very high pH, polynuclear hydrolysis products of H_4SiO_4 may become important, as was discussed for the chemically similar H_3BO_3 (see section on Hydrolysis).

The solubility constants for silicates, listed in Table 9, refer to the reaction:

$$M(II)_2SiO_4 + 4H^+ \rightleftharpoons 2M^{2+} + H_4SiO_4$$

The solubility of metal (II) silicates thus depends strongly on pH.

The dissolution of clay minerals may be represented schematically as follows:

$$\text{Clay mineral} + nH^+ + mH_2O \rightleftharpoons xAl^{3+} + yH_4SiO_4$$
$$+ (Na^+, K^+, Ca^{2+}, Mg^{2+})$$

where n, m, x, and y are reaction constants. If quartz and gibbsite control the aqueous activities of H_4SiO_4 and Al^{3+}, then the stability of clay minerals depends on pH and the activities of a number of relatively mobile cations in solution. If the aqueous activity of one or more of these cations decreases, because of leaching or plant uptake, the clay minerals may become unstable and dissolve, thus releasing trace constituents occluded in these minerals.

In some tropical soils (e.g., Oxisols) this process has left the soil with few weatherable minerals and thus with a poor capacity to replenish micronutrients removed by the crop.

All divalent metals form phosphates of the general form: $M_3(PO_4)_2 \cdot nH_2O$, where n denotes the number of coordinated water molecules. The solubilities of phosphates, listed in Table 9, refer to the reaction:

$$M(II)_3(PO_4)_2 \cdot nH_2O + 4H^+ \rightleftharpoons 3M^{2+} + 2H_2PO_4^- + nH_2O$$

Orthophosphoric acid, H_3PO_4, is a weak acid: between pH 2.2 and 7.2, the predominant aqueous species is $H_2PO_4^-$, and between 7.2 and 12.4, this is HPO_4^{2-}.

When the concentrations of orthophosphates in solution are high, such as in the case of P-fertilizer application, micronutrient elements (e.g., Zn) may precipitate and become unavailable to the plant. Under unfertilized conditions, the levels of orthophosphates in solution are largely determined by adsorption reactions and by Al-, Fe(III)-, or Ca-phosphates. Under these conditions phosphate minerals involving micronutrient elements are not likely to be important.

Most divalent metals form sulfates of the form: $MSO_4 \cdot nH_2O$, which dissolve according to (Table 9):

$$M(II)SO_4 \cdot nH_2O \rightleftharpoons M^{2+} + SO_4^{2-} + nH_2O$$

Most sulfates are too soluble to persist in soils, except in semiarid or arid climates where they may accumulate in soils, mainly in the form of gypsum, $CaSO_4 \cdot 2H_2O$ (log K° = 4.64).

Sulfur is important as a plant nutrient, and in flooded soils (or peat soils) sulfates may be reduced to sulfides. Hydrogen sulfide, H_2S, reacts as a volatile, weak acid. Below pH 7.0, the predominant aqueous species is H_2S, and between pH 7.0 and 12.9 this is HS^-; at pH greater than 12.9, S^{2-} is predominant. The reduction of sulfates to sulfides only occurs under strongly reduced conditions, as follows from:

$$SO_4^{2-} + 8e^- + 8H^+ \rightleftharpoons S^{2-} + 4H_2O \qquad \log K^\circ = 20.74$$

At pe + pH < 2.6, S^{2-} would be the predominant species.

In submerged soils, where the redox potential is sufficiently low for SO_4^{2-} to be reduced to S^{2-}, insoluble metal sulfides may form. The solubilities of sulfides in Table 9 refer to the reaction:

$$M(II)S \rightleftharpoons M^{2+} + S^{2-}$$

Copper is likely to precipitate as chalcocite (Cu_2S) rather than as covellite (CuS) because of the predominance of Cu^+ under these conditions. Iron and manganese may precipitate as the stable bisulfides, pyrite (FeS_2) and hauerite (MnS_2). Zinc is likely to form sphalerite (α-ZnS) [20].

The extent to which sulfides control the solubilities of aqueous metals under low redox conditions depends on the initial concentrations of sulfates and the metals involved, on the solid phases controlling metal solubilities, and on the degree of equilibrium maintained in the system. For example, the equilibrium between magnetite and pyrite may be represented as:

$$Fe_3O_4 \text{ (magnetite)} + 56H^+ + 44e^- + 6SO_4^{2-} \rightleftharpoons 3FeS_2 \text{ (pyrite)}$$

$$+ 28H_2O \qquad \log K^0 = 287.69$$

and:

$$pe + pH = 6.54 + 0.14 \log SO_4^{2-} - 0.27\, pH$$

If equilibrium is maintained, pe + pH is determined by the above relation until all Fe_3O_4 is dissolved and precipitated as FeS_2. Iron contents in soils are in the range of 1% - 10% Fe (Table 1). Even if only 1% of this Fe is present as Fe_3O_4, this would still require initial SO_4^{2-} concentrations of 5 - 50 x 10^{-3} mol/l to precipitate all Fe(II). Typical sulfate concentrations in soils would be of the order of 10^{-3} mol/l, and therefore the formation of pyrite is likely to remove most of the S^{2-} (or: S_2^{2-}) from solution. Redox reactions involving metal sulfides are particularly common in rice lands, reclaimed swamps, and tidal areas [30].

Molybdenum also forms a stable sulfide, MoS_2 (molybdenite), which dissolves according to:

$$MoS_2 \text{ (molybdenite)} + 4H_2O \rightleftharpoons MoO_4^{2-} + 2S^{2-} + 2e^- + 8H^+$$

$$\log K^\circ = -96.49$$

At very low redox potentials, the solubility of molybdates may be determined by molybdenite, but under more oxidized conditions most of the known Mo minerals would be too soluble to persist in soils. However, if the aqueous Ca^{2+} is high enough, calcium molybdate may become important:

$$CaMoO_4(c) \rightleftharpoons Ca^{2+} + MoO_4^{2-} \qquad \log K^\circ = -7.94$$

In calcareous soils, calcium molybdate and calcite could coexist:

$$CaCO_3 \text{ (calcite)} + MoO_4^{2-} + 2H^+ \rightleftharpoons CaMoO_4 \text{ (c)} + CO_2 + H_2O$$

$$\log K^0 = 17.68$$

hence, at atmospheric CO_2 levels,

$$\log MoO_4^{2-} = -21.20 + 2pH$$

A molybdate activity of about 10^{-7} at pH 7 would be in the range of activities expected for soils, but at higher pH or high CO_2 levels, calcium molybdates would probably dissolve in calcareous soils.

The solubility of borates in soils is likely to be determined through adsorption on mineral surfaces, rather than by a distinct boron mineral. Most

borates are too soluble to persist in soils; they form only under arid conditions where they can accumulate in soils as a result of capillary rise of soil moisture and evaporaion on the soil surface [36].

Ion exchange and adsorption

Micronutrient elements may be adsorbed as the aquo cations or anions, or in the form of charged or uncharged complexes. If the adsorption of one or more ionic species is accompanied by the simultaneous desorption of an equivalent amount of other ionic species, this process is called ion exchange or equivalent adsorption. When ions are adsorbed and less than equivalent amounts of other ions are desorbed the process is referred to as superequivalent adsorption (also: 'specific' adsorption). The equivalent adsorption of ionic species does not alter the fixed charge on the solid surface, but the superequivalent adsorption of ionic species may alter the effective surface charge of the adsorbent. The amounts of cations or anions that can be reversibly (or: exchangeably) adsorbed by a solid phase, under specified conditions, are called the cation exchange capacity (CEC) or anion-exchange capacity (AEC), respectively.

When aqueous concentrations of metal ions are of the same order of magnitude as the concentrations of competing ions, adsorptive interactions can be described by the ion-exchange equations commonly used in soil science for alkali and alkaline earth metals [3]. At lower concentrations, however, transition metals and zinc are often strongly preferred over alkali and alkaline earth metals, and this preference tends to increase with decreasing surface coverage by the metal ions and with increasing pH.

At low concentrations, adsorption of metal ions by soils is often described successfully by Langmuir or Freundlich adsorption equations. Both adsorption equations can be derived from ion-exchange considerations which may explain in part their applicability to adsorption of ionic species in soils.

Ion exchange

The adsorption of ionic species A on an adsorbent which is initially in the homoionic B form can be represented as:

$$A + \bar{B} \rightleftharpoons \bar{A} + B$$

where bars denote the adsorbed phase and where it is assumed that both ionic species are of equal valence. Ionic species can occur in two energy states, one associated with the solid phase and one with the solution phase. The thermodynamic equilibrium constant for the A/B exchange reaction, $K^0_{A/B}$, follows from:

$$\Delta G^0_{ads} = -RT \ln K^0_{A/B}$$

where ΔG^0_{ads} is the change in free energy accompanying the exchange reaction under standard conditions. When equilibrium is maintained, it follows that:

$$\bar{a}_A/\bar{a}_B = K^0_{A/B} \cdot a_A/a_B$$

This ion-exchange equation relates the ratio of the ionic activities in the adsorbed phase, $\bar{a}_A/\bar{a}_B$, to the ratio in the solution phase, a_A/a_B. The ratio of the activities in the adsorbed phase is usually replaced by the ratio of the equivalent fractions, q_A/q_B, where q_i is the amount of ionic species i adsorbed from solution (meq/100 g of adsorbent):

$$q_A/q_B = K_{A/B} \cdot a_A/a_B$$

where $K_{A/B}$ is the selectivity coefficient for the A/B exchange reaction. A discussion of the thermodynamics of ion exchange is beyond the scope of the present paper, but the subject has been reviewed by several authors [1, 4, 11]. For the purpose of the present discussion, it is sufficient to note that homovalent ion exchange can be described by an equation of the type presented above, and that the selectivity coefficient may change with the composition of the adsorbent.

The equivalent adsorption of metal ions on clay soils has been successfully described by ion-exchange equations. For example, El-Sayed et al. [9] reported a value of 0.96 for the thermodynamic equilibrium constant for Cu^{2+}/Ca^{2+} exchange on a bentonite clay. In a study on the adsorption of Zn^{2+} and Cu^{2+} on a clay soil containing illitic and smectitic clay minerals, it was found that at low concentrations in solution both metal ions were adsorbed selectively, with selectivity coefficients in the range of 10 to 100 for the Zn^{2+}/Ca^{2+} and Cu^{2+}/Ca^{2+} exchange reactions. At higher concentrations in solution, selectivity coefficients of about 1 were obtained for the same soil. The selective adsorption of Zn^{2+} and Cu^{2+} at low surface coverage was thought to be due to adsorption on surface groups associated with the edges of clay minerals or oxides in soil. The nonselective equivalent adsorption at higher surface coverage was ascribed to competition for planar sites on clay minerals [13].

Adsorption equations

The Langmuir adsorption equation was originally derived [23] to describe the adsorption of gas molecules on a plane surface, having only one kind of elementary site, each of which could hold only one adsorbed molecule. It was further assumed that the binding of a molecule on any one elementary site was independent of the binding on the remaining sites. When applying this equation to the adsorption of ionic species in soils, one has to consider that (a) adsorption sites with a net charge are never 'empty' but always associated with ionic species to balance the charge, (b) a range of different adsorption sites is encountered in soils, and (c) interactions among ionic species in the

adsorbed phase cannot be ruled out and thus the free energy of adsorption may depend on the composition of the adsorbent.

The Langmuir equation as used in soil science can be represented as:

$$q_i = QKc_i/(1 + Kc_i)$$

where q_i denotes the amount of species i adsorbed per unit mass of adsorbent, c_i is the aqueous concentration of species i, Q the adsorption maximum, and K is a constant, which is a measure for the heat of adsorption of species i. The Langmuir equation is usually written in the linearized form:

$$c_i/q_i = 1/QK + c_i/Q$$

The ion-exchange equation describing homovalent A/B exchange:

$$q_A/(Q - q_A) = K_{A/B} \cdot c_A/c_B$$

where Q is the adsorption maximum or cation exchange capacity, can be rewritten in the form of a linearized Langmuir equation:

$$c_A/q_A = 1/K^*_{A/B}Q + c_A/Q$$

where $K^*_{A/B} = K_{A/B} \cdot c_B^{-1}$, which is approximately constant if $c_B \gg c_A$. Thus, the Langmuir equation can be considered as an approximate ion-exchange equation, valid for low surface coverage of the adsorbent. Similar expressions can be derived for heterovalent ion-exchange reactions [13]. In ion exchange only differences between ionic species are measured. Therefore the Langmuir equation would apply to a system where different ionic species would have equal affinities for all adsorption sites, and where interactions between particles in the adsorbed phase would be the same for all species.

An advantage of the use of the Langmuir equation is that only c_A and q_A have to be known. Furthermore, the equation can also be applied to superequivalent adsorption. In the latter case, the physical significance of the constants, K and Q, becomes somewhat obscured, but the results may be of practical significance in a given situation.

Freundlich adsorption equation

The Freundlich adsorption equation represents an empirical relation between the amount of substance i adsorbed, q_i, and the aqueous concentration, c_i:

$$q_i = kc_i^{1/n}$$

where k and n are positive constants, n being greater than one in most cases of practical interest [10]. The Freundlich equation has been widely used to describe the adsorption of ionic and nonionic species in soils. The Freundlich equation can also be written in the logarithmic form:

$$\log q_i = \log k + (1/n) \log c_i$$

Although the Freundlich equation is empirical, several authors have attempted to give a theoretical derivation of the equation. Contrary to the Langmuir equation, which is based on an array of distinguishable, independent, and equivalent sites, the derivations of the Freundlich equation are all based on the assumption of a decreasing heat of adsorption with increasing surface coverage due to surface heterogeneity or to particle interactions [14].

The adsorption of micronutrient elements in soils has often been described successfully with a Freundlich equation of the form:

$$\log q_i = \log k + (1/n) \log c_i + a\mathrm{pH}$$

where a is a constant. The adsorption of aqueous species of Mn, Fe, Cu, and Zn generally increases with increasing pH, whereas in the case of Mo the adsorption has been found to decrease with increasing pH [44].

Mechanisms of adsorption

The reversible adsorption of ions onto a solid surface is likely to involve aquo ions that retain their primary and part of their secondary hydration shell. The coordinated water molecules would thus prevent the ions from entering into specific interactions with the adsorbent surface. The most important attractive forces between ions in a diffuse layer and a charged surface are long-range electrostatic forces of the ion-ion type. These interactions are nonselective, that is, they do not distinguish between ionic species of the same charge.

Ion exchange selectivity may arise from medium- and short-range electrostatic interactions between a charged surface and hydrated or complexed ionic species. Negative surface groups, ionic species, and coordinated ligands, may have permanent or induced dipole moments, or higher moments, such as quadrupoles or octupoles. The attractive forces resulting from these charge distributions are not effective over a long range. When ions approach the adsorbent surface, these attractive forces may become effective and give rise to ion selective or ion specific phenomena, that is, differences in adsorption behavior between different ionic species of equal charge.

Forces that are effective over an intermediate range include ion-(induced) dipole interactions. The interactions between permanent or induced dipoles are referred to as short-range or London-Van der Waals forces. The induction or dispersion interactions depend on the polarizabilities of the elementary particles involved. The polarizability is a measure for the ease with which a dipole moment can be induced in a particle, and increases with mass, size, and number of electrons in the outer shell of the particle. Differences in polarizability between ions may lead to ion-exchange selectivity, and the presence of polarizable ligands surrounding the central ion may enhance this process.

London-Van der Waals forces may play a part in the adsorption of

uncharged complexes, polynuclear hydrolysis products, and metal organic acid complexes. The apolar hydrocarbon parts of organic ligands have low affinities for the polar aqueous phase, and this may help to explain the preferential adsorption of complexes of metals and organic ligands. Oxides are generally strong adsorbents for hydrocarbons and this tendency increases with increasing chain length of the hydrocarbon group.

Ion-exchange selectivity resulting from differences in ion-solvent interactions, hydrated radii, and polarizabilities of ionic species is further enhanced by the rapid decrease in the dielectric constant of water near most mineral surfaces. Therefore, small differences in position of ions or ionic complexes near the adsorbent surface, may give rise to large differences in selectivity between ions.

Other types of bonding that are effective over a short range include hydrogen bonding and coordinate bond formation or ligand exchange. The hydrogen atom can form one covalent bond, and one bond, the 'hydrogen-bond,' which is largely ionic in character. Hydrogen bonds may play a part in the adsorption of organic ligands associated with metals on oxide surfaces. The ability of hydrated metal ions to form hydrogen bonds with surface groups may be correlated with the first hydrolysis constants of the metals (Table 7). This is because the hydrolysis reaction is essentially the proton transfer from a coordinated water molecule to a surrounding molecule, in this case a surface hydroxyl or other functional group.

Coordinate bond formation or ligand exchange is of particular importance for the transition metals and zinc. A coordinate bond between a metal ion and a solid surface may be established by exchange of a ligand, such as H_2O, from the inner coordination sphere of the metal ion for a surface group, such as $-OH$ or $-NH_2$. Coordinate bonds may also play an important part in the adsorption of uncharged complexes.

The ligand exchange reaction between surface hydroxyl groups and aquo ions of divalent Mn, Fe, Cu, and Zn may be visualized as:

$$\text{Surf-O}^- + [M(H_2O)_6]^{2+} \rightleftharpoons \text{Surf-}[OM(H_2O)_5]^+ + H_2O$$

or:

$$\text{Surf-OH} + [M(H_2O)_6]^{2+} \rightleftharpoons \text{Surf-}[OM(H_2O)_5]^+ + H^+ + H_2O$$

In electric fields of high strength, such as those associated with negatively charged surface hydroxyl groups, hydrolyzed species may be more strongly adsorbed than unhydrolyzed species because of their weaker interactions with surrounding water molecules, and hence smaller hydrated radii. For example, James and Healy [18] described the adsorption of Fe^{3+}, Cr^{3+}, Co^{2+}, and Ca^{2+} on SiO_2 as a specific adsorption of first hydrolysis products. Other mechanisms of ligand exchange include the displacement of more than one water molecule in the inner coordination sphere by surface hydroxyls. Whether this can occur depends on steric factors.

The mechanism of the specific adsorption of metal ions on oxide surfaces in soils and the role of hydrolysis are not well established. Most authors seem to agree, however, that the adsorption reaction results in the release of H^+ ions, that adsorption increases with increasing pH, and that the process is highly specific, probably involving surface hydroxyl groups associated with oxide surfaces. Because of acid buffering in soil, the decrease in pH associated with metal ion adsorption as measured in soil solution is usually smaller than would follow from the reaction equation.

The adsorption of molybdate in soils may involve the displacement of a surface hydroxyl group by an oxygen of the molybdate ion:

$$\text{Surf-OH} + MoO_4^{2-} \rightleftharpoons \text{Surf-OMoO}_3^- + OH^-$$

Other mechanisms, including the formation of hydrogen bonds or the displacement of more than one surface hydroxyl group, may be involved in the adsorption of Mo by soils. Iron oxides have been found to be strong adsorbents for Mo, and the adsorption of Mo in soils has been shown to decrease with increasing pH [15, 44].

The adsorption of boric acid in acidic soils generally increases with increasing pH, which may be explained by a reaction of the type:

$$\text{Surf-OH} + B(OH)_3 \rightleftharpoons \text{Surf-OB(OH)}_3^- + H^+$$

where the coordination number of B would increase from 3 to 4. The adsorption of B in soils has been reported to reach a maximum in the range of pH 7 to 9 [15], which may be due to the increasing stability of $B(OH)_4^-$ ions in solution with increasing pH, that is, due to a reaction of the type:

$$\text{Surf-OB(OH)}_3^- + OH^- \rightleftharpoons \text{Surf-O}^- + B(OH)_4^-$$

The adsorption behavior of B in soils is complex and needs further research.

Adsorption reactions play a major role in determining the solubility of aqueous forms of most micronutrient elements in soils. Organic surfaces are of particular importance for Cu(II). The solubility of aqueous Fe and Mn species under oxidized conditions is largely controlled by Fe and Mn oxides, but under reduced conditions adsorption reactions and organic complex formation become of major importance.

Adsorbed species may form chemical bonds with reactive surface groups, resulting in significant changes in the electronic orbital patterns of the species involved. This type of surface interaction can no longer be considered (specific) adsorption, and is referred to as chemisorption or surface precipitation. It probably plays an important role in soils, as is evidenced by the occurrence of many secondary minerals as surface coatings rather than discrete mineral phases. Occlusion of adsorbed metals, such as Cu and Zn, in the growing solid phases of Fe and Mn oxides is probably an important mechanism for the immobilization of these metals in soils [19]. Because of the changing moisture and redox conditions in soils, Fe and Mn oxides tend

to remain in 'active' form, and the occlusion of divalent cations in the oxides results in a net surface charge, which enhances the further adsorption of cations on the oxide surfaces.

Conclusion

The micronutrient contents of soils reflect the composition of the rock materials from which the soils were formed. This is more so in younger soils with a high proportion of primary minerals than in older soils that have been exposed to more weathering and therefore contain a lower proportion of primary minerals.

The processes of weathering and soil formation affect the micronutrient elements in different ways. Under oxidizing conditions, iron is relatively immobile in soils and weathering rocks because of the formation of insoluble ferric oxides. Manganese also forms stable oxides in its higher oxidation states. Under reducing conditions, both elements occur mainly in the divalent oxidation state and behave similar to zinc and copper. The solubility of divalent metal ions is largely determined by aqueous complex formation and adsorptive interactions with solid phases. Molybdenum and boron are relatively mobile in soils and weathering rocks and may be transported over large distances by natural waters.

Soils formed in humid climates may be depleted in mobile elements, such as Mo and B, and low in Zn, Mn, or Cu. Molybdenum and boron may accumulate in soils formed in semiarid and arid regions. Soils in arid regions are often high in pH (calcareous), which enhances the mobility of these elements (Chapter 6).

Intrazonal soils, such as peat soils, reflect the composition of the aqueous environment in which they were formed, rather than the composition of the surrounding rock materials. Copper deficiencies in peat soils (Chapter 3) may be due to low Cu contents in the aqueous medium, possibly because of the precipitation of insoluble copper sulfides under strongly reducing conditions, to the formation of insoluble organic copper complexes, or to the binding of copper by the organic matrix in these soils.

From an agricultural point of view, the plant-available micronutrient contents of soils are more important than the total contents. The total amount of micronutrients, their spatial distribution, and the chemical form in which they occur are generally not directly related to the availability of micronutrients in soils. For example, calcareous soils may be high in total Fe and Mn, but the availability is usually low because of the high pH in these soils and the low solubility of the oxides and adsorbed forms of these elements under those conditions. Hence, in calcareous soils, particularly if they are also low in organic matter, deficiencies of Fe and Mn as well as Zn and Cu may occur irrespective of the total contents of these elements.

Environmental factors, such as soil temperature and moisture conditions, may affect the availability of micronutrients in soils. As is the case for most nutrients, the effective availability of micronutrients tends to decrease with low temperatures and low moisture contents because of reduced root activity and low rates of dissolution and diffusion of nutrients. In soils with low moisture contents, colloidal particles may become immobilized quite readily, which may result in the occlusion of micronutrient elements sorbed on the surfaces of these particles.

Soil factors such as pH, redox potential, biological activity, organic matter, CEC, and clay content are of major importance in determining the availability of micronutrients in soils.

The availability of all micronutrients is affected by pH. The availabilities of Fe, Mn, Zn, Cu, and, under slightly acidic conditions, B tend to decrease with increasing pH, reflecting the decreasing solubility of oxides and surface-adsorbed or precipitated forms with increasing pH and the high stability of complexes with organic matter at high pH. The availability of Mo and of B under alkaline conditions tends to increase with increasing pH.

When the redox potential of a soil decreases, such as in rice soils upon flooding, the availability of Mn and Fe initially increases because of the reduction and dissolution of Mn and Fe oxides in soil. The availability of elements occluded in these oxides, such as Zn, Cu, and possibly Mo and B, would also increase when these oxides dissolve. If the redox potential decreases to very low values, insoluble sulfides of Cu, Mo, Fe, and possibly Mn and Zn may be formed, which would make these elements unavailable to the crop. When submerged soils are drained off and the redox potential increases rapidly, the soil solution may become supersaturated with respect to Fe and Mn oxides, and coprecipitation of other metals with Fe or Mn may become important. The oxidation of metal sulfides may also lower the pH, thus increasing the solubility of metal ions in solution.

The decomposition of organic matter by the heterotrophic biomass may result in the release of complexing organic compounds that can form soluble complexes with elements such as Cu, Zn, Fe, and Mn. Soluble organic complexes may increase the solubility of these elements significantly, in particular that of copper. On the other hand, the formation of complexes with soil organic matter, or the incorporation of micronutrients in the biomass of the soil, may decrease the availability of these elements.

In order to increase the availability of micronutrients to the plant, one could apply the micronutrients directly to the crop (foliar application) or to the soil in a soluble form (e.g., metal chelates). In large areas of the tropics and subtropics, however, the cost of such practices would be prohibitive. Under such circumstances, one could try to manipulate some of the factors that affect the availability of micronutrients in soils, such as pH (by liming), redox potential (by irrigation, drainage), or organic matter and biological activity (by use of manure, crop rotation). Hence, a knowledge of the

chemistry and interactions of micronutrients in soils and an understanding of the factors that determine the availability of these elements in soils are of major importance for good fertilizer and nutrient management.

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2. Micronutrient needs of tropical food crops

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Micronutrient needs of tropical food crops

The essential micronutrients are copper, zinc, manganese, iron, boron, and molybdenum; chlorine is also essential but will not be discussed here since it is rarely lacking in agricultural systems. These micronutrients are essential for plant survival but are only needed in small quantities. In this chapter we will examine the micronutrient needs of tropical food crops. We will review the factors that control micronutrient uptake, the crop's response to this uptake, and the way in which the tropical climate and crop varieties might affect the amounts of micronutrients needed. We will also discuss trends in crop management and yield levels and how these factors affect micronutrient needs.

The tropics are very diverse in both climate and soil resources. The tropics are most commonly defined as the geographic region that extends from 23.5° north to 23.5° south of the equator. This area covers 38% of the land mass area of the world, and it is spread over Africa (43%), South America (28%), Asia (20%), Australia (5%), and Central and North America (4%). Nearly 45% of the world's population lives in this region. The mean monthly temperature of the tropics are 18°C [27], and generally the temperature is favorable for cropping all the year around. However, moisture often limits the number of crops that can be grown per year, particularly in the dry semiarid tropics and wet-dry semiarid tropics with 2.0–4.5 and 4.5–7.0 wet months, respectively.

Many crops are grown in the tropics, but 12 crops are the most important in food production. These twelve and their production statistics are listed in Table 1. Of these, sorghum, millet, wheat, pulses (cowpeas, pigeon peas, chick-peas, beans), and groundnuts are more abundant in dry semiarid tropics and others in wet-dry to humid tropics. In the economy of the tropics, in addition to these food crops there are a number of important commercial crops such as sugarcane, cotton, coffee, tea, cocoa, coconut, oil palm, and bananas. Although we are not discussing the micronutrient needs of these crops, it needs to be recognized that they all show micronutrient deficiencies

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and claim higher use of fertilizers, including micronutrients, because of their commercial importance. It may be observed that the average yields of all these 12 food crops are very low, but the potential for increasing production from them in tropical areas is very high. The introduction of high-yielding varieties, particularly of cereals (rice, wheat, sorghum, maize, millets), is opening up new vistas in agriculture in the tropics and providing new opportunities and potential for production.

Tropical crops are not different from temperate crops in their need for micronutrients. However, the tropical climate, soils, cropping systems, and yield levels are usually quite different from those in temperate regions. Although many crop species are common to both regions, including maize, wheat, soybean, potato, and others, the varieties or cultivars are usually different. As we will see there are significant differences between crop cultivars in the efficiency with which they absorb and utilize micronutrients, and these differences may be one valuable tool for increasing food production on some tropical soils.

Role of micronutrients in crops

The role of micronutrients in the plant has been reviewed by several authors in the last 10 years [36, 38, 62]. Since in this respect tropical crops are probably not much different from temperate crops, only a brief overview follows.

Copper

Copper like most cations, is primarily involved with enzyme activity. Several enzymes that are affected directly by copper deficiency have been identified. The physiological result of copper deficiency is an apparent wilting of leaves. Graham [34] suggests that this wilted appearance is the result of structural weakness of the cell walls in copper-deficient plants and is not related to water stress. However, copper deficiency also reduces root growth more than shoot growth, creating an unfavorable shoot:root ratio [16, 49, 66]. This increased shoot:root ratio could lead to plant/water stress. The two phenomena may work together to create the wilted appearance.

Copper deficiency usually delays maturity and reduces yield by reducing grain size [32, 61]. This reduced grain size is attributed to a lower photosynthetic efficiency caused by increased closure of stomata in copper-deficient plants [34]. When stomata are closed, the diffusion of carbon dioxide into the leaves is slowed or stopped. Also, studies with carbon-14 labeled carbon dioxide show that less carbon is fixed in C_6 sugars, the types that are translocated to other parts of the plant in the phloem [12].

Molybdenum

Molybdenum is needed in the least amount of all the essential micronutrients. It is involved in several enzyme systems including nitrogeneous nitrate

Table 1. Production, area, and yield of the major food crops in the tropics in 1981 [30]

Food crop	Area	Production	Yield	World production
	(millions of ha)	(millions of mt)	(mt/ha)	(%)
Rice (*Oryza sativa*)	100	222	2.2	54
Cassava (*Manihot esculenta*)	14	123	9.0	97
Maize (*Zea mays*)	54	79	1.5	18
Wheat (*Triticum aestivum*)	37	61	1.6	13
Sorghum (*Sorghum spp.*)	35	31	0.9	43
Potato (*Solanum tuberosum*)	2	24	10.6	9
Pulses (various species)	48	23	0.5	55
Millet (*Pennisetum* and others)	36	21	0.6	71
Soybean (*Glycine max*)	11	18	1.6	21
Sweet potato (*Ipomoea batatas*)	2	16	6.6	11
Groundnuts (*Arachis hypogeae*)	16	13	0.8	68
Bean (*Phaseolus vulgaris*)	20	9	0.5	65

reductase, xanthine oxidase, aldehyde oxidase, and sulfate oxidase [62]. The result of Mo deficiency is a disrupted nitrogen metabolism. Nitrate reductase activity is reduced by Mo deficiency. Nitrate reductase is involved in the first step of incorporating inorganic NO_3^- into organic N compounds. Das Gupta and Basuchaudhuri [26] demonstrated that Mo applications to rice increased the amount of reduced nitrogen in the plant tissue.

Mo deficiency results in reduced chlorophyll concentration in the leaves [1, 26] which leads to decreased photosynthetic efficiency. The lack of chlorophyll production is most likely a secondary effect of the disrupted N metabolism since Mo has not been shown to play a direct role in chlorophyll synthesis.

Another role of Mo in N metabolism is in N_2 fixation by legume-*Rhizobium* symbioses. Nitrogenase is a Mo-containing enzyme [13, 87]. It catalyzes the fixation of dinitrogen gas to ammonia, which can be utilized by the host plant. However, examples of Mo deficiencies on legumes in the tropics are rare.

Increased use of N fertilizer increases the need for Mo. The production of nitrate reductase by plant is induced by the nitrate availability. Evans [28] showed that NO_3^--grown plants required more Mo and that all the additional uptake was accounted for by the nitrate reductase enzyme.

Iron

Iron is readily oxidized and reduced between its two oxidation states Fe^{3+} and Fe^{2+}. Its role in plant metabolism is closely linked to this reversible Fe^{2+}/Fe^{3+} oxidation. Many of the reactions associated with Fe are the redox reaction of chloroplasts, mitochondria, and peroxisomes [70, 71]. These reactions include coupled electron-transfer reactions (cytochromes a and b), oxidases (cytochrome oxidase), and peroxidases (catalase and peroxidase) [22]. Also, Fe plays a role in the formation of amino levulinic acid, which is a precursor of chlorophyll synthesis [58]. In addition, a strong correlation exists between the leaf chlorophyll and Fe content as shown in Figure 1 [84]. When Fe becomes limiting, thylakoid development (part of the chloroplast) slows or stops. Then, as the leaf continues to expand, the thylakoid constituents such as Fe and several types of chlorophyll are diluted, resulting in the pale yellow color typical of Fe deficiency.

Zinc

Zinc serves both some structural and some regulatory roles in enzyme activity in plant tissue. Only a few enzymes have clearly been identified as requiring Zn; however, for several others there is considerable indirect evidence of Zn involvement [22, 86]. Zn deficiency is characterized by a reduction in the number of ribosomes and RNA in the plant cells. Plant growth is stunted by zinc deficiency. Like most micronutrient deficiences, Zn deficiency results in an overall reduction in photosynthetic efficiency and disrupted metabolism.

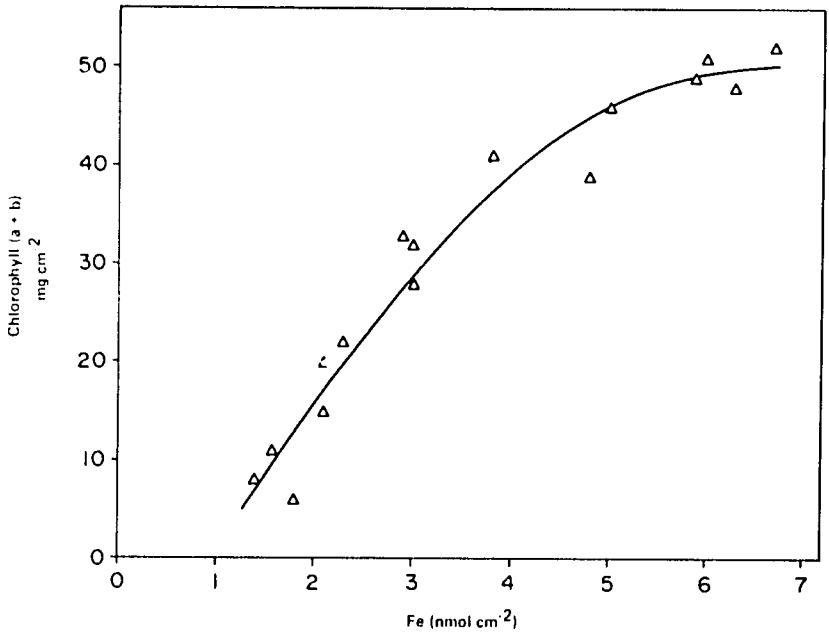

Figure 1. Relationship between leaf iron and chlorophyll contents

Manganese

The role of Mn in plant matabolism is very unclear. Manganese has properties similar to Mg and can substitute for Mg in some enzyme systems. This is probably not a common occurrence in nature since Mg is taken up by crops in much greater quantities than is Mn. Only one system, albeit a very important one, has been shown to require Mn. This is the splitting of water by photolysis in photosystem II [17]. This reaction probably involves a change in the oxidation state of Mn, but the exact structure or functional role of Mn in photosynthesis has not yet been defined.

Boron

The role of B in plant metabolism is not well understood. In fact, no specific function of B has been identified. Only information on the physiological consequence of B deficiency is available to us, and this has been reviewed by Jackson and Chapman [43]. The most pronounced effect of B deficiency on metabolism is a disrupted RNA synthesis. The disruption of RNA metabolism has been studied largely using isotopically labelled RNA precursors in normal and B-deficient plants. An interesting observation is that the results of B deficiency are very similar to those from the application of some plant hormones. This suggests a link between B metabolism and plant hormones. However, our theories of how B functions in plants still have little supporting evidence, and B remains the least understood of the micronutrients.

Species differences

Crop species have shown varying responses to micronutrient availability. A crop such as cassava, which is native to infertile soils, can grow on soil surprisingly low in available micronutrients, whereas crops such as field beans and sorghum seem to require much higher amounts of available micronutrients. Differences between crop species have been recognized for a long time. In 1954, 26 crop species were tested and showed a wide range of sensitivity to Zn deficiency [89]. A more recent complete summary of the likelihood of various crops to respond to micronutrient fertilizer application under conditions conducive to deficiency is shown in Table 2 [54].

Genetic differences between cultivars in their susceptibility to micronutrient deficiencies could be due to several possible mechanisms. Differences occur in (1) the ability to absorb nutrients at low concentration; (2) the excretion of substances by the root to enhance the availability of a micronutrient; (3) the ability to retranslocate ions within the plant; (4) the efficiency of utilization of absorbed nutrients, i.e., the plant's ability to grow well with low tissue concentrations. It is probable that more than one of these mechanisms are responsible for the observed variability.

Table 2. Responses of different food crops to micronutrients under soil or environments favorable to a deficiency [54]

Crop	Zn	Fe	Mn	Mo	Cu	B
Beans	H	H	H	L	L	L
Corn (maize)	H	M	L	L	M	L
Potatos	M	-	M	L	L	L
Sorghum	H	H	H	L	M	L
Rice	M	H	M	L	L	L
Wheat	L	L	H	L	H	L

H = high, M = medium, L = low.

Brown and Jones [8] concluded from their studies that the plant response to micronutrient stress is a genetically controlled adaptive mechanism. The efficient species and varieties exude more H^+ ions and reductants from their roots and thus make some nutrients more available. Christ [19] reported that monocots require higher soil concentrations of iron and are less efficient in iron uptake than are dicots. Much of the difference seems to lie in their abilities to absorb iron in the Fe^{3+} state. In many cultivars severe micronutrient deficiency, such as zinc or iron deficiency, appears in the early stages of growth but disappears or is reduced in intensity with the growth of the root system or rise in temperature. In other cultivars, grown in the same environment, no deficiency symptoms develop. Such cases are common in rice, sorghum, maize, and chick-peas.

Varietal differences

The genetic control of micronutrient uptake and utilization is well documented, if not well understood, by results showing a wide range of efficiency within many crop species [10]. The genetic diversity of the world's crop plants has allowed great expansion in plant breeding activities in the last two decades. The national and international breeding programs have been very successful in developing varieties that have high yield potential, are disease and pest resistant, and respond well to fertilization, primarily nitrogen. The success of these breeding programs has provided hope that, at least to some extent, it is possible to modify the plant to fit in an unfavorable environment instead of trying to change the environment. Randhawa and Takkar [74] have listed the varieties of five cereals (wheat, barley, rice, maize, and sorghum); two pulses (chick-peas and black gram); and two oil seeds (Raya and sunflowers) that have been found tolerant to Zn and Fe deficiency and to Mn and B toxicity (Table 3). Research on improving the efficiency of a crop species by improving its ability to absorb and utilize micronutrients is still in its early stages of development but is expanding. The advances made in developing varieties capable of tolerating high Al, high acidity and toxicity or deficiency of some of the micronutrients have yielded results of practical significance.

Wheat

Wheat seems to be the most studied crop species relative to genetic differences in micronutrient responses. It has been reported [79] that susceptibility to Zn deficiencies among the Indian wheats was closely related to their relative efficiency in the utilization of soil Zn. There were significant differences in the time of appearance and intensity of Zn deficiency symptoms, amount of yield depression, and in tissue Zn concentration. The same authors further reported that tissue concentrations of Zn in cultivars ranged from 4.2 to 28.3 ppm under Zn deficiency conditions and the responses to Zn increased as the inefficiency of utilization of Zn increased. Randhawa and Takkar [74] presented a comparison of three wheat cultivars for their susceptibility to Zn deficiency when three different growth media were used (Table 4). The results show the profound influence that the environmental condition has on the plant's response to micronutrients.

One study [61] compared seven genotypes of wheat, one of barley, and one of oats for their sensitivity to suboptimal supplies of Cu and for their ability to recover from Cu deficiency when Cu was applied at defined stages of growth. The genotypes differed markedly. HALBRED wheat and Clipper barley was less sensitive to Cu deficiency than were the wheat cultivars GABO, GLAIVO, Pinnacle Chotelerma, UP301, Durambia, and the oat cultivar Avon. The author further concluded that genotypes with relatively higher yield potential were less sensitive to Cu deficiency than were those with lower yield potential. There was no apparent association between

Table 3. Varietal tolerance to micronutrient deficiency or excess [74]

Crop	Varieties tolerant to			
	Zinc deficiency	Mn toxicity	B toxicity	Fe deficiency
Wheat (*Triticum aestivum*)	WG377 WL212 UP301	K816	WG357 Vijay	–
Barley (*Hordeum vulgare*)	PL26, 27, 40, 74, 76 RD103 DL40, 70 BG7 BH2 Vijay	–	Vijay Vijay + Jyoli +	K19 Kesri
Rice (*Oryza sativa*)	Sabarmati Ratna Anna Purna Chauvery Madhukar Balmagna Caloro CR10-113 CEB24 BR24 S10-13	– – –	– – –	MTU17 IE71444 IR1561-2283 Karuna – –
Maize (*Zea mays*)	Ganga 2, 3, 4 JML22 T41, TW			
Sorghum (*Sorghum vulgare*)	2077 × 1151 Swarna			
Chick-peas (*Cicer arietinum*)	P6828 N59 S26 BR78			
Black gram (*Vigna mungo*)	T65, 55 Khargaon 3			
Raya (*Brassica juncea*)	T51 AL198			
Sunflower (*Helianthus annuus*)	Aranavisski NP15			

Table 4. Relative tolerance to zinc deficiency of the wheat cultivars [74]

Cultivar	Method of screening		
	Sand culture	Pot culture	Field
Kalyansona	H	M	L
WG357	L	M	H
WP301	L	H	–

H = high, L = low, M = medium

dwarfgrowth and sensitivity to Cu deficiency in wheat. Genotypes with higher grain protein content were potentially more susceptible to Cu deficiency than were those with lower grain protein content.

Generally wheat is more susceptible to Cu deficiency than rye [35]. Crosses between wheat and rye produce *Triticale* which maintains the desirable tolerance to low Cu availability of the parental rye variety. Studies suggest that the copper efficiency trait of rye is carried on a single chromosome and that it should be possible to transfer this trait from rye to wheat, producing Cu-efficient wheat cultivars. There is little doubt that there are genetic differences between cultivars for micronutrient efficiency, but also that these differences are modified by the environment. In wheat there has been a substantial amount of research identifying micronutrient-efficient varieties; however, the mechanism controlling this efficiency and the effects of environmental conditions remain little understood.

Sorghum

Sorghum seems particularly susceptible to Fe deficiency; thus, much of the work on cultivar differences in sorghum has been concentrated on this element. The Fe-efficient cultivars KSS and Pioneer B46 sorghum took up more Fe and contained less P than did the Fe-inefficient cultivar B line and Wheatland [8]. Similarly, it was observed that in Fe-deficient soils SC369-3-IJB sorghum developed Fe chlorosis, whereas NK212 remained green [11]. Under Cu-deficient conditions PS-2 developed apparent Cu-deficiency symptoms, characterized by high P accumulation in the lower leaves. These authors concluded that efficient uptake of P may not be advantageous under Fe- and Cu-deficiency conditions. Kanan [46] observed that the pH of the medium was reduced to 3.5 by the adventitious roots and not by the seminal roots of sorghum CSH5. In his view the signal from the chlorotic leaves was transmitted to adventitious roots which produced more reductants to make more Fe available.

The Zn and phosphorus uptake characteristics of a drought-resistant variety, M35, and a drought-susceptible variety, M47, have been compared [72]. There is little difference in uptake of Zn by the roots of the two varieties; however, M47 is much more efficient at transporting Zn to the shoot. It was also noted that Zn inhibits the uptake of P much less in the drought-resistant variety than in the drought-susceptible variety. This difference may facilitate the survival of M35 under water stress, which also reduces P availability.

Rice

In rice Zn deficiency is quite common; it has been identified by IRRI as the most important nutritional factor, after nitrogen and phosphorus, in limiting rice yields [14]. Giordano and Mortvedt [33] compared 12 rice varieties, some of which were developed in the tropics and others in the United States. A marked difference in their responses to low Zn availability was observed,

with the shortest duration varieties having the least tolerance to Zn deficiency. In experiments at CIAT [15], the Colombian varieties, in general, were found to be more tolerant of low availability of Zn than were those developed at IRRI. However, recent IRRI varieties such as IR42 have proven very tolerant to Zn deficiency as well as many other stresses [42].

Varietal differences in Fe-stress tolerance have also been reported in rice. Shim and Vose [78] ranked the varieties Rebifun, SIAM 29, and Paldal in order of decreasing ability to absorb inorganic Fe. Pandey and Kannan [64] also found that varieties differ in their ability to absorb and translocate inorganic Fe, although this ability was not well correlated with Fe-stress tolerance in the field. They did find, however, that Fe uptake was inhibited by high Ca concentrations in stress-susceptible varieties but unaffected in the stress-tolerant varieties. They classified varieties Basmati, B63 (Basmati mutant), TR23, TR25, PVR1, AU1 (IR8 mutant), and IET144 as tolerant and IR8, Sona, B36 (Basmati mutant), and Jaya as susceptible to Fe stress.

Maize

Genetic variations in the efficiency of uptake and utilization of some micronutrients have also been observed in maize, although the nature of the uptake efficiency is not clear. An Fe-efficient line, WF9, produced H^+ ions and greater reducing conditions in the rhizosphere than did the Fe-inefficient line YS^1/YS^1 [21]. This seems like a plausible explanation for the differences in efficiency. However, when the two varieties were grown together, the Fe uptake and utilization of the inefficient line were not helped by the presence of the efficient line.

Several studies have shown differential responses of maize line to Zn. Shuman et al. [76] concluded that there is little evidence to support the hypothesis that hybrids are more efficient in absorbing soil Zn. In their opinion the differences in responses to Zn are dependent on biological processes involved in the utilization of absorbed Zn. When a Zn-efficient cultivar (Conico Composite) was compared with Pioneer 3369A, a cultivar susceptible to Zn deficiency, it was concluded that the Zn in the tissue of Concio was more biologically active [65]. In another study comparing an efficient and an inefficient cultivar, it was concluded that the inefficient variety translocated less Zn from the roots to the shoot, did not utilize shoot Zn as efficiently to produce dry matter, and accumulated imbalanced quantities of the nutrients P, Fe, and Mn which are known to be associated with Zn deficiency [20]. The low efficiency of translocation and utilization of absorbed Zn, especially when a large quantity of P is available, has been attributed to the immobilization of large amounts of Zn in the cell wall where it is not available for biological processes, which take place within the cell membrane [90].

Legumes

Research on the selection of soybean lines for tolerance to adverse soil environments has been done for many years in the United States. The research

has demonstrated genetic diversity especially in Fe efficiency. One test of 10 soybean varieties showed that Forrest was the most Fe inefficient and Bragg the most Fe efficient [9]. These authors pointed out problems that developed in the midwestern part of the United States as a result of the introduction of some new varieties. Reports of Fe deficiency were not common for soybeans on some marginally low Fe soils while the variety Hawkeye was grown. When new higher yielding varieties were introduced, the incidence of Fe deficiency increased dramatically. This can be expected to occur in other parts of the world also since varieties are usually selected and developed on highly fertile soils without regard to their nutrient efficiency.

Some genetic diversity in micronutrient varietal responses has been reported in other food-grain legumes. Some varieties of Kabuli type (bold seeded) chick-peas are more susceptible to Fe deficiency than are others. In calcareous soils, Fe deficiency becomes visible after 6–8 weeks of seeding and may persist in highly susceptible varieties, even to the point of killing the plants. Sometimes Fe chlorosis reappears in some genotypes after irrigation or rainfall. Genotypic differences in Kabuli type chick-pea cultivars are being recorded at the International Center for Agricultural Research in the Dry Areas (ICARDA), and in a cooperative project between ICRISAT and ICARDA (personal communication from K. B. Singh, 1982) the cultivars tolerant to Fe deficiency have been identified. Likewise in groundnuts, differences in micronutrient sensitivity exist. It has been shown that the use of Fe-efficient groundnut varieties could save the cost of Fe fertilizer applications and still provide high yields [39]. Similar differences in Fe efficiency of dry beans have also been reported in the United States [25].

The genetic potential for improvement in micronutrient utilization in legumes other than soybeans has been exploited very little. There exists a wide variety of legume species and local varieties in the tropics. The collection, characterization, and utilization of this material in breeding programs is increasing and will provide a strong base for the selection of micronutrient-efficient varieties.

Roots and tubers — cassava and potatoes

Cassava is an important crop in the tropics, particularly on the acid infertile, aluminium-rich soils, where toxicity of Al and sometimes Mn is a major problem for most crops. Considerable genetic diversity has also been demonstrated within this crop. Large numbers of varieties of cassava have been screened for their acid tolerance. In a lime and micronutrient trial by CIAT in Colombia it was observed that liming reduced the uptake of Zn, Mn, Cu, and B [41]. High levels of liming greatly reduced yield by inducing Zn deficiency. Trials on the Zn-deficient soils of Punjab (India) [37] demonstrated differences in the responsiveness of potato varieties to Zn fertilizer applications. The varieties Kufri-Chandar-Mukhi and Kufri-Alankar were more responsive than were the varieties Kufri-Sandhuri and Kufri-Joti. The authors

also noted a greater response to Zn in the winter than in the summer which indicated an interaction with climate.

Path of micronutrient uptake

In order to understand the dynamics of the micronutrient needs of tropical food crops, an explanation of the factors that control the rate of uptake and the timing of the needs is necessary. The various micronutrients have different mobility characteristics in the soil, and they are needed in widely differing quantities; in addition, the plants vary in their ability to redistribute the micronutrients from older tissue to new growing points or for grain filling. The mobility of nutrients in the soil and plant, the quantities of micronutrients in the seed, and environmental conditions all affect the quantity and timing of micronutrient needs and uptake.

The amount of uptake of micronutrients from the soil solution is dependent on several factors including (1) the rate and distance of movement of nutrients in the soil; (2) the volume of soil the plant is exploiting; and (3) the plant's capacity to absorb the nutrient [4]. Nutrients move to the plant root by diffusion and mass flow [3]. Diffusion occurs along a concentration gradient. As plant roots absorb nutrients, the soil environment near the root is depleted of the nutrient and the gradient is thus created. As long as root uptake exceeds the rate of movement of nutrients toward the root, diffusion will continue. The rate of diffusion of an ion depends on the physical characteristics of the ion, the soil's volumetric moisture content, soil texture, and reactions between the soil and the ion. Besides the innate differences in mobility of micronutrients in soil, the rate of movement of micronutrients is influenced by the plant's uptake characteristics. Plants that are very efficient at absorbing nutrients at low concentrations will speed diffusion by creating a large concentration gradient.

The other mode of micronutrient movement to the plant is by mass flow. The plant loses water to the atmosphere by transpiration, and this induces a flow of water to the root where it is absorbed. The water moving to the root has nutrients dissolved in it. Thus, the rate of supply of nutrients to the root is related to the plant's transpiration rate. Very high transpiration rates would increase the flow of nutrients to the root, and lower transpiration rates would decrease the nutrient flow. High transpiration rates occur with high temperature, low humidity, and high solar radiation, which are found throughout much of the arid and semiarid tropics as well as part of the humid tropics. This is an oversimplification, though, since soil moisture also limits transpiration. As low moisture decreases transpiration and increases the tortuosity of the diffusion path, nutrient mass flow and nutrient diffusion will both decrease.

Research on nutrient movement to roots indicates that Cu, Fe, and Mn do not move in the soil to any great extent with mass flow [5, 63]. Thus,

nutrients only become available to the plant as the roots explore new volumes of soil and as the relatively slow diffusion process takes place. On the other hand, Mo moves freely by mass flow to the plant root.

Mycorrhizae may play a role in the uptake of these relatively immobile micronutrients. Vesicular-arbuscular mycorrhizae are fungi that infect the roots of most plant species. They have been shown to play a role in P uptake. Their hyphae extend out from the root into the soil and in so doing increase the volume of soil that the plant can deplete of nutrients that are very mobile. A study of mycorrhizae on cassava showed that elimination of the fungus caused about 10% decrease in Zn uptake [88]. Similarly, it was found that the presence of mycorrhizae increased Zn and Cu uptake in both maize and soybeans but had little effect on Mn uptake [51]. The role of mycorrhizae in micronutrient uptake has been studied very little, and the data are inconclusive to date.

The second factor influencing micronutrient availability is the volume of soil being exploited by the crop. The rooting pattern of crops grown in some tropical locations is quite different from that of crops growing in deep fertile soils. In particular, the high aluminium content of the subsoils in large areas of South America inhibits root penetration. As problems of water availability and adaptation of varieties to these environments progress, it is probable that the incidence of micronutrient deficiencies will increase.

A third factor is the plant's capacity to absorb and utilize the micronutrients that are available. The uptake process is best described by the membrane carrier site model. This model depicts sites located on the membrane which actively transport ions from outside the membrane to the cytoplasm. This process utilizes metabolic energy; thus, uptake is affected by temperature, water stress, and respiration-inhibiting chemicals. It seems that Zn, Cu, Mn, and B are absorbed by active uptake [6]. After studying the kinetics of the uptake of these four nutrients, Bowen also concluded that there are three separate uptake mechanisms operating. One actively transports B, another Mn, and the third both Cu and Zn. These two compete for the same uptake sites. Some earlier studies suggested that Zn uptake is passive, but Moore [59] pointed out that this conclusion is probably incorrect because of the way short-term, excised root experiments are often conducted.

The timing of the onset of micronutrient deficiency symptoms is influenced by the seed nutrient reserves and the plant's ability to redistribute nutrients from mature to growing tissue. According to Tiffin [85], seed reserves of micronutrients fall into three classes. The first includes only Mo, which is required in such small quantities that usually the seed contains an adequate amount to allow the plant to grow to maturity. The second group includes Cu and Zn. The seed reserves of these elements are adequate to delay the onset of deficiency, but without an adequate supply of available nutrients in the soil a deficiency is sure to occur. The third group includes B,

Mn, and Fe. The seed reserves of these elements are so small that if soil is low in available nutrients deficiency symptoms will occur very soon after germination.

All of the micronutrients can move through the xylem tissue from the roots to the aerial portions of the plant. However, once in a leaf they differ in their ability to be redistributed to new expanding leaves or the filling grain. Boron is virtually immobile once it reaches a plant organ [85]. Thus, a continuous supply of B is needed by a crop to avoid deficiency. At the other extreme is molybdenum. Mo is readily redistributed via the phloem tissue to the other parts of the plant where it is needed [57]. The other micronutrients Zn, Cu, Fe, and Mn are intermediate in mobility. The deficiency symptoms of all four of these appear first in the youngest leaves. This suggests that the plant's ability to redistribute these micronutrients from mature to growing tissue is limited. It has been shown that in wheat Cu is essentially immobile until a leaf senescences [40]. At that point most of the Cu is redistributed to younger leaves or the grain. It is reported that in sorghum Cu and Zn were retranslocated from the vegetative tissue to the head but Mn was not [44]. In maize at least some Zn is redistributed from the vegetative tissue, mostly the stalk, to the grain [56]. Although some redistribution is evident, it is probable that a continuous supply of each micronutrient except Mo is needed to avoid deficiency and a reduction in yield.

Effects of climate

The two main components of climate affecting micronutrient availability are temperature and moisture availability. The effect of these factors has been studied most extensively in temperate regions; little work on their effects on tropical crops has been reported. Nevertheless, some general conclusions are still possible.

Zinc deficiency early in the growing season is often associated with cool soil temperatures. Sharma and Motiramani [77] reported that the response of rice to Zn applications decreased with an increase in soil temperature. Martin et al. [55] found that high levels of P induced Zn deficiency in cool weather but not in hot weather on soils low in available Zn. Lucas and Knezek [54] suggest that the combination of low light intensity and cool soil temperatures account for the observed greater incidence of Zn deficiency when the weather is wet and cloudy, and Chino and Baba [18] confirm that shading and low temperatures reduce Zn translocation to the plant tops. Lindsay [52] suggests that, in addition to changes in Zn transformations in the soil caused by cool temperature, reduced root development resulting in a less favourable shoot : root ratio may increase the incidence and severity of Zn deficiency. Randhawa and Nayyar [73] observed that in India micronutrient deficiencies are most severe in

cold weather and mild or absent in warm weather on marginally deficient soils.

Soil moisture also affects micronutrient availability. Continuous submergence increases Zn deficiences in rice regardless of the soil pH [14, 81, 83], and the application of Zn fertilizers often produces a dramatic increase in grain yield. Similarly Gangwar and Mann [31] and Brar and Sekhon [7] reported greater responses to Zn applications in rice under flooded conditions than under nonflooded conditions.

Excess moisture increases the availability and uptake of Fe, Mo, and Mn [50]. The increased solubility of Fe caused by flooding may help rice crops, which seem to have a higher Fe requirement than do other crops. In fact, flooding can actually cause Fe toxicity on some soils [75].

Dry soil conditions can cause reduced micronutrient uptake, particularly among those that do not move through the soil by mass flow to the root. The ions of Cu, Fe, and Mn must move to the root by diffusion, as mentioned earlier, through the soil liquid phase. As the soil dries, the tortuosity of the diffusion path increases rapidly. Porter et al. [67] report that the rate of diffusion decreases 6- and 25-fold at 1 and 15 atmosphere of soil water potential, respectively. This, of course, reduces uptake substantially, especially when roots are not growing rapidly enough to exploit new volumes of soil. A more detailed review of the effects of climate on micronutrient availability is given by Lucas and Knezek [54]; however, the effects of climate on both micronutrient reactions in the soil and on crop uptake are not well understood especially under tropical conditions.

Crop management and yield levels

Besides the nature of the crop and its variety, crop management factors and the yield level also influence the frequency and severity of micronutrient deficiencies. The micronutrient removal per ton of dry matter produced by a crop is indicated in Table 5. The introduction of high-yielding varieties, the increased use of high-analysis NPK fertilizers, and increases in cropping intensity can all lead to micronutrient deficiency problems. The principal reason for the increase in deficiencies is the increased demand placed on the soil to supply nutrients for the increased crop yield and the increased number of crops per year. The soil's ability to supply the required quantities of micronutrients may have been adequate for centuries of traditional cropping and traditional low yields, but it is not adequate for high-intensity cropping and high yields.

Reports of micronutrient deficiency are increasing in number. Randhawa and Nayyar [73] reported that in India before 1966, when low-yielding and less-fertilizer-responsive varieties were used, only low-to-moderate responses to micronutrient applications were recorded on a few soils. However, since that time the frequency of responses to micronutrients, especially Zn, has

Table 5. Micronutrients removed by a crop in grams per ton of dry matter

	Fe	Mn	B	Zn	Cu	Mo	Source
Cereals							
Rice	61	270	6	16	7	2	[24]
Maize[a]	1200	320		130	130	-	[48]
Wheat	232	26	18	21	9	0.80	[29]
Sorghum	360	27	27	36	3	1.05	[29]
Pearl millet	264	23	27	22	9	0.84	[29]
Roots and Tubers							
Cassava	200	75	25	75	8	-	[2]
Potato	160	12	50	9	12	0.28	[29]
Pulses							
Mung beans	170	38	32	13	11	1.05	[29]
Chick-peas[a]	57	29	-	38	14	-	b
Pigeon peas[a]	39	14	-	23	13	-	b
Oil Seeds							
Groundnuts	499	39	44	9	5	1.32	[29]
Soybeans	242	147		52	69	-	[68]

[a]Grain only.
[b]Jambunathan, 1983, personal communication.

increased considerably. The mean and range of this response to Zn for a large number of crops are shown in Table 6. The increases in micronutrient responses have also been reviewed by Kanwar and Randhawa [47], Takkar and Randhawa [81], and Katyal and Sharma [48]. Summarizing the thousands of fertilizer response experiments on farmers' fields, these authors reported that 50% 60% of the sites showed a significant increase in grain yield due to Zn applications. In some districts the yield increase due to Zn was as high as 30% 40% with regard to the controls. The responses to several micronutrients in India are given in Table 7.

Table 6. Responses of crops to zinc application in field experiments conducted in India from 1967 to 1980 [73, 82]

	Number of experiments	Range of response (min. & max.) in individual field experiments	Range of mean value of responses in various states	Average response mean of all experiments
		(kg/ha)	(kg/ha)	(kg/ha)
Wheat	1,555	0.0 4,750	330 1,480	370
Rice	799	0.0 5,470	290 1,300	630
Maize	170	1.0 3,090	250 800	520
Pearl millet	207	1.0 670	170 180	150
Sorghum	134	40.0 1,350	180 520	340
Chick-peas	12	100.0 870	230 560	310
Groundnuts	61	50.0 1,210	180- 470	410

Table 7. Yield increases of crops due to micronutrient applications other than zinc in India [73]

Nutrient	Wheat	Rice	Groundnuts
		(kg/ha) (mean)	
Fe	580	1,440	240
Mn	430	360	
Cu	380	530	
B	520	340	
Mo	440		

Reports from other regions of the world have not been so systematic. However, the worldwide trend of increasing both cropping intensity and yields means that the frequency and magnitude of response to micronutrient fertilizer applications are also increasing. Cottenie et al. [23] report that Zn and Cu deficiencies in the Alfisols and Ultisols of West Africa are common. In addition, these African soils are more likely to exhibit Zn and Mn deficiencies with liming and continuous cropping [45]. These are management practices that will become more common as the needs for local food production increase. Lopes [53], while reviewing soil micronutrients as constraints to crop production, concluded that Zn is seriously limited on the Campo-Cerrado soils of Brazil and the Llanos Orientalis in Colombia; B and Zn are limited on some Mollisols of Colombia; B, Cu, and Mo on some Vertisols of Peru; and Mo on some Andosols in Latin America. A survey of soil samples from the Campo-Cerrado region showed 95% below the critical level for Zn, 70% for Cu, and 37% for Mn. Lopes also reported dramatic crop response to Zn applications, in maize, sorghum, and soybeans. As row crops are introduced into new regions in Latin America and as the level of inputs increases in areas that are already in food crop production, the magnitude of the micronutrient deficiency problem will become clearer. On the basis of the limited data available, it seems very likely that the crop needs for micronutrients will exceed the soil's capacity to supply them throughout most of Latin America.

Continuous cropping and high use of fertilizers without adequate amounts of micronutrients also increase micronutrient deficiency. Prasad et al. [68] studied the effect of continous cropping and fertilizer use on the total uptake of micronutrients from the soil. As can be seen in Figure 2, the amounts of Cu, Zn, and Mn removed by four crops in a maize-wheat rotation increased dramatically with increasing rates of NPK applications. In this relatively short-term experiment no decline in soil micronutrient levels was detected as result of this high micronutrient demand. However, in some longer term experiments declines in soil micronutrients are evident. Subba Rao and Ghosh [80] showed that after 7 years of cropping in a pearl millet-wheat-cowpeas rotation, i.e., after harvesting 21 crops, the available Zn in the soil declined by 18.9% 30.6% for the nonfertilized and highest NPK

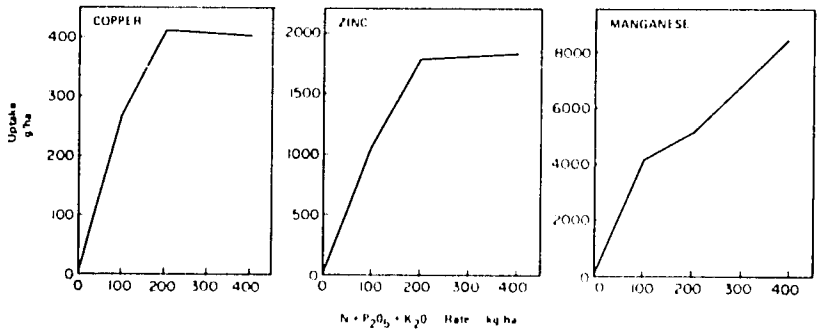

Figure 2. Increase in micronutrient uptake caused by use of N-P-K fertilizer

treatments, respectively. The annual removal of zinc ranged from 173 g/ha in the check to 358 g/ha in the highest NPK treatment. The authors also observed that inclusion of zinc with NPK treatment increased the zinc uptake still more. However, there was only a slight increase in available zinc in the soil due to the continous addition of Zn.

In India [69] it was observed that the changes in the available soil micronutrients took place after 8 years of continuous cropping in a soybean-potato-wheat rotation with various treatments of fertilizer, lime, and manure (Table 8). When farmyard manure was added, the available levels of Zn, Cu,

Table 8. Changes in available micronutrients in soil after 8 years of continuous cropping with a soybean-potato-wheat rotation

Treatment	Available micronutrients (ppm)			
	Zn	Cu	Fe	Mn
Initial value	1.11	2.00	47	57
After 8 years cropping				
No fertilizer	0.58	2.08	28	53
NPK	0.62	2.03	38	68
NPK + lime	0.61	1.98	21	30
NPK + farmyard manure (FYM)	1.29	2.54	54	84

Fe, and Mn all increased. In the other treatments the levels of Zn, Mn, and Fe were significantly reduced by the 8 years of cropping, especially in the NPK and lime treatment. The availability of Cu, however, was not much affected. The addition of FYM with NPK treatment increased all the micronutrients in the soil. This indicates that two ways of eliminating micronutrient deficiency are through the use of farmyard manure and through inclusion of a specific micronutrient fertilization schedule.

The use of NPK fertilizer clearly increases the crop demand for micronutrients. Fertilizer consumption in the tropics has been increasing at a rapid rate, particularly since 1976 (Figure 3). It is already evident that the incidence

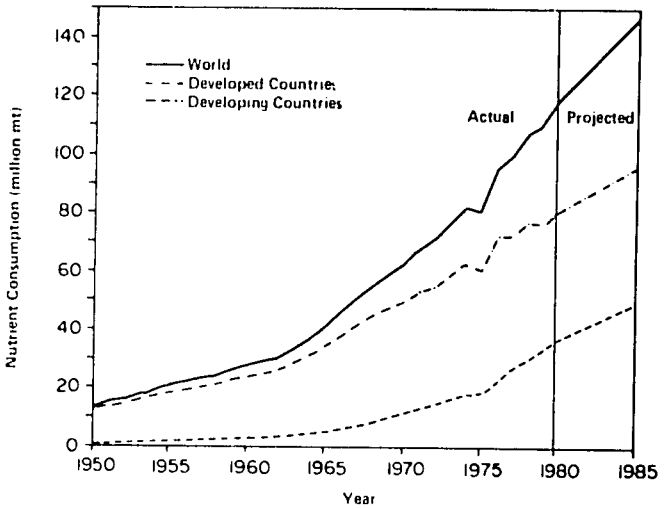

Figure 3. Evolution of total nutrient ($N + P_2O_5 + K_2O$) consumption [60]

of micronutrient deficiencies is increasing in some regions of the tropics. The consumption of NPK fertilizers, the adoption of high-yielding varieties and modern crop management, yield levels, and micronutrient deficiencies will probably all increase.

Micronutrient uptake, hence demand, by important tropical crop for producing the current average yields and the modest commercial or optimum yields are given in Table 9. It may be observed that the micronutrient needs increase in proportion to expected yield; hence, to meet this demand a corresponding input of micronutrients is necessary since the soil may not sustain an adequate supply for years of intensive cropping at high yield levels.

The amount of micronutrient fertilizer required to supply adequate nutrient levels will depend on many factors relating to crop, soil, cropping system, and management. The incidental addition of micronutrients as trace impurities in many fertilizers and irrigation water will be another source of their supply.

It may be concluded, however, that what was once satisfactory for traditional and subsistence agriculture will not remain satisfactory for modern agriculture based on the increased use of inputs required for high production levels. The micronutrient deficiency problems will grow in number and intensity and become more serious, first on those soils inherently deficient in the specific micronutrients, and later even on those soils that are presently marginal in micronutrient supply. These marginal soils will become more responsive because of a depletion of available micronutrients. A survey of world literature shows that Zn deficiency is the most serious micronutrient deficiency in the tropics, and it is becoming as important as deficiencies of N, P, K, S and Ca.

Table 9. Estimates of the current and projected rates of micronutrient removal rates if yields are increased

	Current yield								Projected high yield level						
	Economic	Total dry matter	Micronutrient removal (g/ha)							Micronutrient removal (g/ha)					
			Fe	Mn	B	Zn	Cu	Mo		Fe	Mn	B	Zn	Cu	Mo
	(mt/ha)		(g/ha)						(mt/ha)	(g/ha)					
Cereals															
Rice	2.2	5.5	336	1,485	33	88	39	4.4	6.0	915	4,000	90	240	110	12
Maize	1.5	3.7	1,800	480	–	195	195	–	5.0	6,000	1,600	–	650	650	–
Wheat	1.6	4.3	998	112	77	90	39	3.4	5.0	3,100	350	240	280	120	11
Sorghum	0.9	1.8	648	49	49	65	5	1.9	5.0	3,600	270	270	360	28	11
Pearl millet	0.6	1.2	102	12	–	24	5	–	4.0	680	80	–	160	33	–
Roots and tubers															
Cassava (fresh wt)	9.0	5.4	1,080	405	135	405	42	–	40	4,800	1,800	600	1,800	187	–
Potatoes (fresh wt)	10.6	–	1,700	127	530	95	127	3.0	30	4,800	360	1,500	270	360	9
Pulses															
Mung beans	0.5	1.5	255	57	48	20	17	1.6	3.0	1,530	340	290	120	100	10
Chick-peas	0.5	1.5	29	15	—	19	7	–	4.0	230	120	–	150	56	–
Pigeon peas	0.5	1.5	20	7	—	12	7	–	4.0	160	60	–	100	56	–
Oil seeds															
Groundnuts	0.8	2.4	1,200	94	106	22	12	2.9	5.0	7,500	590	660	140	75	18
Soybeans	1.6	4.8	1,160	706	–	250	331	–	4.0	3,600	2,200	–	780	1,000	–

Conclusions and their implications for further research

Micronutrient deficiency is becoming a constraint to crop production in the tropics. The tolerance of different cultivars to micronutrient deficiency can help in adapting crops and varieties to situations of specific micronutrient deficiency. Intensive research on screening of varieties that are resistant to micronutrient stress, and utilization of this information for breeding varieties having these characteristics deserve high priority. In addition to variety development, some specific research is required to increase our understanding of the micronutrient needs of tropical food crops. This research includes the following:

(1) Long-term studies on the depletion of micronutrients under intensive cropping with high-yielding varieties and moderate-to-heavy fertilizer input.

(2) Studies of the interaction of micronutrients with major fertilizer nutrients, especially N, P, and S, in the nutrition of tropical crops.

(3) Studies on the management of tropical soils and crops to maintain high availability of micronutrients.

(4) Studies to obtain quantitative data on micronutrient removal by different crops in the tropics.

(5) Studies on how the root systems of different crops and varieties affect micronutrient stress.

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3. Micronutrient problems in tropical Asia

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Introduction

The total land area of tropical Asia is approximately 800 million ha. Of this area, around 28%–29% is arable land [39], and this percentage has remained more or less stable over the last decade. Agricultural production, on the other hand, has increased dramatically over the same period. For instance, cereal production in the 11 largest south and southeast Asian countries increased by 30%, reflecting the intensification of agricultural production in tropical Asia. Most of this progress is due to the introduction of high-yielding varieties, increased fertilizer use and irrigation, and other technological improvements. Mudahar [95] estimated the contribution of fertilizers to the growth in rice production alone to be 7% in Nepal and as much as 45% in India, with a regionwide average of 24% for south and southeast Asia.

Increased productivity has greatly increased the demands on the soil for nutrients (see Chapter 2). Whereas traditional fertilizer practices were designed to meet these needs for the major elements (NPK), micronutrients taken up by the crop were generally not replenished. Micronutrient problems in food crops in tropical Asia were observed in rice as early as 1908. Until the mid-1960s, Mn and Fe deficiencies were considered the major problems in rice [3]. During the 1960s Zn deficiency in rice was first identified in tropical Asia [101], and since that time Zn deficiency has been recognized in virtually all food crops [141, 142]. In India alone it is estimated that 47% of the soils are now unable to supply adequate amounts of Zn to the crop [62]. High-yielding varieties combined with intensified land use in tropical Asia have led to an upsurge in the incidence of micronutrient deficiencies, as well as the number of reports on the subject [65].

Climate, geology and soils

The land mass of tropical Asia is small in comparison with that of Africa and Latin America. However, the delimitation of tropical Asia depends on

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the thermal criteria used. By most classification systems tropical Asia extends north of the tropic of Cancer into the foothills of the Himalayas. Other classification systems [103, 161] exclude most of northeast India from the tropics senso stricto because the mean annual temperature range exceeds the mean daily temperature range. Desert environments at the fringe of the intertropical zone are often excluded [162].

Malayasia, Indonesia, and the southern Philippines (Mindanao) are located in the equatorial zone and are surrounded by warm tropical seas. The climate is generally hot and humid throughout the year. Modifications in this general pattern are likely due to topography and geography of the islands. Distinct dry seasons develop only in the southern part of Indonesia as a result of a relatively dry east monsoon. North of the equatorial zone the humid region extends into western Thailand, Burma, eastern Bangladesh, and Assam. In the west it extends into the eastern Philippines. Most of these regions experience a dry season of short duration.

The typical subhumid tropics with $2\frac{1}{2}$ 5 dry months are found in the western Philippines extending westward through south China, Vietnam, Kampuchea, Laos, and parts of India. The rainy season starts in early summer in Sri Lanka and southern India and progressively later further north. In the southern hemisphere, the subhumid tropics are limited to eastern Java and the islands directly east of Java extending to the south-central section of New Guinea.

The most important semiarid regions are found in the Arabian Peninsula, the Indian subcontinent, and in eastern Burma and northeast Thailand. The rainy season is generally less than 7 months. On the Arabian Peninsula the rain diminishes in the northeast direction, while on the Indian subcontinent this gradient is in the northwest direction. The semiarid regions border on desert-type environments in all these cases. An overview of the climatic zones according to Troll and Paffen is given in Figure 1.

In contrast to tropical Latin America and Africa, tropical Asia has a physiography and geology characterized by the absence of vast land masses. The Precambrian Indian and Arabian shields were part of Gondwana land, and the Indian shield remained in place following the breakup during early Eocene.

The four major morphostructural regions of tropical Asia are (1) the Indian shield and Indo-Gangetic plain, (2) the Arabian shield, (3) the Sunda shelf, (4) the Tethys geosyncline and circum-Sunda orogenic system. Small parts of Asia fall within the Sahul shelf area and the circum-Australian orogenic system. A detailed description of these regions can be found in the FAO/UNESCO publications 'Soil Map of the World' [37, 38].

The tropical part of the Arabian shield stretches from the coastal plain bordering the Red Sea to the Oman mountains in the west. The interior plateau consists of calcareous Tertiary rocks, with massive gypsum and marl deposits in the east. Near the coast, soils are formed from sand and siltstone shale, marl, or recent alluvium.

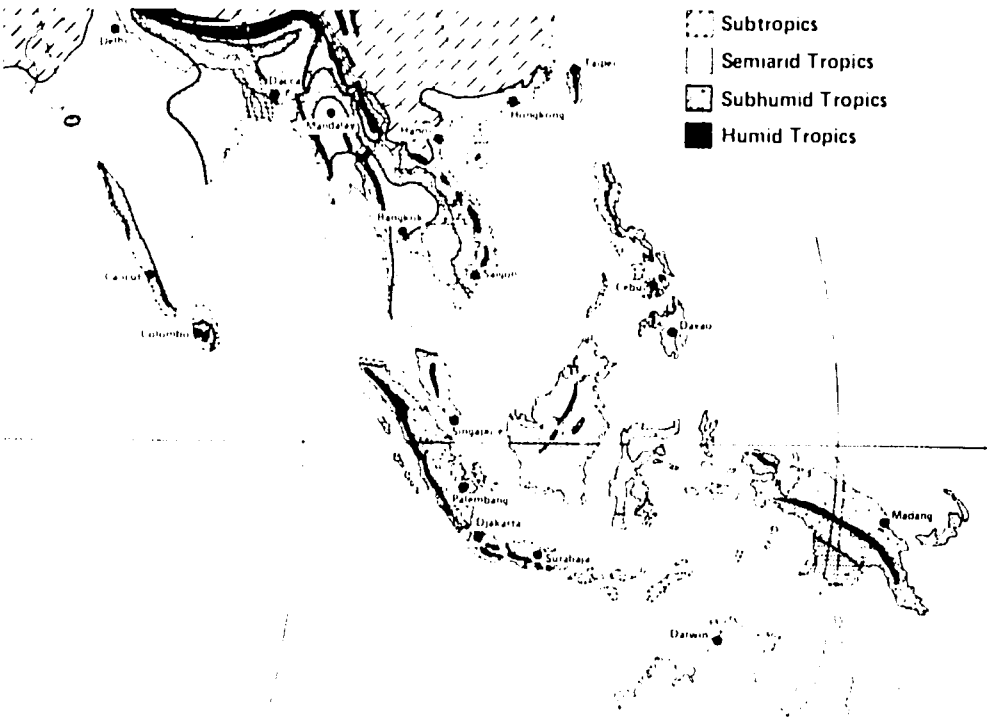

Figure 1. Climates of tropical Asia (after Troll and Paffen, 1966)

The Indian shield is an undulating plateau (200–1000 m) and includes Sri Lanka and the Assam plateau. The basement complex consists of a complex of gneisses and schists, which are exposed over more than 50% of the area. Other parent rocks are the thick basaltic lava beds of the Deccan plateau and northern part of western Ghats mountains and the fluviatile and lacustrine deposits along the Godavari and Mahanadi rivers and scattered throughout Bengal. The remaining part of the Indian shield comprises compacted shale, slate, quartzite, silaceous hornstone, sandstone, and limestone. The shield is bordered by alluvium of the Indo-Gangetic plain. Pleistocene and recent alluvia cover the surface of the Indo-Gangetic plain and coastal lowlands.

Aside from the Brahmaputra Valley, the most important geomorphological regions of the Tethys geosyncline in tropical Asia are the Arakan Yoma range and the Irrawaddy plain. The Arakan Yoma surface is formed from more or less metamorphosed Tertiary shale, sandstone, and limestone. The Irrawaddy geosynclinal is largely filled with sediments that are fluviatile to marine in origin. The Arakan Yoma range continues in the western mountain ranges of Sumatra, across Java, the lesser Sunda Islands, and westward to the Banda arc. Throughout its entire 7000 km, this Sunda mountain

system comprises two concentric belts, the inner volcanic and the outer nonvolcanic. The circum-Sunda orogenic system extends further in the northeast direction to include all of the Philippines. The lithology of the circum-Sunda orogenic system is extremely complex.

The western limit of the Sunda shelf is the Shan Plateau, which is covered with Tertiary and Pleistocene shales, clays, and lacustrine sediments and flanked by gneiss in the west and granite in the east. To the east, the Shan Plateau, which extends into the geosyncline of western Thailand and the Malay Peninsula is composed of partly metamorphosed sandstone and shale. The remainder of Indochina belonging to the Sunda shelf comprises two structures: a region of narrow troughs, known as the Indochinese complex, filled with sediments, and the Indochinese massif comprising the massifs of northeast Thailand, of eastern Laos, Kampuchea, most of Vietnam, and south China. These massifs are largely formed from sedimentary deposits (sandstone, siltstone, shale, and limestone) of various age with some metamorphosis in the most western part. Two Quarternary basis (Mekong and Chao Phraya) contain recent and older alluvium. Away from the continent the Sunda shelf continues in Borneo, the east coast of Sumatra, Banka, and Belitung.

The Sahul shelf is the northern extension of the Australian continent. The coraline Aru islands and the alluvial plain in south New Guinea belong to this shelf. The circum-Australian orogenic system comprises the mountainous area of New Guinea, which consists of sedimentary deposits that have been locally metamorphosed.

The most important soils of tropical Asia are presented in Figure 2. They include the Vertisols and Alfisols in arid and semiarid India, Thailand, Kampuchea, and subhumid east Java. Most of the remaining humid and subhumid regions are dominated by Ultisols and Inceptisols while mountainous regions are complex and undifferentiated. More detailed soil maps exist for some countries, but the only unified map for tropical Asia is the FAO soil map [37, 38].

Distribution of micronutrients in soils

Total micronutrients

Rao [125] reported that total Zn in some soils of India varied between 300 and 600 ppm. As was evident from subsequent investigations, the values of total Zn in fact were much lower. Recent analysis of some benchmark soils of India by Katyal et al. [69] provides typical total Zn values, ranging from 80–89 ppm (Table 1). A range of 20–95 ppm Zn in surface soils of 58 Gujarat soils was reported by Nair and Mehta [97]. Among the different soils analyzed by Lal et al. [79], alkaline Vertisols had the highest total Zn levels (69–76 ppm), whereas the lowest values (24–30 ppm) were found in relatively coarse-textured Oxisols. Sharma and Motiramani [163]

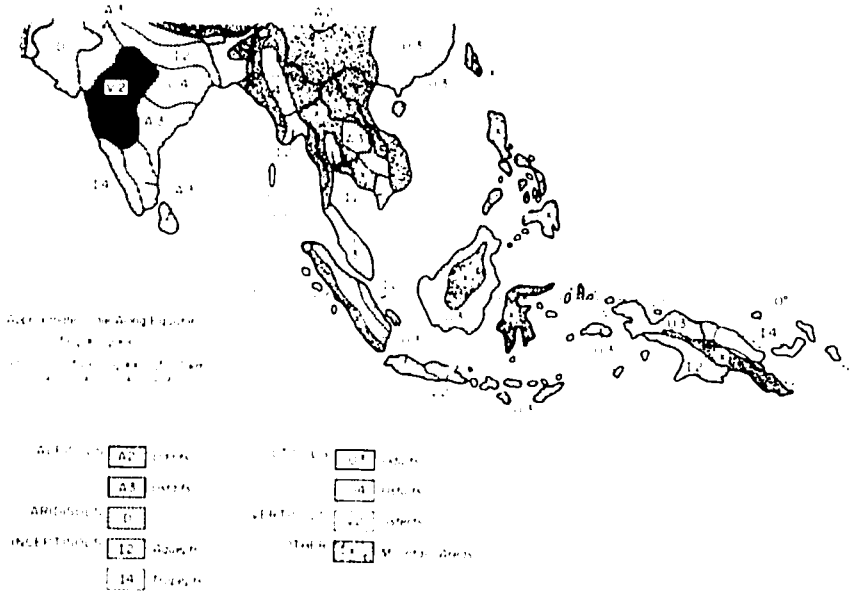

Figure 2. Soils of tropical Asia

Table 1. Distribution of total Zn, Mn, Fe, and Cu in tropical benchmark soils of India [68, 69] (range and mean in ppm)

Soil group	No. of soils	Zn Range	Zn Mean	Mn Range	Mn Mean	Fe Range	Fe Mean	Cu Range	Cu Mean
				Arid-Semiarid					
Inceptisols	5	50–71	62	440–1326	847	2.7–5.4	3.8	19–97	51
Vertisols	9	48–87	64	621–1060	774	3.0–6.1	4.2	41–148	68
Alfisols	5	20–89	49	233–950	488	1.6–6.3	3.3	23–122	50
All soils	19	20–89	59	233–1326	718	1.6–6.3	3.8	19–148	59
				Humid-Subhumid					
Inceptisol	4	46–71	59	38–393	266	2.5–3.1	2.7	23–34	29
Alfisols	3	22–42	33	210–469	347	1.6–2.1	2.0	19–25	22
Oxisols	2	70–74	72	405–800	602	4.6–6.3	5.5	54–58	56
Ultisols	1		43		400		2.0		22
All soils	10	22–74	52	38–800	371	1.6–6.3	2.9	19–58	32

reported that total Zn was the highest in fine-textured Vertisols and the lowest in coarse-textured alluvial soils (Fluvents). Only 7 ppm total Zn was present in certain alluvial soils [40], whereas some deep Vertisols from Maharashtra contained as much as 254 ppm Zn [83].

Raychaudhuri and Datta Biswas [128] showed that soils of Gujarat developed over limestone were richer in Zn than those formed either on sandstone or schists. A highly significant coefficient of correlation existed between lime contents and Zn levels of soils [68]. Similarly, negative

correlation coefficients between total Zn and sand strengthens the belief that soils developed over sandstone are inherently low in Zn.

Katyal [63] determined total Zn in 13 diverse surface soil samples representing major rice-growing areas of the Philippines. The range and mean of total Zn in these soils were 63–135 ppm and 88 ppm, respectively. In his analysis total Zn did not seem to have a significant effect on the incidence of Zn deficiency in rice. Similarly, in Sri Lanka, the range and mean in total Zn contents of wet-patana soils (characterized by high organic matter [OM]) were 35–101 and 75 ppm, respectively [107]. The variations in Zn content of these soils were related to the finer soil fractions. Organic matter level had no effect. Glinski and Thai [42] determined the total Zn content of 20 ferralitic soils of Vietnam ranging from 40 to 485 ppm (mean 102 ppm). Soepartini et al. [152] reported that the total Zn levels in 140 topsoils from Indonesia (Sulawesi and Sumatra) ranged from 33.3 to 173.5, with 25% of the soils containing less than 60 ppm Zn. Although a wide range of soils was sampled, no effort was made to relate total Zn levels to soil type in any of these studies.

Snitwongse [149] reported total Zn levels for 152 soils from Thailand to range from 5 to 158 ppm (average 45 ppm), with the lowest levels found in the northeast (average 20 ppm).

Manganese levels in Asian soils are generally an order of magnitude higher than those of Zn. Among the Indian soils investigated by Iyer and Rajagopalan [51], Vertisols from the Deccan contained more manganese than did the others. Several years later, Biswas [11] confirmed that similar soils were conspicuously rich in total Mn. In comparison, acid Oxisols were characteristically poor. Raychaudhuri and Datta Biswas [128] recorded an average of 1,270, 500, 805, and 368 ppm Mn in black, red, lateritic, and alluvial soils, respectively. These findings are in general agreement with those summarized in Table 1.

Total Mn levels for 20 ferralitic (top) soils from Vietnam ranged from 40 to 4,400 ppm (mean 940 ppm) [42]. Koch [73] analyzed 18 surface soils from rice-growing areas in Sri Lanka which contained Mn values between 24 and 1,204 ppm Mn with a mean of 500 ppm, whereas certain tea soils had less than 15 ppm total Mn [59]. Kalpage and Silva [60] showed that wide variations in Mn in Sri Lanka soils were related to rainfall and parent material. Bleeker and Austin [15] studied the distribution of Mn in six soils of Papua-New Guinea and concluded that Mn levels were greatly influenced by the presence or absence of a fluctuating water table. The transformations of Fe and Mn under anoxic conditions were studied extensively by Ponnamperuma [111, 112, 114].

Finer soil fractions appear to contribute significantly to variability in total Mn in diverse soils [104, 20]. Biswas [12] demonstrated that the concentration of Mn in genetic horizons was principally linked with montmorillonite in the clay fraction. Leaching and lime further modified the distribution

of Mn in soil profiles [14]. Recently, Katyal et al. [69] found that surface soils from the semiarid tropics, where leaching is generally limited, averaged 718 ppm Mn (Table 1). On the other hand, soils from the humid tropics, where free leaching due to heavy precipitation might occur, contained only 371 ppm Mn.

The total Fe content of Indian soils varies from less than 1% to more than 10% with an average of about 3% [65]. Katyal et al. [69] showed that, among the major groups of soils in tropical India, acid Oxisols were the richest in total Fe (Table 1). Next in order were Vertisols followed by Alfisols. One Ultisol showed the lowest amount of Fe. Total Fe in the surface soil increased with the aridity of the climate. Arunachalam and Mosi [6] found that the variations in total Fe in soils depended on OM and the finer soil fractions. In heavily leached lowland soils of the humid tropics, Fe had a tendency to move down and concentrate in the lower horizons [34], whereas it tended to be more uniformly distributed in the soils of arid and semiarid climates [77].

The total Cu content of 28 soils from western India varied between 21 and 101 ppm in the A horizon and between 4 and 32 ppm in the B horizon [52]. Satyanarayan [132] reported a range in total Cu for Vertisols between 63 and 167 ppm. Soepartini et al. [152] reported that the total Cu levels for 14 soils, representing 8 soil orders, from the islands of Sumatra and Sulawesi (Indonesia) ranged from 2.0 to 135.6 ppm. Fifty percent of these soils contained less than 30 ppm Cu. The Cu content of hydromorphic organic soils from Sri Lanka ranged from 15 to 68 ppm with a mean of 38 ppm [107]. Glinski and Thai [42] found the Cu content of 20 ferralitic soils from Vietnam to range from 10 to 143 ppm (mean 57 ppm).

According to Lal et al. [78] and Katyal et al. [69] heavy-textured Vertisols are better endowed with Cu than are lighter textured Alfisols and Entisols (Table 1). Others also had found that copper in soils increases with fineness of soil texture [92, 124, 42]. The level of Cu in the surface horizons appear to be influenced by climate. Soils in a semiarid tropical climate contained more Cu in their surface horizons than did those in humid and subhumid regions (Table 1).

Total B in soils of tropical India varies between 5 and 80 ppm. Iyer and Satyanarayan [52] reported that the average B content of soils changed on the basis of the surface geology as follows: acid lavas 22 ppm, basalt 36 ppm, limestone 13 ppm, alluvium 62 ppm, slate 44 ppm, gneiss 7 ppm, and laterite 37 ppm. Glinski and Thai [42] reported low total B levels in Vietnam soils derived from gneiss (< 20 ppm), crystalline shale (< 5 ppm), and basalt or andesite (< 25 ppm). For all 20 soils studied, the average B content was 45 ppm. Raychaudhuri and Datta Biswas [128] found that loamy Xerochrepts developed on granite and crystalline gneiss contained 8.5 ppm B. A laterite (Aquox) from a more or less similar geologic region contained 25 ppm B. On the other hand, Vertisols and mixed Alfisols and Vertisols

formed over Deccan trap aggite, basalt igneous rock and shales, slates, quartzite, and limestone had between 28 and 57 ppm total B. Certain young alluvials (Inceptisols) from, Bihar contained up to 83 ppm total B [53]. Soil B had a tendency to decrease with the geological age of the rocks from which the soils originate [76] and to increase with tourmaline content [25, 148].

Tyer and Satyanarayan [52] found that heavily leached soils were low in total B. Indeed, Jha [53] reported that coarse-textured soils, apparently vulnerable to leaching, contained less than 20 ppm B. Soils irrigated with high B irrigation waters may accumulate B [88, 80]. Cultivated soils had more B than did virgin soils [52]. High B contents were noted in saline-alkali soils [144]. Accumulation of B in the horizons of a soil profile was affected by lime content [76] and irrigation practices, but B tended to accumulate mostly in the subsoil horizons [144].

In tropical Indian soils total molybdenum contents range between 0.4 to 14.5 ppm. In a majority of the soils, concentrations vary from 1 to 2 ppm. Recent alluvial soils (Fluvents) derived from granite and metamorphic crystalline basalts contained 1.5–5.1 ppm Mo [128]. The corresponding values for Vertisols formed over trap and limestone were 1.5–1.8 ppm. Earlier, Chatterjee and Dakshinamurti [19] reported a range in total Mo between 2.0 and 5.6 ppm, 0.6 and 11.6 ppm, and 1.3 and 2.0 ppm for alluvial soils, Vertisols, and Oxisols, respectively. Verma and Jha [167] and Balaguru and Mosi [8] confirmed that alkaline alluvial soils and Vertisols contained more Mo than did Oxisols and Alfisols. From the study of 46 representative soils from Gujarat, Reddy [129] reported a range and mean of 0.5 to 4.1 and 1.8 ppm Mo, respectively. Recently, Chavan et al. [20] showed that representative soils from Maharashtra contained around 1.9 ppm Mo. Total Mo tends to be higher in neutral-to-alkaline soils. Balaguru and Mosi [8] related the higher total Mo in Vertisols to their high clay contents. Mali and More [84] also reported the highest Mo levels in clay loam and clay soils.

Total Mo in OM-rich mountain soils of Sri Lanka varied between 0.25 and 3.3 with an average content of 2.1 ppm [108]. Ill-drained Deniya soils (low humic gley) contained less Mo in comparison to the well-drained soils in forested areas (Typical wet-patanas).

Available micronutrients

Plant-available Zn generally makes up only a small fraction of the total soil Zn, the size of which may vary with extraction method and soil type. Katyal et al. [69] using DTPA found available Zn to account for no more than 1% of total Zn in various Indian benchmark soils. Using 0.1 *N* HCl on 20 ferralitic soils from Vietnam, Glinski and Thai [42] extracted between 0.2% and 10.6% of the total Zn. They found available Zn well correlated with total Zn ($r = 0.76$). On the other hand, Soepartini et al. [152] found

this correlation to be less ($r = 0.55$) for Indonesian soils, and they reported even lower correlation coefficients using EDTA and dithizone as extractants. Nair and Mehta [97], Sharma and Motiramani [136], and Ganjir et al. [40] found good correlations between available and total Zn in Indian soils; Lal et al. [79] and Rastogi and Rai [126], however, did not.

Judged by the increase in retention of added Zn with the fineness of soil texture [96] and the increase in available Zn with the clay content [44], light-textured sandy soils appear more vulnerable than others to Zn deficiency. Chavan et al. [20] reported that low pH Oxisols contained more available Zn than did neutral-to-alkaline Alfisols and Vertisols. Various correlation studies [119, 45] have confirmed the decline in available Zn with a rise in pH. Zinc deficiency, generally observed in crops growing on calcareous soils, thus seems mostly due to the reaction of the crops to the alkaline soil [65].

The climatic influence on micronutrient availability in soils has been given scant attention. In addition to its effect on soil pH, climate effects the OM level in the soil. Katyal et al. [69] considered low organic matter a cause for generally low DTPA-extractable Zn in arid and semiarid soils (Table 2). Mista and Pandey [93] and Haldar and Mandal [44] demonstrated the favorable effect of OM on Zn availability. Similarly, Pavanasasivam and Kalpage [106, 107] considered the high organic soils (wet patana) of Sri Lanka well supplied with Zn. However, Rajagopal et al. [120] working with high OM soils from Nilgiri Hills, Tamil Nadu, India, reported a reduction in Zn availability when soils contained more than 5.0% OM.

A substantial effort was made by the International Atomic Energy Agency (IAEA) [48] to survey the major rice-growing soils of Bangladesh, Java (Indonesia), the Philippines, and Thailand. Soils were classified on the basis of Zn levels in soil extracts (< 1 ppm) and plant leaves (< 20 ppm). Soils identified as deficient were subsequently selected for greenhouse and field experiments. The survey results proved that Zn content of soils correlated poorly with greenhouse and field results; frequently no yield response and little increase in Zn uptake were obtained from fertilizer Zn. Possibly, the dynamics of Zn in flooded soil prevent adequate prediction of Zn response.

Ponnamperuma [113], Katyal [64], and Haldar and Mandal [45] observed a decline in Zn availability after submergence. Earlier, Katyal [63] demonstrated a reduction in the Zn concentration of the soil solution upon submergence, irrespective of the air-dry soil pH (Table 3). The increase in severity of Zn deficiency with a decrease in altitude along a toposequence reflects the effect of poor soil aeration on Zn availability [164, 166]. On the other hand, mid-season soil drying improves soil aeration and was shown to enhance Zn availability [18].

A highly significant coefficient of correlation has been reported between reducible Mn and total Mn [91, 27]. Glinski and Thai [42] reported that easily reducible Mn levels for various Vietnamese soils range from 5 to 400

Table 2. Distribution of available Zn, Mn, Fe, and Cu in tropical benchmark soils of India [69] (range and mean in ppm)

Soil group	No. of soils	DTPA extractable Zn Range	Zn Mean	Mn Range	Mn Mean	Fe Range	Fe Mean	Cu Range	Cu Mean
				Arid-Semiarid					
Inceptisol	5	0.2–0.6	0.4	7.5–48.8	19.0	3.4–22.8	11.6	0.9–3.6	1.9
Vertisol	9	0.2–1.3	0.4	4.8–16.4	9.8	4.7–9.5	8.0	0.8–2.0	1.4
Alfisols	5	0.3–0.5	0.4	10.3–48.4	24.2	6.7–25.4	17.4	0.9–2.2	1.3
All soils	19	0.2–1.3	0.4	4.8–48.8	16.0	3.4–25.4	11.4	0.8–3.6	1.5
				Humid-Subhumid					
Inceptisol	4	0.3–1.0	0.8	5.1–102.4	40.0	7.9–51.3	30.4	0.2–4.5	2.5
Alfisols	3	0.2–0.7	0.4	17.5–76.0	45.5	14.3–51.2	34.5	0.2–4.9	2.1
Oxisols	2	0.3–1.4	0.9	18.1–155.4	86.8	19.3–26.3	22.8	0.5–2.9	1.7
Ultisols	1	–	0.3	–	40.1	–	17.5	–	0.5
All soils	10	0.2–1.4	0.6	5.1–155.4	51.0	7.9–51.3	28.8	0.2–4.9	2.0

Table 3. Influence of soil pH on the changes of zinc in the solution of flooded soils [63]

Soil	pH	Zn (10^{-2} ppm) Weeks submerged 0	2	4	6	10
Acid sulfate clay (Philippines)	3.7	51	17	21	11	12
Luisiana clay	3.9	30	17	22	8	15
Kalayaan clay loam	5.6	48	15	17	14	9
Antipolo clay	6.0	35	14	13	10	7
Butuan clay	6.8	26	21	21	5	5
Luna clay	7.1	29	18	16	7	5
Maahas clay	7.1	16	13	–	12	7
San Pablo clay	7.4	22	10	14	6	4

ppm (average 113 ppm) constituting 2.7%–26% of total Mn. The lowest levels were found in soils from crystalline shale, acid igneous rocks and elastic materials, and high levels in basalt, clay shale, and limestone-derived soils. Easily reducible Mn in different Indian soils varied from 6 to 820 ppm, i.e., 5%–46% of the total [13]. Reducible Mn, like total, was highest in Vertisols and lowest in Oxisols. Sharma and Motiramani [115] also noted a high content of reducible Mn in Vertisols. The concentration of water-soluble Mn in soils is extremely low [14]. Anaerobic soils, however, are exceptions, and the level of water-soluble Mn may rise to unusually high levels after submergence [111, 64, 58, 98], reflecting the presence of easily reducible Mn in soils. Calcareous soils in the Indian arid and semiarid tropics were generally low in exchangeable Mn [158, 116]. Biswas [13] showed that Oxisols and Alfisols were richer in exchangeable Mn than were Vertisols

and (calcareous) alluvial soils. Sharma and Motiramani [135] reported a range of 1–93 ppm for Vertisols and 2–170 ppm for Alfisols.

Anjaneyulu [4] and Mehta and Patel [91] reported that coarse-textured soils contained more available Mn than did soils with heavy texture. A positive effect of OM content of soils on Mn availability was reported by several workers [171, 7, 2, 127]. On the other hand, Pavanasasivam [105] reported an adverse effect of high OM on Mn availability. Glinski and Thai [42] failed to find a correlation between available Mn and OM at all.

In the few studies that have been conducted [117, 68], the relation between soil-extractable Fe and total uptake or response to added Fe has generally been poor. Iron present in organic combination appears to be the main resource of plant-available Fe [118, 120, 119]. The higher availability of Fe in soils of the humid tropics than in those in semiarid tropics might, in part, be due to higher OM content (Table 2) [69].

Water-soluble Fe, like Mn, is negligible in upland soils but increases after submergence. Mandal [86], Pannamperuma [111], Katyal [64], and Kabeerathumma and Patnaik [55] reported that the magnitude of increase in Fe availability depended mainly on soil pH, intensity of soil reduction, and active iron content. Quickly decomposing green manure treatment enhanced soil reduction, caused more CO_2 production, and brought about early and far greater accumulation of available Fe [110, 43, 87, 64].

The Cu extractable by different reagents has been shown to increase with total Cu in soils [42, 152, 100, 1, 44] and to decrease with a rise in soil pH. A high proportion of clay in soils was found to favor Cu availability [160, 44]. Glinski and Thai [42] found Cu availability correlated with soil OM (r = 0.50) in various Vietnamese soils. Soepartini et al. [152] found no correlation between soil OM and extractable Cu, irrespective of the extraction method employed. Katyal et al. [69] were able to explain 58% of the variability in DTPA-Cu by OM alone in soils of arid and semiarid India. Similarly, any increase in OM seemed to enhance Cu availability in low OM tropical soils [7, 115, 160]. In marked contradiction, Rajagopal et al. [120] showed that in high OM soils from Nilgiri Hills in India OM impaired Cu availability. Peat soils from Malaysia are notoriously low in available Cu [61].

The variations in available B may be traced to various soil factors and certain management practices. Some workers [94, 20] noticed a close association between total and hot water-soluble B, but others [148, 42] could not verify this. Bokde [16] considered 5% of the total B to be plant available. Talati and Agarwal [157] and Chavan et al. [20] noticed an increase in water-soluble B with the fineness of texture. Soil OM seemed to have a favorable effect on B availability [82, 116]. In soils of arid and semiarid Rajasthan, available B increased with increasing pH [88, 94, 82, 157], but alkaline calcareous soils seemed to be exceptions [147]. No correlation with pH was found (r = 0.1) in acid soils from humid and subhumid Vietnam [42].

High clay content, low pH, and large amounts of sesquioxides all tend to reduce Mo availability to plants. To some extent this is reflected in the extractable Mo levels in soils. Plant-available Mo has mostly been assessed by extracting soils with acidic ammonium oxalate. The contents range from traces to less than 1.0 ppm. Based upon the analysis of 1,000 soil samples representing Psamments, Orthents, Vertisols, and Vertic Eutropepts, Duarte et al. [36] reported a range in available Mo from 0.02 to 0.5 ppm. Among the soils studied by Chatterjee and Dakshinamurti [19], Fluvents had the highest available Mo, which varied from 0.10 to 0.34 ppm. Vertisols and Oxisols seldom exceeded 0.05 ppm. On the whole, available Mo was less than 10% of the total. Likewise, in the study of Verma and Jha [167], alkaline alluvial soils exhibited higher available Mo levels than did soils acidic in reaction and sedentary in origin. Balaguru and Mosi [8] also reported certain alluvial soils of Tamil Nadu, India, which analyzed 0.30–0.34 ppm available Mo, to be the richest. High pH Vertisols were relatively poor in Mo availability (0.13–0.16 ppm Mo), and acidic-to-neutral Alfisols were the lowest (0.10–0.15 ppm Mo).

Geographical distribution of micronutrient problems

Semiarid tropics

Zinc – Soils of the arid and semiarid regions of India were found more frequently Zn deficient than those in humid and subhumid zones [69]. Mehta et al. [92] considered a large number of soils from Gujarat Zn deficient. Neutral-to-alkaline red loamy soils (Alfisols) and low-lying alluvial rice soils were more susceptible to Zn deficiency than soils acidic in reaction [74]. As much as 74% of the rice-growing soils (mainly Vertisols and Alfisols) of Andhra Pradesh were found to be deficient in available Zn [195]. Rai et al. [116] showed that on 15%–43% of the black soils from Madhya Pradesh (MP) crops could benefit from Zn treatment. On the basis of available Zn, Rathore et al. [127] classified 69% of the 120 alluvial soils (alkaline Fluvents) studied as Zn deficient. On an overall basis, Katyal and Sharma [67] indicated that on 50% of the Indian soils crops may suffer from Zn deficiency.

Dastur and Singh [32] recorded improvement in yields of cotton on Vertisols resulting from zinc sulfate application. Ramanathan and Nagarajan [123] found that application of 75 kg $ZnSO_4$/ha brought about an increase in yield of cotton on a red loam soil of Tamil Nadu (DTPA-Zn 0.2 ppm). Savithri and Sree Ramulu US [133] were able to raise the kernel yield of groundnut by about 25% through Zn application to a Zn-deficient Alfisol. Solanky et al. [153] also obtained a significant increase in groundnut yield upon Zn treatment of a Vertisol.

On the basis of a micronutrient survey of paddy soils of Thailand [149], the semiarid region (northeast) was considered most susceptible to Zn

Table 4. Summary of field surveys for zinc status in paddy soil in Thailand [149]

Region		DTPA (ppm)	0.05 N HCl (ppm)	Zinc in leaves (ppm)	Total zinc (ppm)	Number of sample	Number of location
Central	Range	0.9–3.4	0.4–1.5	22–52	28–258	36	15
	Average	1.35	0.9	31.7	77.0		
South	Range	0.8–3.0	0.6–1.5	33–45	20–53	7	4
	Average	1.7	0.9	40.1	31.9		
Northeast	Range	0.3–1.6	0.5–2.3	14–30	5.0–120	62	17
	Average	0.8	0.9	20.6	20.1		
Northern	Range	1.0–3.3	0.8–3.5	16–26	10.2–105	47	18
	Average	2.0	1.8	21.3	55.2		

deficiency (Table 4). Four of the ten soils thus identified as Zn deficient showed a response to Zn when cropped to rice in the greenhouse [48].

In the studies of Ramakrishnan and Kaliappa [122], Zn application markedly increased the yield of maize on Vertisol. Deshmukh et al. [35] obtained a 24% increase in sorghum grain yield attributable to 20 kg $ZnSO_4$/ha applied to a Vertisol, (dithizone Zn, 0.82 ppm). On a similar soil Kene and Deshpande [71] reported that the addition of Zn to the NPK (12.5 kg $ZnSO_4$/ha) produced 0.8 ton grain/ha extra sorghum grain. Shinde et al. [138] observed a significant increase in wheat yield on Vertisols from 20 kg Zn/ha supplied as $ZnSO_4$ or ZnO. Field trials conducted in nine villages of North Gujarat (alluvial sandy soils, dithizone-Zn 0.15–0.55 ppm) revealed a wheat yield increase of 5%–25% upon addition of 50 kg $ZnSO_4$/ha [90].

Work done under the ICAR's Coordinated Micronutrient Scheme revealed a response of rice to added Zn in several districts of Andhra Pradesh [155]. Krishnamoorthy et al. [75] obtained an increase of 1.8 tons/ha rice grain yield on a calcareous red soil (pH 7.6, Alfisol) in that state with 10 kg Zn/ha. Studies in Gujarat [156] showed that rice grown on a Zn-deficient soil (dithizone Zn 0.6 ppm) yielded 50% more when treated with 10 kg Zn/ha. In Karnataka, Bhadrapur et al. [10] recommended 50 kg $ZnSO_4$/ha to improve rice yields in salt-affected black soils of the Tung Bhadra Project area. On extremely Zn-deficient Vertisols of Madhya Pradesh (DTPA Zn < 0.30 ppm), yield of rainfed rice was almost doubled upon $ZnSO_4$ treatment [72].

Manganese and iron. Sharma and Motiramani [135] suspected Mn deficiency (less than 3 ppm available Mn) in about 11% of the Vertisols of Madhya Pradesh. Sharma and Shinde [137] also noted low content of available Mn in black soils. However, deep Vertisols from the same state were found adequate in Mn availability [118]. Zende and Pharande [171] did not come across any sample out of 87 soils from the Bombay Deccan that could be considered low in available Mn. It thus appears that, with the possible

exception of alkaline, calcareous Vertisols, Mn deficiency is not a serious constraint to crop production in semiarid tropical India. However, responses to Mn do occur. Dargan and Sahni [26] recorded a 7% increase in cotton yield brought about by Mn treatment of Vertisols. Similarly, Vamadevan and Mariakulandai [163] observed an increase in yield of rice when $MnSO_4$ or MnO was applied to a Vertisol from Tamil Nadu. Bhadrapur et al. [10] recommended $MnSO_4$ application (5 kg Mn/ha) along with Zn and Fe to increase rice yields in salt-affected Vertisols of Siruguppa (Karnataka).

Rai et al [118] concluded that 38%–58% of the soils from the deep Vertisol zone of Madhya Pradesh were deficient (< 2.0 ppm Fe) in Fe. Subsequently, Rai et al. [117] employing the same criteria, classified 47% of the medium Vertisols of Sehore district as Fe deficient. Remarkably all of the 120 alluvial soils (Fluvents) sampled in the same state were considered sufficient in Fe [127]. Widespread deficiencies of Fe, affecting sugarcane in Tamil Nadu (TNAU Scientists personal communication), are being corrected with several sprays of 2%–3% $FeSO_4$ solution. The success of foliar application of $FeSO_4$ in alleviating chlorosis and increasing yield was confirmed by Saxena and Sheldrake [134]. They reported a yield improvement of chickpea grown on a Vertisol near Hyderabad of up to 50%. However, in the case of iron-efficient varieties, no benefit was derived from $FeSO_4$.

Copper. Katyal and Sharma [67], employing a critical limit of 0.2 ppm NH_4OAc-Cu, reported that merely 1% of the 40 000 soil samples from 10 Indian states were likely to be deficient in Cu. However, a majority of the soils (acid-to-slightly alkaline in reaction and well supplied with OM) from Kerala and hilly tracts of Tamil Nadu [120, 119] tested less than 0.5 ppm in *N* NH_4OAc and were categorized Cu deficient. Singh et al. [145] considered 92% of 120 Vertic Eutropepts in the deficient range. They classified a soil deficient if it tested less than 1.0 ppm in *N* NH_4OAc-extractable Cu – an unusually high critical limit. This may explain the virtual lack of Cu deficiency in similar soils (Vertic Eutropepts and Vertisols) in the studies of Kavimandan et al. [70] and Rai et al. [118, 115] who proposed a critical limit of 0.2 ppm NH_4OAc-Cu. On the same basis none of 120 alluvial soils (Fluvents) from Madhya Pradesh were found to be deficient in Cu [127].

Joshi and Joshi [55] reported an increase in rice yield by about 38% upon application of 1 kg $CuSO_4$/ha to certain soils of Ratnagiri district of Maharashtra. Subsequently, on the basis of response to applied Cu in pots, Joshi and Joshi [56] suspected Cu deficiency in the majority of the agricultural soils from the same state.

Boron. Excess B may be more often a problem of soils in the arid and semiarid tropics than is B deficiency, particularly in salt-affected soils. Singh and Singh [146] showed that in saline-alkali soils from south and southwest Bihar water-soluble B was present in toxic amounts (> 1.5 ppm). Moghe and

Maghur [94] also suspected B toxicity in saline soils from arid regions of Rajasthan. In comparison to saline or saline-alkali soils, other soils seldom contain more than 1.0 ppm water-soluble B [53]. On the average, alluvial, black, lateritic, and red soils of Tamil Nadu contained 0.64, 1.03, 0.50, and 0.61 ppm extractable B, respectively [9].

Molybdenum. Indian workers adopted 0.05–0.10 ppm Mo (Grigg's Method) as the critical limit for delineating deficient soils. Of 46 soils from Gujarat studied by Reddy [129], 11 contained less than 0.05 ppm Mo, and crops growing on these soils indeed showed Mo deficiency symptoms. In another survey of the same state, 35% of the 109 soil samples tested below the critical limit of 0.05 ppm Mo [92]. Shinde et al. [140] suspected a need for Mo treatment in 11% of the sugarcane-growing soils from Maharashtra. In general, acid laterites and alkaline black clay soils generally contain a low level of available Mo, and crops, particularly legumes, may benefit from Mo addition to these soils.

On the basis of [illegible]-year study on an experimental farm (available Mo = 0.066 ppm) and on a large number of trials on cultivators' fields (average available Mo = 0.088 ppm) in Aurangabad district of Maharashtra (largely Vertisols), Chavan et al. [21] reported a significant increase in wheat yield from a single foliar spray of 210 g sodium molybdate/1 100 liters of water/ha. Overall wheat grain yields increased by 304 and 120 kg/ha at the experimental farm and in cultivators' fields, respectively. Recently, Shinde et al. [139] working on more or less similar soils observed a yield increase for wheat of up to 20% when treated with Mo.

Humid and subhumid tropics

Zinc. Few efforts have been made in Asia to use available Zn as a tool to map Zn-deficient areas. Soepardi et al. [151] delineated micronutrient-deficient soils from northern central plains of West Java representing an area of about 2 500 000 ha. Judged by the available Zn level of 162 soil samples and actual yield response, 29% of the soils were categorized as Zn deficient. A soil map of zinc deficiency in Java has since been published by Soepardi [150]. He proposed that if soils tested less than 1 ppm 0.05 *N* HCl-Zn or DTPA-Zn or rice plants analyzed below 15 ppm Zn, a Zn deficiency was likely. However, Ismunadji et al. [49] considered 0.15 ppm Zn extractable in 0.1 *N* HCl the critical limit and concluded that many upland soils of Indonesia (alluvial, Regosols, Lithosols, and Aridisols) were likely to be deficient on that basis. The extent of Zn problems in Java has been confirmed through response studies with corn and rice [46, 47].

De and Chatterjee [33] observed an increase of 42% in pod yield of groundnut when 20 kg $ZnSO_4$/ha was supplied to an acid-leached sandy loam soil of West Bengal (total Zn 12–14 ppm). De and Chatterjee [34] obtained more than 20% improvement in rice yield through Zn application

on these soils of West Bengal. Regardless of soil, benefits from Zn application were greater in cold, dry seasons than in hot, wet seasons [131, 121]. Application of 6.25 kg $ZnSO_4$/ha yielded 245 kg extra wheat grain on an alluvial soil of West Pengal [89]. On the basis of the 0.1 *N* HCl test, Chowdhury et al. [23] judged most soils from south and southeastern Bangladesh to be adequately supplied with Zn, whereas Zn deficiency was common in the northern parts of the country. Response to Zn fertilization is observed in the north.

Juang et al. [57] reported a significant increase in cane and sugar yield on four tropical soils of Taiwan (pH 6.4–8.4, 0.1 *N* HCl-Zn 1.0–7.9 ppm). The lower the soil Zn content, the higher was the efficiency of applied Zn. On an overall basis cane and sugar yield increased by about 10% through Zn treatment. In China calcareous paddy soils, especially with impeded drainage, gave a significant response of rice to Zn application [85].

In the Philippines responses to added Zn have been spectacular. Katyal [63] reported Zn deficiency in rice on certain Hydrosols to be so severe that Zn treatment meant the difference between yield and no yield. Even fertilization of such soils with NPK + Zn was of no avail (Table 5) [66]. However, an increase of 4.4 tons/ha rice grain was obtained on these soils through dipping seedling roots in a 2%–4% ZnO suspension, equivalent to about 1 kg ZnO/ha. Yoshida et al. [170] recorded a yield increase of 4.8 tons/ha through an application of 50 kg Zn/ha to calcareous soil. Several other examples of response of rice to added Zn, and information on methods, sources, levels, and time of application can be obtained from some recent reviews [18, 54]. It is estimated that about half a million hectares of current and potential rice land in the Philippines alone are zinc deficient [102, 48].

Preliminary research from the subhumid zone of Sri Lanka by Nagarajah (personal communication) indicates a region of severe Zn deficiency (0.224 ppm Zn in 0.05 *N* HCl) in the area near Matale on slightly acid soil which is representative of approximately 10 000 ha. A crop response to Zn was observed after the first rice season.

Manganese and iron. Deficiencies of iron and manganese have rarely been reported for humid and subhumid tropical regions. Deficiency of these elements in lowland rice is unlikely [159], but iron deficiency in upland rice may present a major problem in some soils [113]. Pillai [109] reported a response to Mn for rice grown on an Oxisol in India when seeds were presoaked in an 8% $MnSO_4$ solution. Iron toxicity was identified as a major problem to wetland rice [165, 5].

In West Bengal pod yields of groundnut were improved by about 40% with 40 kg $FeSO_4$/ha applied to an acid-leached soil (total iron 1.0% in 0 to 30 cm depth) [33]. Recently, Ismunadji et al. [49] reported Fe chlorosis in several crops growing on high pH calcareous upland soils of Indonesia.

Table 5. Yield of rice with or without NPK and/or zinc treatment in eight farmers' fields [66]

Treatment		Grain yield (tons/ha)							
		Farm number							
Zinc	NPK	1	2	3	4	5	6	7	8
No	No	1.6	3.0	1.0	4.1	3.1	2.5	2.6	0.0
No	Yes	0.0	2.2	1.8	3.9	4.8	3.7	1.4	0.0
Yes	No	3.9	5.1	5.4	4.7	4.0	3.7	4.7	4.2
Yes	Yes	3.1	6.1	6.7	5.1	5.0	4.6	4.2	4.9

Copper. Ponnamperuma [114] showed that the concentration of Cu in the soil solution decreased after submergence. Despite this, Cu deficiency, unlike Zn deficiency, has seldom been encountered in the Philippines. Response of rice to application of Cu (0.13% $CuSO_4$ foliar spray) on a clay soil has been recorded in Bangladesh [17]. Sreedharan and George [154] noted an increase in both grain and straw yields of rice on a high OM, acid red loam soil of Kerala as a result of Cu application. Samui and Bhattacharya [130] obtained an additional 324 kg grain/ha from $CuSO_4$ treatment of Boro rice (spring rice) on an acid-leached soil of West Bengal, whereas the Kharif rice (summer, wet season rice) did not respond to Cu. On more or less similar soils, De and Chatterjee [34] reported an 18% increase in yield of upland, direct-seeded rice, attributable to 5 kg $CuSO_4$/ha. The performance of flooded transplanted rice, however, remained unaffected. Rice-growing alluvial soils from West Bengal are considered adequately supplied with Cu [44].

Micronutrient studies in Malaysia have concentrated on peat soils, which occupy extensive areas of southeast Asia. Deficiency of Cu is the most widespread on these soils. Coulter [24] found that palms growing on peat and showing yellowing or browning symptoms were characteristically low in Cu ($\leq$ 3 ppm). Such symptoms in palms are known as 'peat yellow' and are easily controlled by $CuSO_4$ application before planting or even by top-dressing. Kanapathy [61] reported a significant increase in yield of maize on a peat testing 7 ppm total Cu. So pronounced was the Cu deficiency that he considered Cu to be an indispensable component of peat reclamation. One application of 30 kg $CuSO_4$/ha was able to check Cu deficiency in nine successive crops. In the studies of Chew et al. [22] conducted on two peats (total Cu 6.5 and 5.6 ppm, Mn 43 and 32 ppm, and Zn 25 and 20 ppm), significant responses to Cu application were confirmed. In Indonesia, the wide coastal plains of eastern Sumatra, western and southern Kalimantan, and the southern coast of West Irian are covered with swamp forests with thick peat layers. On these peat soils, the yield of corn was almost doubled through Cu treatment [49].

Boron. If soils test less than 0.5 ppm hot water-soluble B, they are considered incapable of supplying sufficient B to support normal plant growth. On this basis the majority of the Indian soils are well supplied with B except in certain humid and subhumid areas, such as various parts of Bihar [148]. Ghani and Haque [41] reported that available B in 26 soils from Bengal ranged from 0.4 to 2.0 ppm. Soils frequently flooded with sea water contained higher B than those free from marine influence.

In the southern parts of tropical China, B-deficient soils have been found in large areas [81]. These soils are derived from low B granite and other acid igneous rocks, gneiss, etc. Symptoms of serious B deficiency were observed on these soils in many areas of 11 provinces in southern China. An application of B increased the yield of rape and other B-sensitive crops.

Molybdenum. Relatively little research has been conducted on Mo in humid and subhumid tropical Asia. To some extent this may reflect the inadequacy of available soil tests for Mo. For instance, in spite of the acid nature of a number of Sri Lanka soils tested, a majority of these soils contained more than 0.5 ppm (Grigg) extractable Mo and were suspected to be adequately supplied [108]. However, a beneficial effect from Mo treatment was obtained on soybeans grown on an acid (pH, 5.3) Oxisol. These benefits, due to enhanced N_2 fixation, were measurable in terms of N content as well as yield [168, 169].

Similarly in India, Das Gupta and his associates [31, 28, 29, 30] reported advantages of Mo application to rice not only in terms of yield but in N utilization as well. In variance, Nayar et al. [99] were not able to confirm the usefulness of this treatment for rice grown on an acidic alluvial soil. Except in the findings of Ponnamperuma [114], who reported a positive response of rice to Mo application on an organic soil, no report of Mo deficiency in the Philippines has come to our attention.

A very low dose of Mo (0.5 kg sodium molybdate/ha) applied to foliage at late tillering stage of wheat grown on some alluvial soils of West Bengal brought about a 30% increase in grain yield [131].

Conclusions and future research needs

The interest in micronutrient research in tropical Asia increased following the development of modern crop varieties and Nene's discovery in 1964 of Zn deficiency in rice. Except in India and the Philippines, research on micronutrients is of recent origin and is mostly directed to Zn nutrition of rice. Obviously, there is need to extend this research to other nutrients and crops. In the tropical climate several crops of commercial value such as coconut, coffee, tea, rubber, and cocoa are widely grown. In view of their economic value, studies on micronutrient requirement of these crops should

be an important aspect of future research strategies of this region. The role of Cu in peat reclamation needs to be investigated further.

The work on distribution of micronutrients is very sketchy. Rarely an attempt is made to associate micronutrient problems with the parent material, climate, or other soil-forming factors. From all the studies reviewed here, we can merely conclude that total B levels appear low in gneiss, granite, shale, and basalt of the Indian shield, as do Zn levels in the sandstones and schists of the Indo-Chinese massif. Copper deficiency is a problem in peats of the Indonesian archipelago. Information on the basis of well-defined soil classification units is largely lacking. A better knowledge of the micronutrient distribution on this basis would make it possible to delineate geographical areas where micronutrient deficiencies are likely to be constraints to crop production. Large-scale sampling of typical soils and plants of diverse physiographical, climate, and landscape characteristics and evaluation of their micronutrient status in the laboratory and greenhouse would probably be desirable. The existence of micronutrient deficiencies, however, can be proven only through simple field experiments.

Research on micronutrients in tropical Asia is primarily conducted in India and the Philippines. Coordination of research among countries is nonexistent. Aside from the recent effort by IAEA [48] and FAO [143], micronutrient surveys are regional in scope. The organization of a micronutrient workgroup involving all tropical Asian countries to establish unified testing procedures and organize data collection and storage would greatly facilitate the transfer of information among countries and allow for a continuous assessment of the role of micronutrients in this most populous part of the world.

The information gathered thus far points out that for alleviation of micronutrient disorders, treatment of soil with the deficient nutrient is the standard remedy. Few attempts have been made to develop management practices capable of minimizing the use of micronutrients, although this is an important strategy in light of the poor economic conditions of the Asian farmer and the escalating costs of amelioration. The role of organic manures in preventing nutrient deficiencies needs critical evaluation. Selection of varieties tolerant to micronutrient stresses and their adoption on deficient soils can save on nutrients. Finally, because specific genes control a plant's capacity for nutrient absorption, varietal tolerance to available nutrients can be incorporated in the breeding objectives.

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4. Micronutrient problems in tropical Latin America

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Introduction

The agricultural production of tropical Latin America is astonishingly low. The land area in Latin America that is suitable for crop production from a topographical standpoint varies from 95% in the plains to 75% on the plateaus, 25% in the hills, and 5% in the mountains. However, less than 5% of the total land area in tropical Latin America, approximately 1600 million ha, was under cultivation by 1950, largely because of adverse soil, geographic, or climatic conditions. Regionally the percentage of land under cultivation varied from 17% in the Caribbean Islands, to 9% in Central America and Mexico, down to 3% and 2% in Colombia and Brazil, respectively. According to estimates at the time, only 40% of the potentially arable land was being cultivated.

Developments over the last 3 decades have drastically changed this picture. The total harvested area of Latin America doubled from 53 million ha in 1950 to 97 million ha in 1976, with 10 million ha brought into production between 1973 and 1976 alone. The major part of this increase occurred in Brazil (17.5 to 44 million ha) while Paraguay, Panama, Mexico, Ecuador, Bolivia and Costa Rica also substantially expanded their harvested area [48]. By 1979 around 50 million ha of cereals, tubers, and pulses were harvested in tropical Latin America [49].

Although crop production in Latin America has risen by 3.5% annually since the early 1950s, yields have risen only by 1.1%, reflecting the emphasis on new lands. If Brazil were excluded, however, changes in yield would account for 50% of the increase in crop production. The increase in fertilizer use by a factor of 20 over the last 25 years gives an indication of the intensification of land use (Table 1).

The role of micronutrients in agriculture has been recognized only recently in Latin America. Even though the essentiality of various micronutrients has been known or suspected for a long time, few agricultural scientists appreciated the importance of these elements in the quest for increased yields.

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Table 1. Indicators of agricultural modernization, Latin America and selected countries [48]

Country	Fertilizer use (thousand tons)						Annual rate of change (%/year)		
	Average 1948–52	Average 1961–65	1970	1974	1975	1976	1948–52 to 1976	1961–65 to 1976	1970 to 1976
Latin America	278	1239	2922	4289	4440	5258	20	12	10
Brazil	35	224	961	1716	1791	2371	30	20	7
Chile	30	95	148	158	94	116	9	2	4
Colombia	13	121	144	249	214	247	20	6	9
Mexico	21	260	593	922	1158	1165	29	12	12
Peru	63	94	84	142	104	129	5	3	5

The extent of micronutrient research in tropical Latin America is rather limited. The three countries from which subtantial research in this area is reported are Colombia, Brazil, and Costa Rica, but even within these countries the available data have a great regional bias. The data reported from Colombia and Costa Rica provide some insight into the status of micronutrient problems of the Andes region, while data from Brazil are largely limited to the 'Cerrado' and São Paulo state. Thus, huge sections of the continent remain largely untouched, particularly the Amazon and Guyana highlands.

Early reports from Puerto Rico on micronutrient problems in tropical Latin America date from the mid-1950s. Reports from Brazil and Colombia followed in the 1960s [87, 124]. The results of these early studies were generally inconclusive and indicated considerable differences in response to micronutrients by the different crops in different locations [42]. An escalation in micronutrient research occurred in the late 1960s and 1970s as more intensive land use as well as infringement on less fertile land raised the incidence of micronutrient deficiencies. Textbooks undoubtedly contributed to greater awareness of the role of micronutrients in agriculture [148, 115] as did the introduction of atomic absorption spectrophotometers in the region.

Geology and soils of tropical America

The main surface features of tropical America are the Andean Cordillera and its continuation in Central America and Mexico; the Guyana and Brazilian shields, the Orinoco, Amazon, and Paraná basins, and the Caribbean Islands [141].

The Andes and their counterparts in Central America and Mexico extend as a unit through 8800 km in the western edge of tropical America. The Andes formation occurred during the Tertiary period, associated with great volcanic activity. Volcanic activity is still present in parts of the area. Intermountain valleys with high population density, although relatively narrow, are locally important. Some examples of these valleys are Mexico City Valley, the Guatemalan Altiplano, the Meseta Central of Costa Rica, the 'Sabana' of Bogotá, the Cauca Valley of Colombia, and the Mantaro and Cajamarca Valleys in Peru [141].

To the east, the Guyana and Brazilian shields consist of very old crystalline rocks (mainly granite and gneiss), most of them greatly worn down and partially covered by stratified rocks, mainly sandstone. The formation of these shields occurred during Archean and Paleozoic periods, and they are considered the oldest surfaces in tropical America. The Brazilian shield covers about 1 500 000 km^2.

The Amazon Basin forms an enormous drainage area of 6 900 000 km^2 bounded by the Andes to the west, the Guyana shield to the north, and the

Table 2. Approximate extent of major soil suborders in tropical America

Order	Suborder	Area (million ha)	Area (%)
Oxisols	Orthox	380	22.7
	Ustox	170	10.2
Aridisols	All	50	3.0
Alfisols	Ustalfs	135	8.0
	Udalfs	15	0.9
Ultisols	Aquults	40	2.4
	Ustults	35	2.1
	Udults	125	7.5
Inceptisols	Aquepts	145	8.7
	Tropepts	75	4.5
Entisols	Psamments	90	5.4
	Aquents	10	0.6
Mollisols	All	50	3.0
Mountain areas		350	21.0

Source: Sánchez [141], from calculations by M. Drosdoff, Cornell University, based on maps of Aubert and Tavernier [4].

Brazilian shield to the south. The ancient platform of primary rock that underlies the area is covered with layers of alluvial sand and clay to form an immense plain of low undulations. Many of the present sediments originated from erosion of the Andean uplifts, and some are derived from the shield areas. The Orinoco Basin, also called the 'Llanos' extends between the coastal ranges of the Venezuelan Andes and the Guyana shield and is covered with alluvial brought down by the Andean torrents. The Paraná Basin occurs to the south and is rich in basic and ultra-basic rocks, primarily basalt.

The Caribbean Islands were formed primarily from uplifted limestone or volcanic deposits, with present volcanic activity limited to the lesser Antilles.

The major soils of tropical America at the suborder level of the Soil Taxonomy are presented in Table 2. Although these are very generalized data and subject to substantial modifications, they represent, according to Sánchez [141], a first attempt to quantify the distribution of soils in tropical America. Oxisols and Ultisols are by far the major soil orders in this region of the world (44.9%). However, recent calculations from the FAO-UNESCO [47] world soil maps indicate that these two soil orders cover 64% of tropical South America and 10% of Mexico, Central America, and the Caribbean [143]. Data in Table 2 also show the great variability of soils in tropical America, even at order and suborder levels. This variability reflects differences in parent materials, pedogenic processes, rate of weathering, and climate that will definitely influence micronutrient availability for food crops being cultivated on these soils. Vertisols, Spodosols, and Histosols do not occupy large enough areas in tropical America to appear as mapping units at a scale of 1:50 million (base used in Table 2). However, they are present and are locally important in smaller areas. Also the mountain area

soils are not differentiated at this level of generalization; consequently the extent of important groups such as Andepts (volcanic ash soils) are not estimated.

Agroclimatology of tropical America

Nineteen of the Latin American countries lie partly or totally in the tropics as defined by astronomers, and five of these are crossed by the Tropic of Cancer or the Tropic of Capricorn. Since this geographical definition ignores climatic criteria for the tropics, it only roughly indicates the global extent of this zone. Various efforts have been made to define the tropics on a climatic basis [96, 132, 156, 51, 127]. The usefulness of these classifications depends on their purpose. We will adhere to the definition of the tropics by Tricart [158] as the zone free of thermal seasons and with a mean temperature of every month in excess of 20 °C. This zone is further characterized by an annual temperature range of less than 10 °C and a daily temperature range that is higher than the annual temperature range. By this definition tropical Latin America extends from southern Mexico down to a line through southern Peru and Rio de Janeiro.

The climatic diversity of 'tropical' Latin America is due to the presence of the Atlantic and Pacific Oceans, separated by a few to thousands of miles, and to the presence of the Andes mountain chain. The Andes serves as an effective climate barrier and at high altitudes may provide temperate climate conditions. Delineation of the various climatic zones and subzones depends on the criteria used, which can be based solely on climatic information [99, 66] or on a combination of climatic and vegetative information [97]. Clearly, the climatic classifications are as diverse as the characteristics of the various climatic zones.

Three major climates are distinguishable in tropical Latin America: (1) the arid and semiarid regions including the Peruvian coast, the interior of the Brazil northeast; (2) periodically humid regions comprising the Brazilian Cerrado and the Venezuelan and Colombian Llanos; and (3) the humid tropics with the Amazon Basin, the Pacific coast of Colombia, the southern Atlantic coast of Brazil, and the lowlands of Central America. These regions roughly correspond with the Troll and Paffen classifications as tropical wet and dry-desert climates' (3, 4, 5), 'tropical humid summer climates (2), and 'tropical rainy climates' (1), respectively (Figure 1).

Major food producing areas and crops

Around 575 million ha in Latin America is estimated to be suitable for cultivation, of which less than 25% is presently used. However, much of the unused land is subject to major constraints. For instance, it is estimated that 90% of the soils in the Amazon region, one of the most important frontiers,

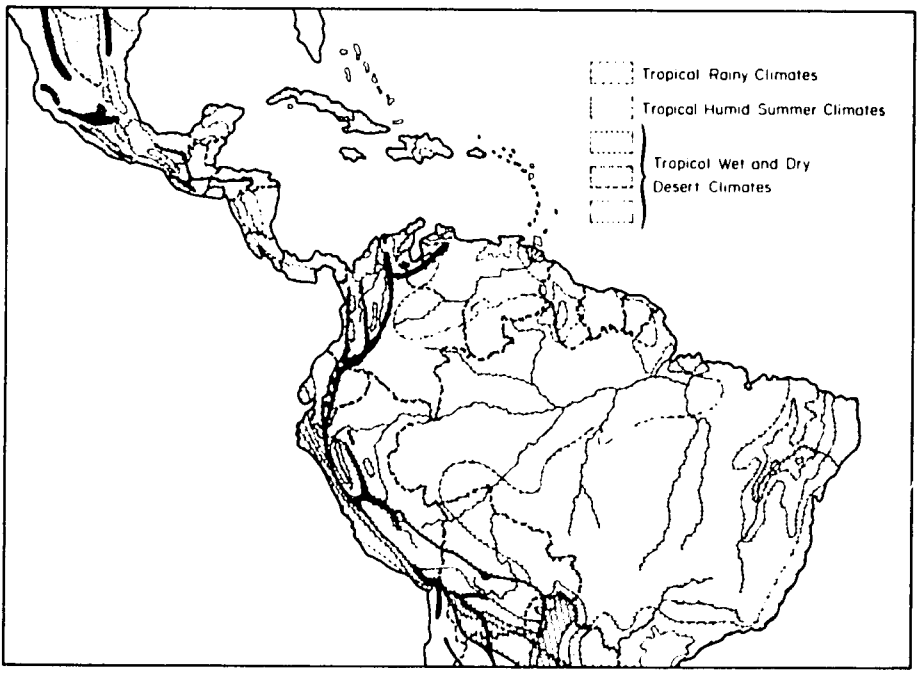

Figure 1. Seasonal climates of tropical Latin America. Tropical rainy climates; tropical humid summer climates; tropical wet and dry-desert climates. Scale 1:45 000 000. Source: Adapted from Troll [160]

suffer from low natural fertility [142]. Although extension of agricultural frontiers still offers possibilities for increasing food production, most of the easily occupied land is already in use, and intensification of land use appears to be of increasing importance. This holds particularly true for Mexico and the Andean region where prospects for expanding cropland are dim.

The croplands of tropical Latin America are generally found near the coastal areas, and the heaviest concentrations are in the areas with the milder climates and the more favorable soils and topography. These areas also support the highest density in populations [47]. Although the major grain-producing areas of Latin America fall outside the tropics, more than 45% of the staple crops harvested in 1979 in the tropics were cereals. Most of these are produced in the valleys and on the plateaus of the Andean region of tropical South and Central America and Mexico, as well as in the southern states of Brazil.

Shifting cultivation through slash and burn is the major crop production system in humid tropical America (Amazon and Orinoco Basins). Livestock ranching is typical of the 'Cerrado' in Brazil and the 'Llanos Orientales' in Colombia. Settled subsistence farming is the major system along the Andes Cordillera in South America and Central America. Modern plantation systems

are common in São Paulo State and coastal forested areas in northeast Brazil, in spotted areas in the Andes, Guyanas, Venezuela, and throughout the Central American and Caribbean countries. These plantation systems are mainly dedicated to export crops such as sugarcane, coffee, cacao, rubber, bananas, and pineapple.

A considerable effort was made in the late 1970s, mainly in the 'Cerrado' area in Brazil, to extend advanced plantation-type production systems to some food crops (mainly soybeans, wheat, rice, and beans) similar to those already used south of the tropical region. This program, however, was seriously affected by the high investments in fertilizers required to actually 'build' a soil to support adequate yields and by the decline in government subsidies.

Since our interest lies in food crop production, a summary of the main food crops in tropical America is presented in Table 3. Not considered in this summary are the plantation crops and the 282 million ha devoted to pastures and meadows for animal production.

Micronutrient contents in soils of tropical America

Arid and semiarid regions

Data about micronutrient contents in arid and semiarid tropical America are too limited to draw a conclusive picture relating micronutrient problems to parent material, climatic conditions, soil properties, weathering and other soil-forming processes.

Some work was conducted in these regions by Horowitz and Dantas [74] who studied 12 typical soil profiles from the 'Sertao' region in Pernambuco State, northeast of Brazil. They observed that all soils contained sufficient amounts of easily reducible manganese (about 20 ppm) according to Jones and Leeper's [94] criteria. The authors attribute these high levels in the region to low rainfall, low organic matter content, and relatively acid pH. Similarly, the physiographic area called 'Agreste' in the same state is well supplied with soluble zinc and soluble molybdenum. Horowitz et al. [78] observed only 3 of 12 soil profiles with less than 1.25 ppm Na_2-EDTA-soluble zinc [19]. Dantas and Horowitz [40] data average 0.46 and 0.37 ppm of ammonium oxalate-soluble molybdenum in surface layers of Oxisols and Ultisols in this area, well above the 'critical level' of 0.16 ppm suggested by Grigg [69].

Toxic levels of boron and molybdenum have been found in alluvial, calcareous, nonsaline soils under a desertic climate; however, zinc and manganese deficiency can be quite common in the same soils. Data presented in Table 4 are a summary based upon analysis of 29 samples from the Copiapo Valley in northern Chile. These soils have a pH of about 8.0 and organic matter contents ranging from 0.1% to 2.6% [9]. However, no criteria were presented to interpret the levels of the micronutrients studied.

Table 3. Major food crops produced in tropical America countries ('000 mt) based on 1981 data (FAO, 1982)

Country	Rice	Corn	Wheat	Potatoes	Sweet potatoes	Cassava	Sorghum	Soybeans	Dry beans
Peru	684*	628*	117F	1627*	151F	410*	56*	13*	91
Bolivia	100*	250*	50*	950*	15F	230F	15F	40	19F
Ecuador	402	246*	41	349*	3F	236*	1*	39*	42
Venezuela	708*	486*	1*	200*	4F	360F	578*	–	67
Colombia	1799	880	62	2100	–	2150	532	89	138
Paraguay	60	600F	80F	9F	115F	2000F	10F	600	86F
Brazil	8261	21098	2207	1911	800F	25050	212	14978	2401
Guyana	289*	3F	–	–	2F	8F	–	–	2F
Suriname	244*	–	–	–	–	3F	–	–	–
Panama	192*	68*	–	13F	–	43F	–	–	7
Costa Rica	210	88	–	28	–	18F	42	–	12
El Salvador	52*	487	–	6F	–	25	139*	1F	37*
Nicaragua	65*	250	–	2F	–	27F	70F	1F	60*
Honduras	40*	338*	1F	5F	1F	7F	45*	–	42*
Guatemala	46	1052	45	37F	–	8	67	–	90
Mexico	644	14766	3189	868	33F	22F	6296	712	1820
Cuba	518F	95F	–	239	327F	328F	1F	–	26F
Dominican Rep.	430*	50*	–	27*	85*	180*	45*	–	75
Haiti	90*	180F	–	9F	270F	255*	110*	–	87
TOTAL PRODUCTION	14834	41525	5793	8380	1806	31360	8218	16473	3001
Area under production (million ha)	8.0	24.0	3.2	0.8	0.3	2.7	2.9	9.3	8.9

* Unofficial figure
F = FAO estimate.

Table 4. Total and extractable micronutrients (in ppm) in aluvial soils from Copiapo Valley, desertic region of Chile[a]

	Fe		Zn		Mn		Mo		B	
	Mean	Range	Mean	Range	Mean (ppm)	Range	Mean	Range	Mean	Range
Total[b]	45 600	38 840 52 700	148	76–309	1050	744–2109	3.39	1.9–14.5	238	158–307
Extractable	14.7[c]	2.1–44.9	2.55[d]	0.8–12.3	–	–	0.78[f]	0.30–2.57	4.3[g]	1.9–7.9
Easily reducible	–	–	–	–	198[e]	38–688	–	–	–	–
Exchangeable	–	–	–	–	2.4	0.2–9.1	–	–	–	–

a. Adapted from Bernardi et al. [9].
b. Fusion with sodium carbonate.
c. 1 *N* ammonium acetate pH 4.8.
d. 1 *N* ammonium acetate + dithizone 0.01% in carbon tetrachloride pH 7.0.
e. 1 *N* ammonium acetate pH 7.0 in 0.05% hidroquinone.
f. Ammonium oxalate-oxalic acid pH 3.1.
g. Hot water.

Blasco and Soto [12] reported micronutrient deficiencies in the arid and semiarid regions of Nicaragua, Central America, in soils close to the volcanic mountain range.

Periodically humid regions

Most of the available data on micronutrient contents in periodically humid tropical America are from São Paulo State and the forest region of Pernambuco State of Brazil. Data of Table 5 are a summary of a series of papers concerning 28 soil profiles of 14 soil units in São Paulo State in Brazil. For all four micronutrients studied there is a good relationship with the parent material. Soils derived from basic-igneous rocks had the highest levels of cobalt, molybdenum, copper, and zinc, and those derived from sandy sediments had the lowest. For total molybdenum, soils derived from modern sedminments contained the highest level [7, 161, 162]. Levels of < 0.14 ppm soluble molybdenum indicate possible molybdenum deficiency in all these soils [69]. The authors observed good correlations for total copper and total zinc with Fe_2O_3 ($r = 0.79^{**}$) total molybdenum with soluble molybdenum ($r = 0.54^{**}$), and soluble molybdenum with clay ($r = 0.75^{**}$). Similar results were observed by Brasil Sobrinho et al. [15] in 16 soil series from the Piracicaba region where Oxisols derived or influenced by basic igneous rocks contained about 100 ppm total zinc and above 1.0 ppm available zinc, as determined by the ammonium acetate-dithizone method [150].

Total and hot water-soluble boron in São Paulo State do not show as good a relation with parent material as the other micronutrients. Surface horizons of 7 profiles contained a range of 31.3 to 54.0 ppm and a mean of 42.9 ppm total boron, and from 0.06 to 0.32 ppm (mean 0.16 ppm) for hot water-extractable boron. Extractable B showed a definite tendency to decrease with depth in the soil profile [16]. The great variability in the total/soluble boron ratio from one great soil group to another indicates that the soluble level depends not only upon the total boron level. Other factors such as parent material, pedogenic process, and organic matter level seem to have a great degree of influence on the hot water-boron level.

The geochemistry of some micronutrients has also been studied in a systematic way in the forested coastal area in Pernambuco State, in the northeast of Brazil [74, 75, 76, 77, 79]. A summary of the results obtained for copper, molybdenum, boron, and zinc for surface horizons is presented in Table 6. Most of these soils are derived from acid rocks (granite, gneiss) with only one soil derived from andesitic basalt and trachyte.

Total copper levels (Table 6) are surprisingly high for these soils considering the generally acidic parent material. The metal is probably present in a moderately stable form in the lattice of ferro-magnesian minerals — mostly biotite and hornblend [75]. The authors also observed that only 4 of 11 soils studied presented less than 0.6 ppm 0.05 *M* EDTA-extractable copper — the suggested deficiency level for cultivated crops.

Table 5. Micronutrients (total and/or soluble) levels (in ppm) at the surface horizon of twenty-eight soil profiles in the state of São Paulo, Brazil[a]

		Mo				Cu		Zn	
		Total		Soluble[c]		Total		Total	
Parent material	Soil units[b]	$\bar{X}$	Range	$\bar{X}$	Range	$\bar{X}$	Range	$\bar{X}$	Range
Basic rocks	(Lib, TE LRe, LRd)	1.79	0.51–2.86	0.10	0.09 0.13	189.5	89.0 334.7	194.6	87.0–315.3
Alluvial and coluvial	(Hi)	0.82	0.78–1.17	0.12	0.09–0.16	27.2	25.6 28.8	68.6	53.0–84.2
Modern sediments	(LE, LV, LH, PV)	2.20	0.50–5.72	0.07	0.05–0.12	22.4	6.3 49.2	29.3	29.3–65.2
Bauru sandstone	(Pin, Pml)	0.31	0.21–0.38	0.03	0.03–0.04	5.2	3.4 6.9	21.4	16.4–30.4
Sandy sediments	(LEa, LVa, R)	0.46	0.09–1.74	0.02	0.01–0.05	8.1	1.6 12.8	7.9	1.0–17.2

a. Adapted from Valdares [161], Valdares and Catani [162], and Bataglia et al. [7].
b. (Lib, TE, LRe, LRd = Inceptisol, Alfisol, Oxisols; Hi = Histosol or Inceptisol; LE, LV, LH, PV = Oxisols, Ultisols; Pin, Pml = Ultisol; LEa, LVa and R = Sandy Oxisols and Entisols).
c. Ammonium oxalate pH 3.3.

Table 6. Total and soluble micronutrients (in ppm) at the surface horizons of eleven soil profiles in the coastal-forested area of Pernambuco State in northeast Brazil[a]

	Cu		M		B		Zn	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Total	25.1	2.2–79.4	0.90	0.06–2.13	–	–	53.3	19.0–189.0
Soluble	0.85[b]	< 0.1–1.6	0.07[c]	< 0.01–0.12	1.47[d]	0.42–3.39	1.52[e]	0.38–3.75

a. Adapted from Horowitz et al. [74, 75, 76, 77, 78, 79].
b. EDTA 0.05 *M* [112].
c. Ammonium oxalate pH 3.3 [69].
d. Hot water [72].
e. Na_2 EDTA-1% [19].

Horowitz [79] pointed out that while half of these topsoils are well supplied with total molybdenum (> 1 ppm), all of them are below 0.14 ppm available molybdenum, the level considered critical [69]. A poor relationship existed also between soil molybdenum and molybdenum in the parent material. The low levels of available molybdenum suggest problems in molybdenum nutrition of plants in the acid natural soils (pH 4.2 to 5.9). However, in some cases this can be overcome by adequate liming of these soils.

Boron and zinc do not seem to present serious problems in the topsoils of the coastal forested area in Pernambuco State. Only 1 of the 11 soils studied contained less than the 0.5 ppm hot water-extractable boron that is considered deficient [76], and 4 of 11 showed zinc deficiency (less than 1.25 ppm) by the Na_2-EDTA (1%) method [77]. However, levels of available manganese for these soils were found to be rather low [74, 39]. According to these authors only 1 of 20 soil profiles analyzed presented easily reducible manganese [94] above 20 ppm, a level considered critical for normal plant growth.

Other areas of the periodically humid tropics in Latin America have not been studied for micronutrients from a geochemical point of view. Instead, information was obtained from greenhouse and field experiments in order to evaluate crop response to one or more micronutrients.

Humid tropics

Data from the humid tropics on total available micronutrient contents of soil are limited. Data presented in Table 7 are a summary of the results of studies on soils from Brazil (Bahia and Amazonas), Peru (Pucallpa and Yurimaguas), eastern Ecuador, Venezuela (Upper Orinoco River Basin), Colombia (Amazonas and Pacific Coast), Costa Rica (Northwest and South Pacific coast, and Central Plateau), and Jamaica.

Santana and Igue [144] studied the distribution of different forms of zinc, copper, manganese, iron, and molybdenum in eight typical soil profiles from the cocoa region of Bahia, Brazil. The highest micronutrient reserves were found in young soils (Alfisols) with a high content of silt and clay and the presence of primary minerals in the subsurface horizons. In Oxisols, with highly weathered parent materials, the authors found the lowest concentrations of zinc and copper. Molybdenum (not shown) was relatively low, ranging from 1.09 to 2.82 ppm in A_1 horizons. If one considers the critical level of zinc to be 1.4 ppm extracted with 0.1 *N* HCl [122] and the critical level of copper to be 0.2 ppm extracted with NH_4OAc pH 4.8, the two Oxisols from Bahia can be classified as zinc and copper deficient. According to the data presented by the authors, the Ultisols present a possible copper deficiency. Apparently zinc, copper, manganese, and iron deficiencies are unlikely in soils of the Cacao region of Bahia, which are classified as Alfisols, Vertisols, Inceptisols, Ultisols, and hydromorphic soils.

Scarce information is found relating to micronutrients in soils of the

Table 7. Total and extractable micronutrients (in ppm) at the surface horizons of soils of the

Region	Extractant	No.	Zn Range	Zn Mean	Mn Range
Bahia, Brazil	Digestion with H_2SO_4 · $HClO_4$	8	13.7–82.6	40.4	110.2–4082
	HCl 0.1 *N*		0.5–44.8	5.8	1.5–2646
Parana dos Ramos, Amazonas, Brazil (Varzea soils)	HCl 0.05 *N* + H_2SO_4 0.025 *N*	13	6.2–11.8	8.4	22–100
Pucallpa, Amazonas, Peru, Ultisol	HCl 0.1 *N*	1	–	5.4	–
Yurimaguas, Amazonas, Peru (30 months after clearing)	HCl 0.05 *N* + H_2SO_4 0.025 *N*	3	–	1.5	–
Leticia, Amazonas Colombia	HCl 0.05 *N* + H_2SO_4 0.025 *N*	10	–	0.51	–
North Center and Southeast Ecuador	EDTA $NaHCO_3$		0.5–37.6	5.2	0.7–50
Pacific Coast, Colombia (forest)	NH_4OA NH_4OA_c *N* pH 7	5	0.38–1.25	0.75	Tr.–6.7
Upper Orinoco River Basin, Venezuela	HCl 0.05 *N* + H_2SO_4 0.025 *N*	6	0.16–0.70	0.41	0.53–7.25
Northwest Pacific Coast, Costa Rica	$NaHCO_3$ 0.5 *N* + EDTA 0.01 *N* pH 8.5	76	0.8–12.0	2.02	6–175
Central Plateau Buenavista, Costa Rica	$NaHCO_3$ 0.5 *N* + EDTA 0.01 *N* pH 8.5	75	0.6–13.0	3.96	12–2175
South Pacific Coto Colorado Costa Rica	HCl 0.1 *N* for Cu and Zn, NH_4OAc *N* pH 7 for Mn	10	0.1–20.0	9.0	0.1–69.0
Jamaica, Purple Conglomerates	HCl 0.1 *N*	–	1.6–5.0	2.9	9.0–120.0

humid tropics of Latin America

	Cu		Fe		
Mean	Range	Mean	Range	Mean	Author
800.9	2.7–24.6	15.0	3488–27 686	11702.6	Santana and Igue [144]
288.4	1.3–5.2	2.3	46.4–396.6	170.6	
56.0	2.9–6.3	4.3	250–1470	1039	Correa and Bastos [33]
8.0	–	–	–	–	Villachica et al. [166]
5.3	–	0.9	–	650	NCSU Trop. Soils program An. Rep. [119, 120, 122, 123]
0.82	–	0.30	–	80.1	León, Unpublished data
8.7	–	–	–	–	Bejarano et al [8]
3.7	3.5–6.5	4.8	850–2819	1905	Agreda et al. [1]
2.13	0.17–0.26	0.20	–	–	Zusevics and La Brecque [169]
53.4	1.0–31.0	6.7	2.0–86.0	13.4	Castillo Muñoz R. [24]
506.8	2.0–25.0	10.0	8.0–244.0	87.0	Castillo Muñoz R. [25]
17.0	2.0–14.0	8	–	–	Flores et al. [54, 55]
59.0	1.4–4.4	2.6	–	–	Weir [167]

Amazon River Basin. Table 7 shows data obtained for extractable micronutrients in Pucallpa, Yurimaguas, eastern Ecuador, Leticia, and Parana dos Ramos. Brazilians separate the Amazon into two basic geological formations: 'Terra firme' (precambic shields of Brazil and Guyana formed by igneous and metamorphic rocks, north and south of the Amazon Valley), and 'Varzeas' (recent river lowland, periodically flooded by the Solimoes and Amazonas Rivers). Correa and Bastos [33] studied 13 soil profiles of 'Varzeas' soils of Parana dos Ramos. Summarized data (Table 7) show that contents of extractable zinc, manganese, and copper are very high in these 'Varzea' soils according to critical levels established by Salinas [30, 31]. This is not surprising because these soils were developed from transported materials from the Andes, and the main minerals of the original sediments were montmorillonite and illite [149]. Soils from other formations of the Amazon watershed, probably most of them 'Terra firme', vary in their micronutrient content. For instance, the Ultisol from Pucallpa, Peru, studied by Villachica et al. [166] showed a content of zinc well above the critical level. On the other hand, soils from Yurimaguas, Peru, and Leticia, Colombia, presented zinc, manganese, and copper contents approaching and below the critical levels established by Salinas [30, 31], respectively.

The study performed by Bejarano et al. [8] in soils of eastern Ecuador (north, center, and south) showed a wide variation in micronutrient availability according to Padilla's [126] critical levels. Zinc and manganese were low in the northeastern soils, zinc was high and manganese low to medium in the central eastern soils, and zinc was low to medium and manganese variable in the southeast soils. These findings confirm the general idea that 'Terra firme' soils have low fertility compared with 'Varzea' soils. As a matter of fact, work done by Barros et al. [6] showed low availability of copper, cobalt, and zinc in 'Terra firme' soils of the Amazonas State in Brazil.

Table 7 also presents analytical data from soils of the Upper Orinoco River Basin in Venezuela [169]. According to the Howeler's [82] and Salinas [30, 31] critical levels of 1, 5 and 0.5 ppm for zinc, manganese, and copper, respectively, these soils can be classified as low in extractable zinc, manganese, and copper.

Agreda et al. [1] worked with soils from the flat lands of the humid Pacific Coast of Colombia under crops, forest, and pastures. Table 7 shows some of the data obtained. Although boron is not presented in Table 7, the authors found that the soils were low in boron under the three conditions studied. Zinc, copper, and iron seem to be adequate in these soils, but there are possibilities of finding manganese deficiencies in some of them.

Studies done in soils of Costa Rica, Central America, and Jamaica, Caribbean, by Castillo Munoz [24, 25], Flores et al. [54, 55], and Weir [167] show that a high percentage of the soils analyzed are low in available Zn,

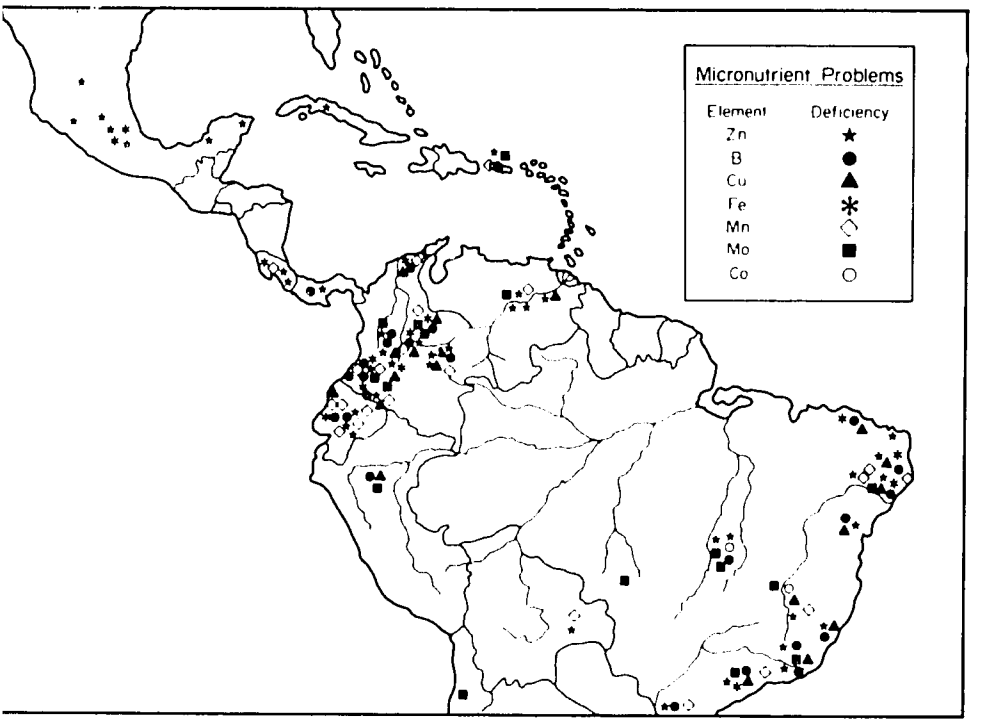

Figure 2. Location of micronutrient deficiencies in tropical Latin America

followed by Mn, Cu, and B. Some soils of the southern Pacific coast of Costa Rica are very high in available Cu [55].

Major micronutrient problems in tropical America

Reports on micronutrient deficiencies observed in tropical Latin America, either by greenhouse or field experimentation, are summarized below. This information is also mapped in Figure 2 to provide a picture of where information regarding micronutrient deficiency problems has been recorded. To a great extent the density of points on this map is a reflection of where micronutrient research in tropical Latin America has been conducted.

Arid and semiarid regions

The major agroecological regions in arid and semiarid tropical America comprise northeastern Brazil, the Pacific coast of southern Ecuador and Peru, the northern tip of Colombia, and the Yucatán Península of Mexico. Information about micronutrient problems in these areas, obtained through greenhouse and field experiments, is extremely limited.

Some studies from the dry coastal area in southern Ecuador seem to

point to problems with iron and manganese, most likely associated with high pH soils [90, 91, 92]. Research results are lacking on micronutrients in the agriculturally important regions of coastal Peru and in the Yucatán Península where conditions for iron and manganese deficiency seem to exist as well. Calcareous soils of other parts of Mexico have shown considerable increases in divalent iron when subjected to preplant flooding. This method of overcoming iron deficiency has been recommended only when the level of available manganese is adequate [67, 130]. Inceptisols and Alfisols of the arid and semiarid regions of Panama are deficient in B and Zn [118].

Climatic variability in the inter-Andean valleys is high, ranging from arid to humid. The major part of the agriculturally important Cauca Valley in Colombia is classified as a tropical dry to very dry [35]. The most representative soils are Mollisols and Vertisols formed from calcareous sands and clayey sediments. Entisols, Inceptisols, Aridisols, and Histosols also occur. Some factors that may adversely affect growth of cultivated crops in these soils are heavy texture, poor drainage, alkaline pH (due to sodium and/or carbonates), salinity, and adverse Ca/Mg relationships [64]. Some of these soils have shown micronutrient problems: boron in leguminous plants; boron and zinc in corn [83]; zinc in cotton [61], in beans [82], and in flooded rice in soils with excess salt; and zinc and copper in soybeans [83, 85].

Boron seems to be the most limiting for beans, alfalfa, corn, and sorghum [28, 52, 53, 84, 85, 133, 135]. On a high-pH Mollisol, bean (Phaseolus vulgaris) yields were seriously limited by boron deficiency, and application of 2–4 kg boron/ha gave optimum yields for two and three successive crops [80]. It is interesting to note that mung beans (Vigna radiata) were highly tolerant and showed, in the same area, negative response to boron application [80]. These differences in behavior stress the need to work with different plant species when evaluating critical levels of micronutrients in soils and plants.

Possible causal relationships of boron deficiency in soils from the Cauca Valley in Colombia have been proposed by Garavito and León [64]. They associated boron deficiency in these soils with the following soil chemical characteristics: hot water-soluble boron < 0.3 ppm, low level for total boron (approximately 15 ppm), high levels of calcium carbonate, pH above 7.3, and low percentage of organic carbon. Physical and mineralogical characteristics associated with the same problem were high bulk density (1.4 g/cc or more), development of vertic characteristics in the profile, lack of tourmaline or other boron bearing minerals, a high level of 2:1 clays, and a high proportion of vermiculite in the clay fraction. In a study of Bingham et al. [11] with selected amorphous soils from Mexico, quite different from the soils of the Cauca Valley in Colombia, they found a very high boron adsorption, significantly correlated with amorphous Al_2O_3.

Inceptisols located in the area of the 'Sabana de Bogota' in the Andes

of Colombia, classified as 'Low Montano Dry Forest' [57] have also shown some micronutrient problems. Lora [104] reports boron deficiency for various crops in 10 of 16 soils studied in this area. In five soils series, levels of available soil manganese, iron, and zinc were considered adequate, whereas available copper and boron were low, according to criteria set by Cox and Kamprath [38] and Ortega and Lora [125]. In this study, however, oats showed little response to micronutrients. Monsalve and Lotero [113], working under greenhouse conditions with a similar soil, did observe a significant increase in the dry matter yield of white clover due to use of 30 kg borax/ha and 10 kg copper chloride/ha. In these studies rates above 0.5 kg sodium molybdate/ha and above 10 kg copper chloride had a depressive effect on yield. These data emphasize once more that with micronutrients, the line between deficiency and toxicity can be quite narrow.

Cauliflower (Brassica oleracea) cultivated in an unlimed Aquic Andic Eutropept, with 0.14 ppm extractable molybdenum, showed a significant increase in yield with seed treatment of up to 32 g sodium molybdate/ha and with normal fertilization of up to 1 kg sodium molybdate/ha [116].

Periodically humid regions

Two major regions in periodically humid tropical America are the 'Cerrado' in Brazil and the 'Llanos Orientales' in Colombia, but also large regions of Central America can be considered part of this region. Micronutrient problems have been studied in these areas mainly through greenhouse and field experiments, however, in some cases the use of simple mixtures of micronutrients did not allow the researchers to identify which one is a problem [154, 134, 71, 59, 110].

Among the various micronutrients, zinc is the one that shows the most widespread deficiency in the 'Campo Cerrado' region of the central plateau of Brazil and also in Costa Rica, Guatemala, Mexico, and Peru [88]. Most of the soils of the 'Campo Cerrado' are highly weathered, acid, low CEC Oxisols and Ultisols. Zinc deficiency has been confirmed for the most diverse locations in this region for the following crops: corn [87, 60, 17, 18, 129, 120], rice [153, 20, 63, 62], sorghum [2], lettuce [56], soybeans and cotton [18], cassava [131], and perennial soybeans [58]. Because most of these studies lack analysis for soluble or extractable zinc, they fail to relate the degree of response to zinc fertilizers to zinc soil test levels. In the cases where this information does exist, the most pronounced response occurs in soils with less than 1 ppm zinc in 0.05 *N* HCl + 0.025 *N* H_2SO_4 extractant solution [121, 63, 62]. If this level is used as a critical level for Zn, data summarized on Table 8 indicate that 95% of 518 topsoil samples from the 'Cerrado' region were below the zinc critical level — a finding that suggests a high probability of response to zinc fertilizers in soils in this area of Brazil [103].

Some studies from the 'Cerrado' region failed to show a response to zinc

Table 8. Summary of the range of some micronutrients observed in 518 topsoil samples under 'Cerrado' vegetation in Brazil (includes 16 samples under forest vegetation)

Micronutrient[a]	Accepted Critical level[b] (ppm)	Samples below Critical level (%)	Range (ppm)	Medium
Zinc	1.0	95	0.2 - 2.2	0.6
Copper	1.0	70	0.0 - 9.7	0.6
Iron	?	-	3.7 - 74.0	32.5
Manganese	5.0	37	0.6 - 92.2	7.6

a. Extracted by 0.05 *N* HCl + 0.025 *N* H_2SO_4.
b. According to soil testing services in the State of Minas Gerais, Brazil.
Source: Lopes and Cox [103].

fertilization. Martins and Braga [111] observed no response of soybean variety UFV-1 to zinc fertilizer in five Oxisols and Ultisols from the Triangle of Minas Gerais. Also a leguminous plant, *Leucaena leucocephala*, did not show any response to zinc when cultivated in a clayey Oxisol from Planaltina, Federal District [147]. In both studies there were no data on soil-available zinc. Lack of response to zinc was also observed with perennial soybean (*Neotonia wightii*, IRI 1394) in three Oxisols and one Entisol from the State of Mato Grosso do Sul; the levels of zinc extractable in 0.05 *N* HCl + 0.025 *N* H_2SO_4 ranged from 0.9 to 1.3 ppm [23]. These data suggest that species and varietal differences in relation to zinc fertilization in these soils should also be taken into account.

Meanwhile, zinc deficiency is a serious nutritional problem in the 'Cerrado' region in central Brazil. Rates of zinc fertilizers required to achieve adequate yield response are quite low — about 3 - 5 kg zinc as zinc sulfate/ha for most grain crops [129, 120, 20, 62] as well as cassava [131].

Data from Table 8 [103] show the range for copper extractable in 0.05 *N* HCl + 0.025 *N* H_2SO_4 to be from 0.0 to 9.7 ppm, with a mean of 0.6 ppm for the soils under 'Cerrado' vegetation in central Brazil. Omission of copper in the missing element technique failed to show any detrimental effect on several crops growing in these soils [2, 111, 63, 23, 62, 131] even though the double acid-extractable copper was only 0.9 ppm in the two studies where such data were reported. The lack of response to copper in these experiments suggests that using the critical level of 1 ppm (Table 8) may overestimate the problem of copper deficiency in these soils.

Iron and manganese seems to be adequate for most food crops in the 'Campo Cerrado'. As was the case with copper, omission of iron and manganese from a complete treatment did not affect growth or yield of several crops. Virtually no iron or manganese fertilizers have been used in these soils. Data from Table 8 show ranges from 3.7 to 74.0 and from 0.6 to 92.2 with medians of 32.5 and 7.6 for extractable iron and extractable manganese, respectively. The data suggest that most of the Oxisols and Ultisols in the central plateau in Brazil are well supplied with available

manganese. On the contrary, Fassbender and Roldan [50] found that more than 11% of the soils that they studied in Central America (Guatemala, El Salvador, Honduras, Nicaragua, Costa Rica) were deficient in available manganese.

Boron and molybdenum availability in soils of the 'Campo Cerrado' have not been evaluated in any survey. Results of various experiments are somehow conflicting and do not provide a complete picture about these micronutrients in these soils. No response to these micronutrients was observed when using the missing element technique in several studies with soybeans [111], rice [63], cassava [131], and rice and corn [62]. Most of these studies were conducted in low-base Oxisols. Similar results (lack of response) in relation to the use of boron and molybdenum were obtained for beans [105] and for perennial soybeans, a leguminous forage crop, in two low-base Oxisols from Minas Gerais [146] and in three Oxisols from Mato Grosso du Sul [23]. However, a Quartzpsamment included in this last study showed a definite increase in dry matter production due to the use of these micronutrients. Perennial soybeans also showed an increase in dry matter yield due to the use of 3.5 kg boric acid/ha in an Oxisol at Sete Lagoas, Minas Gerais [58]. Male sterility in wheat due to B deficiency was reported on an Oxisol from around Brasilia [41]. Only the work by Santos et al. [146] provided data on total and available soil molybdenum and boron. (Values around 0.036 and 0.020 ppm for molybdenum and 37 and 0.90 for boron, respectively). Few studies with other food crops in these soils have shown response to boron, cobalt, and molybdenum. Positive effects on tomato yields and quality due to use of 20–40 kg borax/ha were observed in a clayey, dark-red Latosol near Brasilia, DF [106]. In the same soil, lettuce did not respond to 20 kg of borax/ha but did indicate a significant effect of 2 kg sodium molybdate/ha [56].

Similar to the situation in the 'Cerrado' region of Brazil is the situation in the 'Llanos Orientales' of Colombia, where zinc deficiency is the most striking micronutrient problem [29]. A similar situation exists in the andepts from the Central Plateau of Costa Rica [128, 70, 108, 26] and in northwestern Puerto Rico [5]. Most of these soils of the 'Llanos' are Oxisols and Ultisols; they are highly weathered, have a low CEC, and are extremely low in bases. Only 5 kg Zn/ha as zinc sulfate increased cassava yield from 8.3 to 12.7 t/ha and from 1.7 to 8.4 t/ha for two varieties growing in a Typic Haplustox (clayey, kaolinitic, isohyperthermic, pH 4.5) at Carimagua [29]. Zinc deficiency is aggravated in these soils when high rates of lime are used; however, higher rates of zinc can offset the lime. Howeler et al. [81] observed that 20 kg of zinc/ha was effective in overcoming zinc deficiency induced by the use of 6 t lime/ha for cassava. The treatment with nitrogen, phosphorus, and potassium + 20 kg zinc/ha gave the same yield (16 t/ha) as nitrogen, phosphorus, and potassium + zinc + molybdenum + manganese; thus the limiting micronutrient clearly was zinc. Zinc deficiency

is also reported from the Venezuelan section of the Llanos for sorghum, maize, and peanuts [100, 139, 142]. Few studies have been conducted on soils of the Llanos to evaluate micronutrient dynamics under flooded conditions. These soils are high in iron (Fe_2O_3), and the poor growth of rice plants under flooded conditions has been associated with high iron absorption and a decrease in absorption of other nutrients [117].

Some possible problems with micronutrients have been identified in other subhumid areas of tropical Brazil that are not considered part of the 'Cerrado' region. Soybean yields were enhanced by 382 kg/ha due to the use of 13 g MoO_2/ha in a Cambic red-yellow Podzolic (Ultisol) in the forest region of Minas Gerais State [168]. Also in the same soil, Braga [13] observed a linear effect of boron up to 0.69 kg/ha and a quadratic effect of molybdenum with maximum bean yields at 13.5 g Mo/ha. The most striking response to cobalt and molybdenum with beans in this region was observed by Junqueira Netto et al. [95] when applications of 12.9 g Mo/ha and 0.25 g cobalt/ha, applied to moist seeds, increased grain yields by 100% and 130%. Together molybdenum and cobalt were as efficient as ordinary superphosphate. However, greenhouse work with beans in three soils from the same region failed to show any response to cobalt (rates up to 0.4 g cobalt/ha), and the response to molybdenum (up to 16 g Mo/ha) varied from positive to negative, depending on the soil [145]. Lack of soil chemical analysis for these micronutrients precludes a complete soil characterization and thus makes interpretation of these results impossible.

Soils from the region around Piracicaba, São Paulo State, mainly used for sugarcane production, failed to show any response to boron fertilization either in greenhouse or field work [44, 14, 45]. The fact that most of these soils contain more than 1.0 ppm hot water-extractable boron suggests medium or no B deficiency [22].

Soils from Alajuela, Costa Rica, showed response to boron application when cultivated with broccoli (*Brassica oleracea*) [27]. Steep Ultisols from Puerto Rico, used for plantain production, responded to B fertilization but failed to show response to Zn [151].

Lowland soils (alluvial, low humic gley, humic gley, and organic soils) included in the periodically humid and semiarid agroecological zones present a great potential for food crops production, mainly through the use of irrigation. These soils are complex by nature, and research on evaluation of micronutrient problems is scarce. In Brazil, Coqueiro et al. [36] observed little response of wheat to a mixture of micronutrients in an alluvial soil from Minas Gerais State. However, 4-year data with wheat in the same soil showed a 9.8% increase in yield due to the use of 10 kg borax/ha. Manganese and zinc had a negative effect on yield [37]. Boron and molybdenum applied to beans and soybeans as seed coatings increased nitrogen content and plant growth in a gley hydromorphic soil from Rio de Janeiro State; this response suggests low availability of these micronutrients under these

conditions [137, 138]. Organic soils from the Paraiba Valley in São Paulo State have shown a definite response to boron fertilization with potato [65, 101, 73].

Lowland soils located in other countries in tropical America also have shown some responses to application of micronutrients. Bertsch et al. [10] found responses to Cu, Fe, Mo, and B in soils of Guamacaste and Corredores in Costa Rica. Nodulation and N adsorption by tropical legumes are affected by B and Mo deficiencies in Ultisols [159] and other soils [46] from Costa Rica. Rates of 60, 30, and 15 kg/ha of iron sulfate, zinc sulfate, and borax, respectively, increased yield and quality of tomato in an alluvial soil from the Cauca Valley in Colombia; however, copper sulfate had a depressive effect on the yields [93]. Lowland soils (Entisols) from the eastern plains of Bolivia showed considerable increases in yield of sugarcane due to use of 8 kg manganese and zinc/ha [32].

Humid tropics

The humid tropical region of South America is presently of limited agricultural importance. Shifting cultivation normally recycles adequate quantities of micronutrients to supply the subsistence crops. Because of the lack of interest in this agroclimatic zone for intensive agriculture, the number of micronutrient studies is limited. The same situation is found in the humid tropical region of Central America. In the humid tropical regions of Costa Rica, located in the South Pacific and Atlantic coasts, after P and N deficiencies, micronutrients are the main problems for an adequate crop production [109].

Few studies were conducted in the Amazon region. In Peru these included greenhouse studies at Pucallpa and field experiments at Yurimaguas [166, 119, 121, 122, 123, 142]. In Brazil only a few studies from around Manaus were found to represent the vast Amazon basin [43, 6, 33, 34]. The main problem was identified on a Paleudult near Yurimaguas where copper deficiency was consistently found in greenhouse and field; the deficiency was particularly associated with the liming effect of burning or with lime additions. Additionally, a response was obtained to boron and molybdenum with peanuts and to boron with soybeans. Zinc and manganese fertilization showed no response. At Pucallpa a study on an Ultisol with Pangola grass showed negative response to zinc even after three cuttings and heavy applications of phosphorus. Unfortunately, no other micronutrients were considered in the study. In the area of Manaus, on the 'Terra firme', a 3-year missing-element trial on an Oxisol that was cropped with maize showed no effect of omitting boron, copper, zinc, manganese, or molybdenum. The surprising lack of acute deficiency problems on these sedimentary Amazon soils is possibly due to their recent regeneration during bush fallow.

Other humid tropical regions in South America comprise the eastern

foothills of the Andes, the inter-Andean valleys and slopes, and the coastal regions of western Colombia and southeastern Brazil. Micronutrient studies in the eastern Andean foothills include two studies by Sanchez [86, 140] near Villavicencio, Colombia, on rice grown on an Ultisol and Entisol. The Ultisol showed some response to zinc and copper but none to manganese; a zinc response was observed in the Entisol of the Ariari River. The latter response was, however, lime induced since these fields are flooded by the highly alkaline waters of the Ariari. In Peru a greenhouse study was carried out with an Inceptisol from the Chanchamayo Valley in which no effect was observed to additions of molybdenum, manganese, zinc, and boron [164, 165]. Micronutrient studies from the Magdalena Valley are remarkably scarce. Various studies from in and around the Medellin Valley showed little if no response to micronutrients [114, 136, 104].

Although relatively little research has been conducted in Ecuador, boron deficiency has been reported for several crops on some volcanic soils [157]. In the coastal region a series of greenhouse evaluations showed some problems with iron and copper on some of the soils planted with coffee, whereas on those planted with sorghum, deficiencies were rare [89]. Such greenhouse evaluations are to be considered tentative at best. Field studies indicated iron deficiency with peanuts [3]; manganese and zinc deficiencies with maize, beans, coffee, and guinea grass [92]; and boron deficiency with cocoa [98]. Loor [102] and Tergas [155] reported manganese, boron, zinc, iron, and molybdenum deficiencies on *siratro* and *centrosema pubescens* after two to four cuttings.

Micronutrient studies from the humid tropical Atlantic coast of Brazil are limited. Viana [163] reported boron and zinc deficiencies in coffee. In the Cacau region of Bahia no response to zinc, copper, boron, or molybdenum was obtained with cassava or bean [68, 21]. Similar results were obtained with cassava in the State of Sergipe [152].

Table 9 lists the most common micronutrient deficiencies for the humid tropics in Brazil according to a revision made by Malavolta [107]. The most common micronutrient deficiencies, zinc and boron, are found in the States of São Paulo, Espiritu Santo, and Bahia, mainly in coffee, citrus, and vegetables.

Summary and research needs

Tropical America comprises a total land area of 1683 million ha. The cultivated area is less than 10% of the total, and the average per capita is 0 3 ha. The main surface features in this region are the Andes, the Guyana and Brazilian shields, and the Orinoco, Amazon, and Parana Basin. Oxisols and Ultisols are the major soil orders (44.9%), but considerable areas are formed by Alfisols, Inceptisols, Entisols, and Aridisols. The major food crops in terms of production are corn, cassava, rice, soybeans, potatoes, and wheat.

Table 9. Most common micronutrient deficiencies in the humid tropical region of Brazil. Adapted from: Malavolta E. [107]

Element	State	Crop and frequency[a]
Boron	Bahia	Coffee (3)
		Vegetables (3)
		Sugarcane (1)
	Espiritu Santo	Coffee (3)
		Cotton (2)
		Vegetables (2)
	Rio de Janeiro	Vegetables (4)
		Citrus (2)
	Pará	Papaya (3)
		Maceira (2)
	São Paulo	Coffee (4)
		Vegetables (4)
		Potatoes (3)
		Cotton (2)
		Sugarcane (2)
		Oranges (2)
		Eucalyptus (2)
		Pinus (2)
		Grapes (2)
		Papaya (1)
Copper	Bahia	Coffee (1)
		Oranges (1)
	Espiritu Santo	Coffee (2)
	Rio de Janeiro	Coffee (1)
		Sugarcane (1)
	São Paulo	Oranges (2)
		Coffee (1)
		Vegetables (1)
Manganese	São Paulo	Citrus (3)
		Coffee (1)
Molybdenum	São Paulo	Vegetables (3)
		Coffee (1)
		Oranges (1)
		Soybeans (1)
		Forage legumes (1)
	Pará	Leucaena (1)
Zinc	Bahia	Coffee (4)
		Oranges (4)
		Rice (2)
		Sugarcane (1)
		Maize (1)
		Sorghum (1)
	Espiritu Santo	Coffee (4)
	São Paulo	Coffee (8)
		Oranges (8)
		Maize (3)
		Cassava (3)
		Rice (3)
	Pará	Rubber tree (1)

a. Arbitrary scale: max = 10, min = 0.

There are few data in relation to micronutrient contents (total and available) for soils of the humid, periodically humid, and semiarid and arid tropical America as a whole. For the periodically humid regions, soils derived from basic igneous rocks contain the highest level of micronutrients compared with soils from other parent materials. In some cases even soils derived from acidic parent material show surprisingly high levels for copper, zinc, cobalt, and boron. For the semiarid region the available information suggests a complex situation. Although toxic levels of boron and molybdenum have been found, iron, zinc, and manganese deficiencies due to alkaline pH can also be a problem.

With the information available to date, only a rough picture of the micronutrient status of the soils of humid tropical Latin America can be sketched. Since such vast regions as the Amazon basin have hardly been studied, the picture is incomplete. Moreover, virtually no information is available to relate micronutrient problems to basic parameters such as parent material, climatic conditions, soil type, or soil characteristics. Therefore, the value of the reported information is often site related and does not allow for extrapolation. At present the best one can do is to speculate by using existing data in combination with a general knowledge of the agroecology of the region.

Soils under 'Cerrado' vegetation in Brazil and from the 'Llanos Orientales' in Colombia, most of them Oxisols and Ultisols, have definitely shown problems of zinc deficiency for most food crops. This zinc deficiency problem is associated with low levels of zinc in the parent material and is aggravated by high rates of lime. One ppm of zinc extractable in 0.05 *N* HCl + 0.025 *N* H_2SO_4 seems to be a good estimation of the zinc 'critical level' in these soils. Rates to overcome deficiency are about 3–5 kg zinc/ha as zinc sulfate or zinc oxide. When high rates of lime are used, the need for zinc fertilizers to achieve adequate yield is considerably higher. Boron deficiency also seems to occur in some of these soils, but the picture is not so well defined. The fact that omission of other micronutrients, as in using the missing-element technique, has not seemed to have any detrimental effect on food crops in most of these soils suggests sufficiency. However, with continuous cultivation of these soils other micronutrient problems may soon occur.

Data on micronutrient problems in the semiarid region of tropical America are extremely limited. The reported iron, zinc, and manganese deficiencies are a problem associated in general with high pH soils. Some cases of boron deficiency have been reported. The area with the most prominent boron deficiencies is the Andes region. It appears that these boron problems are associated with volcanic deposits low in boron.

Lowland soils (alluvial, low humic gley, humic gley, and organic) have received little attention in relation to micronutrient studies. The situation becomes even more complex in the case of continuous flooding. The

dynamics of micronutrients have not been evaluated in depth under such conditions in Latin American soils.

Based upon data of this literature review some future research needs could be summarized as follows:

Areas with lack of information about micronutrient problems should be surveyed. Soil survey samples are, in general, stored after characterization for this specific purpose. Analysis of stored samples for total and available micronutrients and correlation with other chemical, physical, and mineralogical characteristics may give considerable information about the micronutrient status of these soils. Selective greenhouse studies should be conducted to verify this information.

Since most of the 'critical levels' for micronutrient interpretations were obtained in temperate regions, these levels should be reestablished for the tropics through adequate correlation and calibration studies that take into consideration differences in parent material, soil, climate, weathering stage, management, and other factors. Establishing the critical levels would thus involve studies with extractant solutions and different crops through successive cropping under greenhouse conditions.

Areas that have already passed through the preliminary survey phase should be studied in more depth; representative sites should be selected on the basis of preliminary data obtained under laboratory and greenhouse conditions. Such studies may consist of missing-element trials followed by studies on rates, sources, and methods of application. In all cases complete chemical, physical, and mineralogical characterization of the soils must receive high priority.

To achieve these goals there is an urgent need for improved laboratory facilities as well as highly trained technicians to work with precision and accuracy. There is also a need for trained personnel (M.S. and Ph.D level) in this specific area.

With the increasing awareness of the role of micronutrients and a greater number of scientists and laboratories dedicated to this topic of research, the number of reported problems is bound to grow; the reports will eventually provide a more detailed picture of the extent and magnitude of micronutrient problems in tropical Latin America. However, if real progress is to be made in understanding the relations between micronutrient problems and the agroecological environment, coordination of such research to assure uniformity in data collection and reporting will be essential.

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5. Micronutrient problems in tropical Africa

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Introduction

Micronutrient investigations in tropical Africa started during the late 1940s and early 1950s, particularly in West Africa. Though some of the early investigations carried out with food crops indicate few micronutrient problems, if any [16, 94], investigations with perennial cash crops showed distinct responses to micronutrient applications. Greenwood and Hayfron [37], for instance, reported deficiencies of iron and zinc in cocoa in Ghana, and Ferrand et al. [32] observed deficiencies of boron, copper, and manganese in the Congo.

The widespread occurrence of micronutrient problems in Africa south of the Sahara was also shown by the results of a survey conducted by Schutte [89], who concluded from his study that soils in Africa, in general, have a low micronutrient status. In a more recent review on micronutrient investigations in west Africa, Kang and Osiname [55] stated that boron, molybdenum, and zinc problems are more prevalent and of more economic importance than those of copper, iron, and manganese.

Despite the more than three decades of micronutrient investigations, the role of micronutrients in crop production in the various regions of tropical Africa has not yet been studied systematically. Many of the past investigations are either incidental or exploratory in nature, which makes it difficult to obtain a real assessment of the magnitude of micronutrient problems in the region. Moreover, the lack of precise soil characterization of many of the studies prevents extrapolation of the results to wider areas.

In this paper the authors will review the status of micronutrient investigations in tropical Africa in the region between the tropics of Cancer (23½°N) and Capricorn (23½°S) in an attempt to better understand the micronutrient problems in the area.

Geology, soils, and climate

With the exception of some river basins and coastal plains, most of tropical Africa consists of upland plains [47]. The African plateau can be subdivided

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into a number of large basins (e.g., Chad, Zaire, and Bahr el Ghazal) and the higher regions in the southern and eastern part of the plateau. The Ethiopian Highlands and East African Plateau are volcanic in origin and are dissected by the Great Rift Valley that runs south from the Red Sea to Lake Malawi. Residual highlands are found throughout the continent as inselberge or as the more extensive divides between plateau basins (e.g., Cameroon Highlands) or residual plateaus. The last uplift of the African continent was so recent that rivers have not had the time to dissect the surface. A great number of short streams flow from the edges of the plateau, while a third of the continent has no drainage outlets. The major rivers of tropical Africa are the Zaire (formerly Congo), Nile, Niger, Senegal, and Zambezi.

Compared with the geology of other continents, the geology of Africa is relatively simple. The continent is a vast crystalline Precambrian plateau consisting primarily of granite, gneiss, and schists of the basement complex rocks overlain by various sedimentary formations (quartzites, limestones, dolomites, and phyllites)[30]. These formations cover about a third of the continent. In the course of the Paleozoic era, various marine sediments were laid down, mostly in north Africa with uneven extensions to the south. In west Africa sandstones cover major portions of Ghana, Togo, Benin, Mauritania, Senegal, Mali, and Guinea. Paleozoic outcrops are virtually absent from equatorial and southern Africa. The only formations of the Mesozoic era in tropical Africa are the Jurassic sandstones and gypsum-carrying clays extending south of the Ethiopian massif, the Cretaceous limestones and clays in Nigeria, and scattered remnants of the late Triassic volcanic activity. Old Tertiary surfaces, sometimes covered by ferruginous crusts, subsist in west Africa to the south of the Niger and Chad basins; between the basins of Chad, the Nile-Bahr el Ghazal, and the Zaire; and around the basins of Lake Victoria and Lake Kioga. The Kalahari deposits consisting of polymorphous sandstones, aeolian and fluviatile sands, and lacustrine calcareous lenses, crop out extensively in Botswana, Namibia, Zimbabwe, Angola, the Congo, and Zaire. The Tertiary period is also characterized by volcanic activity, principally in east Africa.

The greater part of the superficial deposits are of Quarternary formations. Volcanic formations border the faulted areas. Aeolean sand deposits form the loose formations of the south Sahara and the Kalahari, extending as far north as the equator. As in other locations, the Quarternary period in tropical Africa was characterized by frequent climatic changes of alternate wet and dry periods. It was during this period that extensive ferralitization or lateritization of the vast Sudanian zone took place. It is this alternating in climates in combination with the parent rock that, to the greatest extent, has influenced the pedology of tropical Africa.

The parent materials of the soils are not necessarily similar to the weathered bedrock [24]. In fact many parent materials in tropical Africa are polygenetic residues, reworked and exhausted sediments, or aeolean sands, and

the nature of the original parent rock is difficult to establish. In general, parent materials currently exposed to pedogenesis in tropical African landscapes are poor in alterable minerals. The most favorable exceptions are parent materials formed directly from underlying rock or volcanic ashes, the black tropical clays of the Nile-Bahr el Ghazal and Chad basins, and various recent alluvia.

Soil-mapping efforts in Tropical Africa are limited. The most comprehensive soil maps are the map produced by D'Hoore [24] on a scale of 1:5,000,000 and its successor produced by FAO/UNESCO [30]. A soil map, using U.S. soil taxonomy units, is shown in Figure 1. From this 1:50,000,000 soil map of Africa [6], it appears that the Aridisol is the most extensive soil group. It is estimated to cover approximately 36.8% of the total area. Alfisols cover about 24.0%, Ultisols and Oxisols approximately 22.6%, and Entisols 14.1%. Inceptisols and Vertisols cover 2.5% and 2.1% of the total area, respectively. These figures are expected to change as more detailed information on the distribution of the major soils in tropical Africa becomes available.

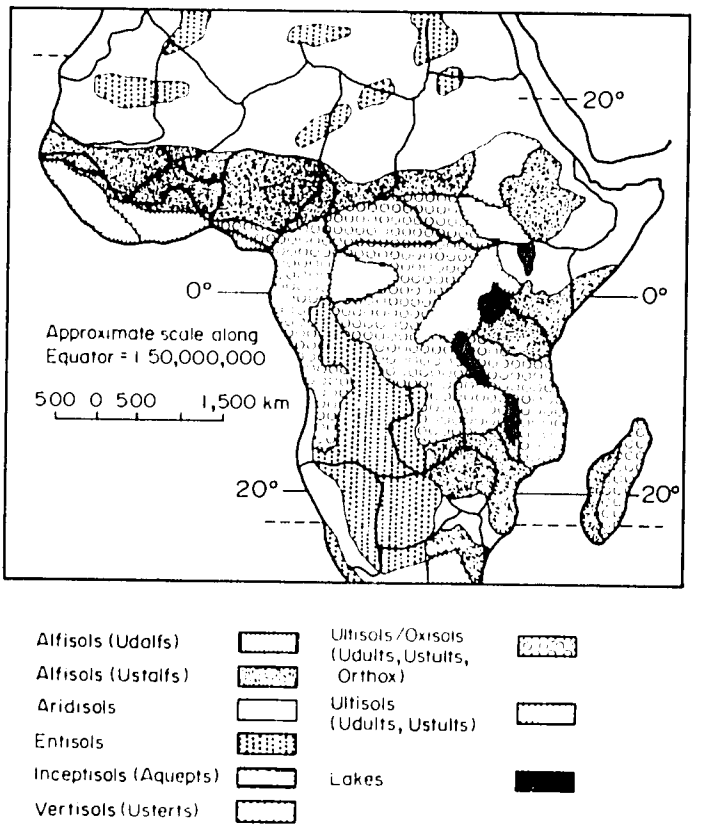

Figure 1. Soils of tropical Africa (Adapted from Aubert and Tavernier, 1972 [6])

As much as two-thirds of the 30.4 million km^2 of the African land area is situated between the tropics of Cancer and Capricorn. The equator runs more or less through the center of the continent where it spans a distance of about 7,000 km. Three factors dominate the climatic pattern in Africa: the size of the continent; the high altitude of Ethiopia, east Africa, and parts of central and south Africa; and two cold Atlantic ocean currents and the warm Mozambique Current.

Figure 2 depicts the main climatic types in tropical Africa: (1) the humid tropical and equatorial region of southern west Africa, the Zaire Basin, and the east side of Madagascar; (2) the periodically humid regions to the north and south of the humid tropics; and (3) the semiarid and arid regions including the Sahel region, Somalia and parts of Ethiopia, and the Kalahari. The

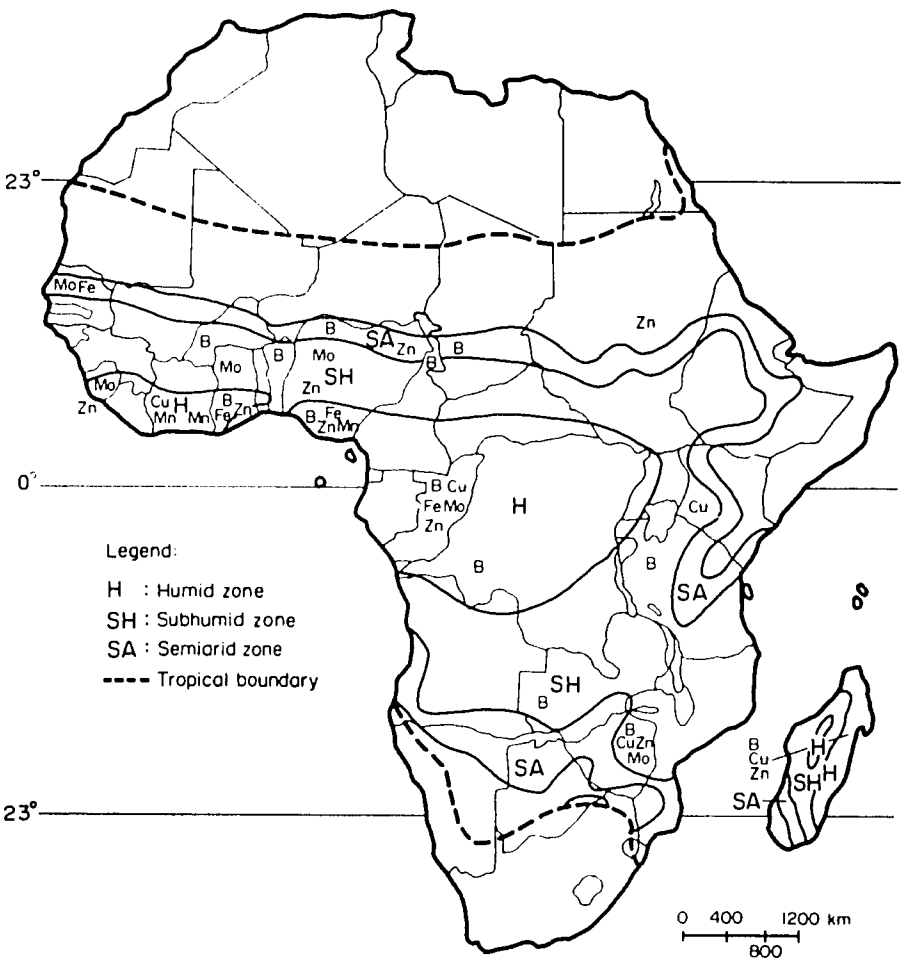

Figure 2. Location of micronutrient deficiencies in tropical Africa [27].

length of the rainy season and the reliability of rainfall, as well as the amount of rain diminish with increasing distance from the equator provided the maritime influence is negligible. It is the scarcity of rain in combination with poor reliability of rainfall that poses a major constraint to food production in much of the semiarid tropical regions of Africa.

Micronutrient content of soils

Total micronutrient content

Despite the increasing importance of micronutrients in agriculture in tropical Africa, few published data are available on the total content and distribution of micronutrients in tropical African soils. Detailed data on the total micronutrient contents of soils from some countries in tropical Africa are summarized in a publication of Aubert and Pinta [7].

Reports from different countries in tropical Africa show that there is a strong relationship between parent material and micronutrient content of the soils, though pedogenesis may have a modifying effect [7]. Results from a survey of representative Ghanian forest soils by Burridge and Ahn [18] showed that the micronutrient levels in the fine earth fractions (< 2 mm) are related to the underlying geological formations. Nalovic and Pinta [69] observed that soils of Malagasy formed on crystalline metamorphic rocks are richer in manganese and copper than soils formed on sedimentary rocks (Table 1). Similarly, Cottenie et al. [21] noted that Nigerian soils derived from basic rocks such as basalt and amphiboles are richer in micronutrients than those derived from acid granites and sandstones. Parent rock was the most important factor in determining both the total and available (hot-water-soluble) boron in Nigerian soils [11]. The range of extractable boron content was 1.26 to 1.50 ppm for soils derived from sandstones compared with 1.12 to 2.75 ppm for soils derived from basement complex rocks (Table 2). Nyandat

Table 1. Total manganese and copper contents of selected soils from Malagasy [69]

Soil description	Parent rock	Mn (%)	Cu (ppm)
Ferralitic soils	Basalt	0.093	50
	Marble	0.770	65
	Limestone	0.458	20
	Gneiss	0.235	53
	Granite	0.047	46
	Acid rocks	0.100	34
	Volcanic ash	0.084	22
Ferruginous soils	Limestone	0.119	22
	Basic rocks	0.230	54
	Schist	0.013	26
	Shells	0.075	24
	Sands	0.045	24
	Sandstone	0.025	23

Table 2. Total boron content of selected soil profiles from Southern Nigeria [11]

Soil series/taxonomy	Soil depth (cm)	Total B content (ppm)
	Derived from sandstones	
Onne	0–13	1.26
(typic paleudult)	13–42	1.86
	42–72	1.68
	72–153	3.48
	153–180	1.44
Alagba	0–8	1.56
(oxic paleustalf)	8–23	0.84
	23–48	1.38
Iju	0–20	1.26
(tropaquept)	20–39	1.26
	39–80	0.78
	80–160	0.78
	Derived from basement complex rocks	
Egbeda	0–13	4.68
(oxic paleustalf)	13–30	5.52
	30–66	7.92
	66–127	7.16
	127–183	9.24
Olorunda	0–18	6.12
(oxic paleustalf)	18–38	6.36
	38–71	9.60
	71–122	4.00
	122–183	4.92
Owena	0–20	0.78
(oxic paleustalf)	20–30	1.32
	30–64	3.36
	64–122	1.50
	122–194	3.30

and Ochieng [71] found that the total copper content in selected Kenyan soils was greatly dependent on the parent rock from which the soil was derived. Soils underlain by volcanic rocks contained less total copper (8.6–25.0 ppm Cu) than did soils underlain by metamorphic rocks (26.6–103.1 ppm Cu). The total copper content of soils underlain by sedimentary rocks was found to vary greatly, between 9.4 and 100.6 ppm Cu.

Cottenie et al. [21] have shown that within a soil association, the position of a profile in the toposequence has a stronger influence on soil micronutrient status than does parent material. Upper slope profiles were found to contain more boron, copper, iron, manganese, and zinc than do the lower members of the toposequence. Cottenie et al. [21] also found wide ranges in total micronutrient contents of selected Nigerian soil profiles (Table 3). The mean total iron ranged from 0.63% to 7.36% and manganese from 0.02% to 0.19%; copper ranged from 7 to 59 ppm. The means in the profiles for boron, copper, molybdenum, and zinc were 12–212, 29–79, 3–42, and 26–189 ppm,

Table 3. Mean total amount of seven micronutrients in the surface horizon of selected well-drained soil profiles from Nigeria [21]

Soil series/taxonomy	Fe	Mn	Cu	Zn	B	Mo	Co
	(%)		(ppm)				
Nkpologu (typic paleudult)	1.83	0.04	10	28	122	42	48
Iwo (oxic paleustalf)	3.55	0.12	37	68	135	31	63
Apomu (psammentic usthorthent)	0.63	0.04	7	26	22	41	52
Adio (aeric tropaqualf)	0.74	0.02	8	45	12	20	29
Aramoni (udic rhodustalf)	7.36	0.19	59	189	212	3	70
Alagba (oxic paleustalf)	1.28	0.05	23	52	87	26	29
Atan (plinthic paleustalf)	0.94	0.03	8	49	18	29	30

respectively. Iron content increased while manganese decreased with depth within the profile. Where concretion existed, the manganese content tended to increase with depth.

Osiname and Kang (unpublished data) observed a range between 12 and 45 ppm zinc for the forest region and 9–35 ppm zinc for the savanna region of Nigeria. They also observed that the total zinc content increased with depth. Banjoko [9] and Banjoko and Ashaye [10] reported lower total iron content in surface horizons (0–30 cm) of Inceptisols (0.55%–0.88% Fe) as compared with the associated well-drained uplands soils (2.12%–3.39% Fe) of southwestern Nigeria.

Analysis of selected top soils in Ghana by Acquaye et al. [1] showed total manganese to be rather low (0.015%–0.24%), whereas iron was medium (0.13%–4.6%). The ranges for copper and zinc were 21–77 and 19–116 ppm, respectively (Table 4).

Nalovic and Pinta [70] reported low levels of total boron (3.3–18.2 ppm), copper (7.3–54.0 ppm), and manganese (0.044%–0.24%) in surface horizons of Alfisols, Ultisols, and degraded Aridisols. Pinta and Ollat [83] also showed very low levels of total copper (< 1.0–4.0 ppm) and manganese (0.013%–0.20%) in surface horizons of Alfisols and Ultisols from Benin. The total zinc content of surface horizons ranges from 40–280 ppm.

Data from surface soils from Mali [80] indicated very low contents of total boron (0.12–0.31 ppm), copper (7.3–55.0 ppm), molybdenum (0.44–0.75 ppm) manganese (75–600 ppm), and zinc (1.9–4.8 ppm).

Lack of a detailed soil map of tropical Africa constitutes a major problem in attempts to relate micronutrient status with the major soils of the region. Some investigators [89, 55] have therefore found it easier to discuss the micronutrient problems of tropical Africa on a geographical basis.

Table 4. Total manganese, iron, copper, and zinc contents of selected top soils from Ghana [1]

Soil description	Fe (%)	Mn (%)	Cu (ppm)	Zn (ppm)
Forest oxysol on biotite granite schist	1.53	0.033	37	116
Forest ochrosol on granite	0.27	0.010	21	103
Tropical black clay on hornblend gneiss	4.59	0.240	77	94
Forest oxysol on biotite granite	0.56	0.015	21	33
Forest oxysol on phyllite	0.13	0.085	26	92
Savanna oxysol on alluvium	0.82	0.075	30	87
Savanna gleisol on alluvium	1.88	0.190	46	72
Forest ochrosol on phyllite	0.72	0.043	35	45
Groundwater laterite on shale	0.61	0.010	26	42
Savanna acid gleisol on phyllite	1.60	0.050	35	53
Forest acid gleisol on phyllite	0.80	0.056	30	34
Savanna ochrosol on quartzite/sandstone	0.68	0.015	30	41
Forest oxysol on tertiary sand	0.66	0.015	30	41
Savanna and gleisol on shale	0.26	0.015	26	19

Extractable micronutrient levels

A number of investigations were carried out in the various ecological zones of tropical Africa to determine the extractable micronutrient status of the soil as a means for delineating micronutrient problem areas. Several extractants were used to assess the micronutrient availability to crops in tropical African soils.

Dabin and Leneuf [23] determined the levels of 2.5% acetic acid-extractable copper, iron, manganese, molybdenum, and zinc in 58 different soils collected from the main banana-growing areas of the Ivory Coast. They observed low copper content in the younger peat soil. Extractable iron was low in soils derived from basic rocks. There was also an indication of possible manganese deficiency in soils of peat and lacustrine alluvial origins. All the soils investigated, except the organic and hydromorphic soils, were low in molybdenum. Soils derived from Tertiary sands, granites, schists, and alluvial materials were also low in extractable zinc.

Ashaye [4] found ample extractable manganese levels (Tamm, and easily reducible) in a toposequence in southwestern Nigeria with soils derived from sandstones. On the other hand, Cottenie et al. [21], studying the micronutrient status of selected benchmark soils from the humid zone of southern Nigeria and Togo, observed low manganese levels by various extraction methods in soils derived from sandstones and sedimentary material. They reported high extractable manganese levels in upland soils derived from basement complex rocks. The soils studied by Cottenie et al. [21] also showed rather low levels of hot water-extractable boron, ammonium oxalate-extractable molybdenum, and ammonium acetate/EDTA-extractable zinc. Haque et al. [40, 41] investigated the copper, iron, manganese, and zinc status of some upland and lowland soils from humid Sierra Leone. They

observed generally high levels of extractable iron, low levels of manganese in some of the lowland soils, and low levels of zinc in all samples. In a survey of the levels of acetic acid-extractable copper, iron, managanese, molybdenum, and zinc of a number of soils from Zaire, Vancompernolle et al. [107] also observed generally low zinc levels with some of the soils showing low iron and manganese status.

From the drier zones, Chamberlain and Searle [19] reported high neutral ammonium acetate-extractable manganese levels in soils from Kenya, particularly those derived from basement complex rocks. Pinkerton [81] observed low extractable (perchloric acid digestible) copper levels in soils from the Rift Valley region of Kenya. This finding was subsequently verified by the investigations by Nyandat and Ochieng [71]. Ibrahim [45] studied the micronutrient status of three major soils from the Gezira scheme in Sudan. He reported low levels of extractable molybdenum in these soils, whereas the levels of the other extractable nutrients were adequate.

As part of a global study on soil micronutrients, Sillanpaa [90] investigated the micronutrient status of a large number of soils from Ghana, Nigeria, Sierra Leone, Malawi, Tanzania, and Zambia, using a variety of extraction methods (c.f. Chapter 6). He reported generally low to deficient levels of boron, copper, molybdenum, and zinc and normal to excessive levels of manganese in these countries.

Geographical distribution of micronutrient problems

Various field experiments were carried out in tropical Africa to determine the micronutrient problems for crop production. From the results of a number of carefully conducted experiments in the subhumid region of northern Ghana, Stephens [94] concluded that, with the possible exception of molybdenum, micronutrients appear not to be needed for food crop production. Stephens [95] also reported negligible responses to micronutrients in extensive field investigations conducted between 1959 and 1965 at high elevation at nine locations in Uganda. Jones [49] reported increased yield with zinc fertilization in two of eight trials, and with molybdenum fertilization in one of four trials at Luve (Swaziland), and concluded that 'the need for zinc and molybdenum were not confirmed.' Also, Jones [50] concluded from 20 trials conducted at Malkerns that copper and manganese availability are almost certainly adequate, but that zinc, molybdenum, and boron availabilities are marginal. He comments that 'the need for zinc and molybdenum fertilization is incompletely understood' and that 'interactions between these nutrients, soil pH, and phosphate deserve more investigation.' He also indicated the need for further investigations on boron at Malkerns Station.

Despite negligible micronutrient response in some of the field trials with food crops as discussed above, field responses were reported on a number of other crops at other locations [89, 55]. Because of the economic importance

of cash crops, more is known about the problems in such crops as banana [23, 68, 20], groundnuts [63, 35], cotton [87, 17, 43], cocoa [37, 22, 5, 29], and oil palm [32, 33, 75, 66].

To better illustrate the micronutrient problems in tropical Africa, the geographical distribution of reported field cases based on published data including those from Schutte [89] is shown in Figure 2. It appears that the micronutrient problems may be more prevalent in the subhumid and semiarid regions than in the humid region. The following discussion provides a more detailed review of the problems of each of the micronutrients for various crops according to their importance in the different agroecological zones.

Boron

Humid zone.[2] Boron was first found to be of practical importance in west and central Africa in oil palm. A positive response to boron was first reported by Ferrand et al. [32] in oil palm grown on depleted sandy soil at Etoumbi, in the Congo. Significant responses to boron application were also reported in oil palm grown in the Kasai region of Zaire [33], in the Ivory Coast [75, 66] and in southern Nigeria [73]. Martin [66] observed that oil palm will respond to boron application if the available boron content of the soil falls below 0.1–0.2 ppm. In the Ivory Coast boron deficiency in this crop can be corrected by annual application of 50–75 g of borax per tree.

Boron deficiency was observed in adult cacao plantations (cultivating Amazon variety cacao) in the Tafo and Bunso areas of Ghana [5] and in southwestern Nigeria [29]. Egbe and Omotoso [29] also reported low available boron content in surface samples from the cacao belt soils of western Nigeria, ranging from 0.01 to 0.44 ppm boron soluble in hot water. This boron content in the soil is considered insufficient to satisfy the boron needs of the early-maturing and high-yielding Amazon variety cacao.

Charpentier and Martin-Prevel [20] reported boron deficiency in banana in the Ivory Coast. They felt that the problem was due to increased soil pH resulting from excessive liming.

Subhumid and semiarid zones. Boron deficiency is common in cotton grown in tropical Africa. Le Mare [58] states that boron deficiency occurs widely in Tanzania, especially on light-textured soils and in the wetter areas. Rothwell et al. [87] observed widespread occurrence of boron deficiency in cotton in the Magoye district of Zambia. According to a 1968 unpublished report from the research branch of the Zambian Ministry of Agriculture, boron deficiency occurs in cotton in soils with less than 0.4 ppm boron soluble in hot water. The importance of boron for cotton production in central and

[2] Agroecological boundaries adapted from Dudal [27], humid zone length of growing period (LGP > 270 days); subhumid zone (LGP, 150–269 days); semiarid (LGP, 75–149 days).

west Africa was also demonstrated by the survey conducted by Braud et al. [17]. From leaf analysis they confirmed boron deficiency in field-grown cotton at Yaone and Tikem in Chad, Marona in Cameroon, and Tantega in Benin. The problem in Tikem in Chad was observed following application of high rates of fertilizers. Smithson [92] and Smithson and Heathcote [93] reported that boron deficiency covers a wide area of the cotton belt of northern Nigeria. The deficiency is particularly associated with drift soils in the north-central and northwestern regions. There are considerable variations in the severity of the problems even within a small area because of moisture stress, varieties grown, and dosage of fertilizers applied, particularly that of nitrogen. Though foliar boron application in cotton gives satisfactory results [87], soil application as borax or boronated superphosphates is equally effective in correcting the problem [87, 43].

Fenner and Goldring [31] reported significant yield increases in maize with boron application in one of seven trials conducted in Zimbabwe and observed yield improvement in three of the trials. In an additional 19 trials conducted between 1971 and 1973, one experiment showed a positive response to boron, whereas 4 trials showed significant negative responses [12]. Following the discovery of severe boron deficiency in cotton in the Magoye district of Zambia, Honisch [44] conducted some field trials with maize. He was, however, unable to show any boron response in three years of observations. Velley et al. [108] reported a boron response in maize grown in ferrallitic soil derived from gneiss in Malagasy.

Oliver et al. [74] working with three hydromorphic soils from the Malagasy highlands around Tanarive observed low boron levels. In a pot trial, wheat grown in these soils responded to boron application. Velley et al. [108] reported that after several years of intensive cropping in Malagasy boron deficiency was observed in groundnuts and wheat grown on ferrallitic soil derived from gneiss. Very serious problems were observed in wheat grown on recent alluvial soils and on ferrallitic soils derived from basalt. The importance of boron for groundnuts in northern Zimbabwe was reported by Smart [91].

Boron deficiency was also observed in other crops such as sisal [25] and eucalyptus in northern Zimbabwe [88] and in Bobo Dioulasso in southern Upper Volta [13].

Copper

Humid zone. Investigations by Ferrand et al. [32] on depleted sandy soil at Etoumbi in the Congo showed a significant yield increase in oil palm with copper application. Dabin and Leneuf [23] in a survey of the micronutrient status of the banana region in the Ivory Coast observed low copper levels (acetic acid, 2.5%) ranging from 0.2 to 1.5 ppm Cu. The lowest copper levels were observed in the younger peat soil. Charpentier and Martin-Prevel [20] also reported copper deficiency in banana grown on peat soil in the Ivory Coast.

Subhumid and semiarid zones. Osiname [76] observed low extractable copper levels in various sandy soils from the subhumid region of south-western Nigeria. Despite the low copper levels observed, field-grown maize did not respond to copper application.

In East Africa, copper deficiency was observed in wheat, mostly on soils of the Rift Valley area in Kenya. Considerable laboratory and greenhouse work was carried out to elucidate the factors contributing to the copper deficiency problem in the Njoro-Nakuru area [82, 81]. Pinkerton [81] examined copper deficiency in soils derived from various parent materials and observed that deficiency was associated with soils derived from recent ash and pumice. On the basis of greenhouse and field trials, Wapakala [109] reported that phosphate application reduced copper uptake, whereas nitrogen application improved the efficiency of copper to wheat yield. Nyandat and Ochieng [71] conducted a countrywide survey to estimate the copper content and availability in both arable and range lands of Kenya based on results of greenhouse trials. They observed no deficiency in wheat grown in soils with more than 1.0 ppm EDTA-extractable copper and confirmed that most of the deficiencies occurred in plants grown in soils derived from ash and pumice.

Copper deficiency in irrigated winter wheat grown on sands derived from granite in northern Zimbabwe was reported by Tanner et al. [101]. The copper problem appeared to be aggravated by the high zinc concentration in the soil. Velley et al. [108] also observed copper response in maize grown on ferrallitic soil derived from gneiss in Malagasy.

Iron

Humid zone. Iron deficiencies are more of a local problem. For instance, Greenwood and Hayfron [37] reported an iron deficiency in cacao seedlings planted in a farmer's plot that had been burnt over. Egbe and Omotoso [29] reported some minor iron deficiency problems with cacao grown in south-western Nigeria. Kang et al. [53] observed iron chlorosis in upland rice grown on land after extensive burning of plant residues. They observed differential varietal responses to iron deficiency, with the short varieties being more susceptible to iron deficiency than the tall varieties.

The deficiencies following burning are attributed to high pH resulting from burning, which renders the iron less available [37, 22, 53]. Although heating of the soil at low temperatures ($\leq 200\,^{\circ}C$) increases the amount of DTPA-extractable iron, heating at high temperatures ($\geq 500\,^{\circ}C$) decreases the amount of extractable iron [56]. The iron chlorosis can be successfully corrected with foliar spraying in cacao [37, 22], as well as in upland rice [53]. Soil treatment has been less successful.

Iron toxicity can be of importance in some of the flooded rice-growing areas in the humid zone as reported from Liberia [46] and Sierra Leone [61]. This problem can be partially solved by breeding varieties tolerant to iron toxicity [46].

Subhumid and semiarid zones. Iron chlorosis was reported in sorghum grown in sandy soil in Bambey, Senegal following irrigation with calcium- and magnesium-containing water [15]. Accumulation of carbonates in the soil surface horizons increases soil pH and this induces the iron deficiency.

Manganese

Humid zone. The role of manganese in the nutrition of groundnuts and oil palm has been widely studied in west Africa and was reviewed by Prevot [84]. Manganese deficiency is, however, of minor importance in west Africa.

A significant response to manganese application was reported by Ferrand et al. [32] in oil palm grown at Etoumbi in the Congo. Bachy and Fehling [8] observed that fusariosis, a wilt disease caused by *Fusarium oxysporium*, was associated with low manganese contents (< 100 ppm Mn) in mature palm leaves at Dabou in the Ivory Coast. A similar observation was also made by Prevot [84] in southern Nigeria, where application of manganese sulfate reduced the number of affected plants.

Okoye [73], in a preliminary assessment of the micronutrient responses on a sandy Ultisol from east-central Nigeria, found that manganese application had the greatest effect on maize yield. This soil, which is derived from sandy sedimentary materials, is known to have a low total manganese level [106]. However, Amon and Adetunji [3], conducting trials on similar soils in southwestern Nigeria, could not obtain any manganese response.

Liming was shown to reduce the yield of pineapple grown on acid ferrallitic soil in the Ivory Coast [62]. This was in part attributed to reduced manganese uptake. Similar effects of liming in reducing manganese uptake which resulted in deficient levels were observed in pot experiments with maize [50], cassava [28], and cowpeas [52] grown on a sandy and highly acid Ultisol from southeastern Nigeria.

More important is the problem of manganese toxicity, which has been widely observed in the humid as well as the subhumid and semiarid regions. Prevot et al. [85] observed manganese toxicity in groundnuts at the Niari Valley in the Congo. This toxicity, the result of a reduction in soil organic matter [84], was corrected by liming [64]. Ngo et al. [72] reported manganese toxicity on a ferrallitic soil in Malagasy. Many of the upland soils derived from basement complex rocks have high levels of manganese [19, 21]. Upon further acidification with the use of acid-forming fertilizers, these soils may release high concentrations of manganese, potentially leading to toxicity for a variety of crops such as maize, cowpeas, and cotton [36]. Manganese toxicity problems can be prevented and corrected by liming [59] or by application of farmyard manure [48].

Molybdenum

Humid zone. Although Dabin and Leneuf [23], in a survey of banana-growing areas in the Ivory Coast using acetic acid (2.5%) extraction, observed

low molybdenum levels in the soil, there are no reports of molybdenum problems in the area. In Sierra Leone, Haque and Kamara [39] reported that an increase in dry-matter yield and nitrogen uptake of groundnuts grown on an Oxisol resulted from molybdenum application. They, however, failed to obtain an increase in seed yield. Rhodes and Kpaka [86] did obtain significant increases in dry-matter and seed yield with molybdenum seed dressing in cowpeas grown on an Oxisol in Sierra Leone.

In a series of trials to investigate the effect of various micronutrients on cane growth in Mauritius, Parish et al. [79] obtained a significant response only to molybdenum in a low humic Latosol. Subsequent studies have shown, however, that this was an isolated case [110].

Subhumid and semiarid zones. Molybdenum deficiency occurs widely in groundnut-growing areas in northwest Senegal [65], northern Ghana [94], and northern Nigeria [42]. Webb [110] in pot trials observed molybdenum deficiency in some Gambian soils, but Maremah [63] was unable to confirm this in field trials with groundnuts. Molybdenum application on the sandy aeolian soils in the semiarid zone of west Africa has led to improvements in growth, nodulation, nitrogen fixation, and seed yield of groundnuts [65, 35].

Greenhouse trials [96] have shown molybdenum deficiency to be a major growth-limiting factor on a red clay-loam soil in Zimbabwe. Results of field trials with molybdenum at 13 locations suggest that molybdenum deficiency occurs in soil with pH < 4.8 [105]. Application of molybdenum was effective in improving early maize growth in soils with pH between 4.4 and 4.8. With maize, symptoms of molybdenum deficiency only develop when the seed has a low molybdenum content [100]. Although deficiencies can be corrected by foliar sprays or seed dressings [99, 14] there is some evidence that these treatments will not fully correct problems caused by use of low-molybdenum seed. Molybdenum deficiency coupled with late nitrogen top-dressing has been shown in Zimbabwe to cause premature sprouting of maize grain on the cob [98].

Zinc

Humid zone. Osiname [76] considered zinc levels low in some soils from the humid zone of southern Nigeria. Greenhouse trials on 10 soils from that zone showed a response to zinc on most soils when cropped to maize [57]. However, field trials with maize did not show any response to zinc application [77, 78]. Response to zinc was obtained in maize grown on ferrallitic soil derived from gneiss in Malagasy [108]. Zinc deficiency problems were observed in oil palm grown in the depleted sandy soil at Etoumbi in the Congo [32] and in cacao in isolated places in Ghana [37] and in western Nigeria [29]. Greenwood and Hayfron [37] noted that zinc deficiency in farmer's fields in Ghana appeared to be mainly confined to the vicinity of refuse heaps and husk dumps and to seedling beds made from soils scraped from the surface

beneath matured cocoa trees. They attributed the problem to high soil pH (> 7.0) and unusually high contents of phosphorus and potassium.

Liming the soil from pH 4.5 to above 6.5 induced zinc deficiency in field-grown banana in Guinea [67], in spite of the high zinc content of the soil. Charpentier and Martin-Prevel [20] made a similar observation in the Ivory Coast. Friesen et al. [34] also showed in pot trials with kaolinitic Ultisols from southeastern Nigeria that a combination of high rates of lime (to pH 7.0) and phosphorus induced zinc deficiency and depressed dry-matter yield of maize. Zinc deficiency was also observed in flooded soil in Sierra Leone [38].

Subhumid and semiarid zones. In field investigations on sandy soils in the subhumid zone of southwestern Nigeria, Osiname et al. [77] obtained large maize grain yield increases with the application of zinc at low rates. Significant zinc responses were limited to soils with extractable zinc levels of less than 1 ppm. The importance of zinc deficiency in this zone had earlier been established by Agboola et al. [2]. They reported an increase in maize yield by about 33% with zinc application. In pot experiments Kang and Okoro [54] confirmed that zinc deficiency is common in rice grown on Vertisols (pH 6.7) from northeast Nigeria (Chad Basin). The importance of zinc for crop production on Vertisols in the Gezira region of the Sudan was also reported by Magar and Babikir [60]. Seed dressing seems insufficient to correct zinc deficiency in these soils [54].

The importance of zinc for production of maize grown on sands in Zimbabwe was shown by the various reports from Tanner and Grant [102, 103]. There is, however, no indication of the extent and location of the problem area. Tanner and Grant [102, 103, 104] reported that zinc can be effectively applied as zincated fertilizers either spot-placed or banded at a location lower than the maize seed.

Conclusions and recommendations

Although much of the early fieldwork on micronutrients in tropical Africa was mainly concerned with annual and perennial cash crops, during the last two decades an increasing number of investigations have been carried out with food crops.

From the published information discussed in the preceding sections of this paper, it appears that micronutrient deficiencies are generally related to parent material. Because of the generally low total and extractable levels of boron, copper, molybdenum, and zinc in the soils, deficiencies of these nutrients are rather prevalent. Boron and zinc problems are commonly observed throughout the region; copper problems are of particular importance in the Rift Valley area of Kenya, and molybdenum is a problem in the legume-growing belt of the semiarid zone of west Africa. Deficiencies of iron and manganese in tropical Africa are rare but may be of local importance. More important is the

occurrence of iron toxicity in flooded rice soils and manganese toxicity in upland soils following soil acidification resulting from fertilizer use.

As shown in Figure 2, more of the micronutrient problems are encountered in the subhumid and semiarid zones than in the humid zones. This is not unexpected, since the bush fallow system, which is still widely practiced in the humid zone, usually provides sufficient micronutrients to supply the needs of the subsistence crop. The problem is more serious in the drier areas where there is less nutrient recycling during the fallow period. However, this assessment may be somewhat biased as it appears that more research work has been conducted in the subhumid and semiarid areas.

Micronutrient problems are expected to increase in the future because of the increase in cropping intensity, the use of high-yielding varieties, and the greater use of nitrogen, phosphorus, and potassium fertilizers [26]. A greater effort should therefore be made to conduct systematic micronutrient investigations in the region, particularly in the drier areas. Research workers should be encouraged to use the recent advances in soil taxonomy by correlating the results of their investigations with the soil type used in the investigations, in order to get wider applicability of their research findings.

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6. Micronutrients and the agroecology of tropical and Mediterranean regions

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Introduction

The status of micronutrients in soils and their availability to plants are the result of a complex of factors related to parent material, soil type, and climate. Some progress has been made in understanding the effects of several individual factors on the availability of micronutrients; however, the possibility of identifying areas of potential micronutrient problems on the basis of existing information on soils and climate is still remote. Such areas, therefore, are identified through site characterization based on surveys of micronutrient deficiency symptoms, extensive micronutrient soil testing, or selective micronutrient trials.

Attempts to compile maps of areas with micronutrient deficiencies in the tropics have been virtually nonexistent. The value of such maps is, in fact, questionable since their scale would not allow delineation of actual areas of deficiency. Moreover, new information being generated would rapidly render such maps obsolete [11]. Finally, huge areas of the tropics remain entirely unexplored while existing information is heavily biased toward commercially produced, high-value crops.

As is evident from the previous chapters, making an inventory of the micronutrient problem areas in the tropics would not provide a data base large enough to allow extrapolation to regions yet unexplored. Except in India, micronutrient studies in tropical countries have been sparse, and even in India most studies have been conducted in the subtropical region in the north. In an attempt to collect a broad data base on micronutrients, FAO initiated a global study, involving 30 countries, to produce fresh information on the problems of a number of micronutrients under different soil, climatic, and cultural conditions. Twenty-four of these countries are situated partly or totally in the tropics or Near East. The results of this study appeared as FAO Soils Bulletin, No. 48 [22], and they form to a large extent the basis of this chapter.

It is tempting to assume that areas with potential for micronutrient problems can be recognized solely through information on the agroecology of

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an area, including its parent materials, soils, and climate; such information at present is available on a global scale. If the validity of this assumption could be established, it would greatly facilitate the work of research institutions, particularly in the less explored tropics and subtropics, in directing their research priorities, and it would increase the readiness of governments and industry to deal with micronutrient problems as they arise.

In this chapter we will try to show, with the help of data collected in the Global Study, what progress has been made in relating the micronutrient status of soils to agroecological conditions of the area. We also want to place the information discussed in Chapters 3–5 in a global context.

The global study

Topsoils were collected from 3538 fields cultivated in wheat or maize in 30 different countries around the world. These samples were analyzed at the Institute of Soil Science, Finland, for a host of physical and chemical characteristics including particle size distribution, CEC, pH, free carbonates, organic C, volume weight, and available macro- and micronutrients. Subsamples of these soils were also planted to wheat (Var Apu) under greenhouse conditions in Finland. Correlation studies between the content of micronutrients in wheat and selected extractable micronutrient levels were used to select the best soil test. The soil tests selected for this study and the respective correlation with pot-grown plant concentration are listed below.

Zn	DTPA	Lindsay and Norvell [14]	r = 0.732
Mn	DTPA	Lindsay and Norvell [14]	r = 0.552
Fe	AAAC-EDTA	Lakanen and Ervio [13]	r = 0.325
Cu	AAAC-EDTA	Lakanen and Ervio [13]	r = 0.664
B	Hot water	Berger and Truog [2] (modified)	r = 0.741
Mo	AO-OA	Tamm [24] (modified)	r = 0.245

Sillanpää [22] corrected the values of the extractable Mn, Cu, B, and Mo to improve the reliability of these micronutrient soil tests. The Mn and Mo tests were corrected for soil pH, the B test for CEC, and the Cu test for organic C. These corrections took the form of:

$$k(pH) = 10^{7.06 - 2.20\,pH + 0.164\,pH^2} \quad \text{for Mn}$$

$$k(pH) = 10^{-2.45 + 0.36\,pH} \quad \text{for Mo}$$

$$k(CEC) = 10^{0.466 - 0.026\,x + 0.000273\,x^2} \quad \text{for B}$$

where x = cation exchange capacity (CEC)(me/100 g)

$$k(\text{org C}) = 10^{-0.491 \log x + 0.470 (\log x)^2} \quad \text{for Cu}$$

where x = soil organic carbon (%)

which, when multiplied with the soil extraction value, provided the corrected value. Correlations with plant uptake were thus improved to 0.713, 0.731, 0.826, and 0.696 for Mn, Cu, B, and Mo, respectively.

In the Global Study, data sets of micronutrients in soils and plants were plotted on log graphs in which five zones (based equally on both the plant and soil analyses) were identified to represent very low (I), low (II), intermediate (III), high (IV), and very high (V) micronutrient status. Zones I, II, IV, and V each contain 5% of the total sample population (n = 3538), and zone III represents the remaining 80%. The demarcations between zones I, II, and III, however, are not to be considered as critical limits.

The sample population from various countries ranged from 16 (Lebanon) to as many as 298 (Turkey). Moreover, some countries were sampled only in a particular region (e.g., Brazil, India), whereas other countries were sampled throughout (e.g., Turkey, Mexico). Soil test values and micronutrient contents of plants for each country were averaged in an attempt to give a general idea of the geographic differences in the micronutrient status of soils. Figure 1 summarizes the results of the Global Study on a country basis. Regression lines were calculated for the total sample population (n = 3538) and compared with the country averages plotted in Figure 1. It should be pointed out that the country averages represent only part of the situation because there is wide internal variation within most countries. For example, 12% of data for B falls in India into zone I, 8% into II and 12% into zones IV and V, but the Indian average remains in zone III giving an impression that all B values in India are more or less normal. Therefore, the majority of the countries are grouped in the intermediate zone. Some notable exceptions are Sierra Leone for Mo and Cu, and Malta for Fe and Mn. When generally accepted critical soil test levels (Chapter 7) are applied to B and Zn, several countries can be considered dangerously low in B (e.g., Nepal, Zambia, Nigeria, Malawi, and Philippines), while low Zn levels seem typical of the semiarid countries (Iraq, Turkey, India, Pakistan, Egypt, and Lebanon). Published information on many of these countries is available to substantiate this conclusion (Chapters 3–5; [4]).

Some countries with reportedly widespread micronutrient deficiency are not identified as such in the Global Study. The Philippines, for instance, with widespread Zn deficiency problems on rice (Chapter 3), is characterized as 'high Zn' in Figure 1. This discrepancy is probably due to the random sampling scheme employed in the Global Study in arriving at the average soil test value. More detailed information regarding the various countries is obtained from the country reports [22], where data sets for individual sites are plotted. The plot for Zn in the Philippines, shown in Figure 2, reveals that over 40% of the sites (n = 194) contained less than 1 mg/l of DTPA-extractable Zn.[1] Unfortunately, the rice-growing areas of eastern Mindoro where Zn deficiency is widespread [7] were not sampled in the Global Study.

[1] As in the Global Study, all soil nutrient contents are expressed on a soil volume basis

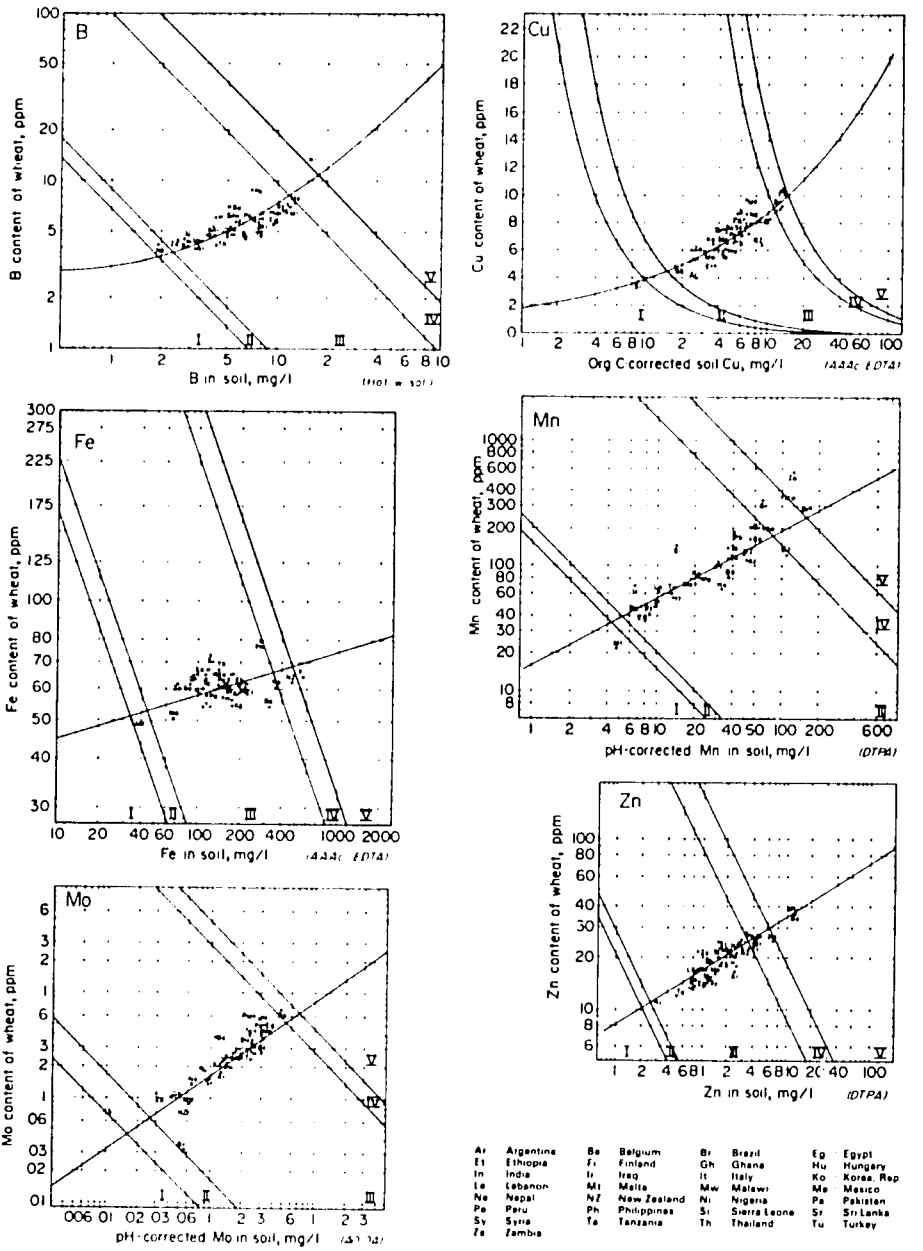

Figure 1. Regression of country-averaged micronutrient contents of pot-grown wheat (Y) on extractable soil test values (X). Global study

Climate and micronutrients

Geographically, the tropics are confined to the region between the tropics of Cancer and Capricorn. This description, however, is of little use for ecological purposes since it lacks strict climatic criteria. Various other criteria

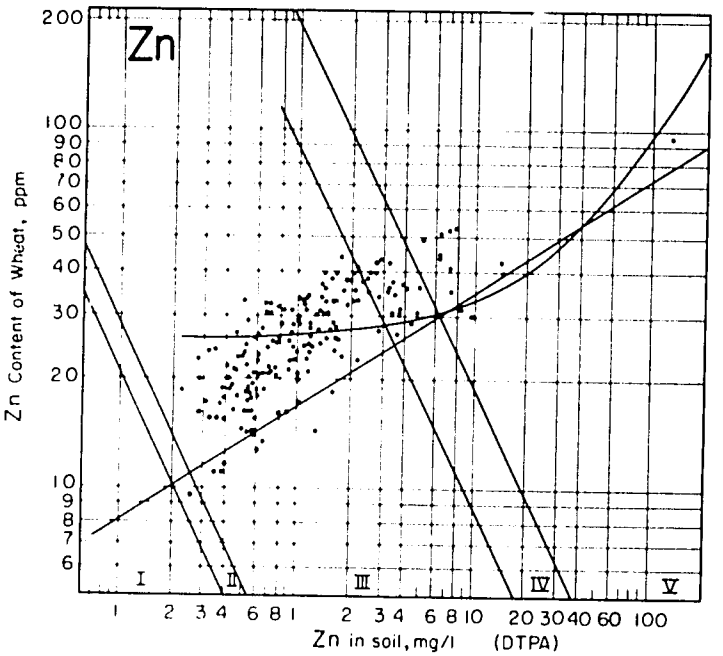

Figure 2. Regression of Zn content of pot-grown wheat (Y) on DTPA-extractable soil Zn (X), Philippines

to delimit the tropics have been proposed. Kuchler [12] defined the tropics as the area in which the temperature of the coldest month is above 18.3 °C. Tricart [27] offered a more elaborate definition: the zone free of thermal seasons and with (1) a mean monthly temperature in excess of 20 °C all year, (2) an annual mean temperature range of less than 10 °C, and (3) a daily temperature range greater than the annual range of the daily means. Yet other climatic definitions of the tropics were proposed by Koppen [9], Thornthwaite [26], Flohn [8], Paffen and Troll [17], and Papadakis [18]. The classification criteria selected by these authors generally suited the purpose for which the classification system was designed, whether for medical, biological, or socioeconomic studies.

Temperature and precipitation are the major determinants for the climatic adaptability and distribution of crops. On the basis of this premise, FAO [6] developed a climatic classification for its Agroecological Zones Project using temperature criteria dictated by the requirements of the major food-crops of the world. The tropics were defined as the region with mean monthly 'sea level-normalized temperatures' higher than 18 °C to account for the effect of latitude on temperature. The effect of altitude was taken into account by subdivision of the tropics into regions with various degrees of coldness during the growing season. This thermal delimitation of the tropics and subtropics will be adhered to in this chapter.

The moisture factor forms the basis for further subdivision of the major climatic zones. For the purpose of this study, the Tropics have been subdivided into humid, subhumid, and semiarid regions according to the number of wet months [17] the humid tropics $> 9\frac{1}{2}$ months wet; the subhumid tropics 7 $9\frac{1}{2}$ months wet; and the semiarid tropics < 7 months wet. The delimitation of the humid and subhumid tropics according to these criteria more or less coincides with the separation between the tropical rainforest and moist forest on the one hand and the semideciduous forest and moist savanna on the other hand [12]. Figure 3 summarizes the delineation of the climatic zones based on humidity, relevant to the area of study.

Figure 3. Climatic regions of the tropics and subtropics based on Paffen and Troll [17]

Data sets from selected areas of the Global Study (Tropics, Middle East, and North Africa) were grouped according to the various agroclimatic zones represented by this sample population.

Table 1 lists the mean and median values for extractable Zn and B for all sites and for the seven climatic zones of the tropics and Mediterranean regions. The number of sites sampled in each zone varies greatly (19 708), and the lowest categories, cool humid tropics (n = 19) and cool semiarid tropics (n = 61), are assumed not to be properly represented.

The mean value for extractable Zn ($\bar{Zn}$) for all sites (n = 2096) is 1.69 mg/l, but 50% of the sites contained less than 0.72 mg/l ($\tilde{Zn}$), or a mean/median ratio ($\bar{Z}/\tilde{Zn}$) of 2.35. This large difference is due to the large number of sites ($\cong$ 20%) with higher (> 2 mg/l) Zn levels. In the case of B less than 5% of the sites contained in excess of 2 mg/l B, and the $\bar{B}/\tilde{B}$ ratio was only 1.43. Excessive Zn and B levels appear more common in some climatic zones, leading to $\bar{Zn}/\tilde{Zn}$ ratios varying from 3.36 to 1.58 and $\bar{B}/\tilde{B}$ ratios between 1.1 and 1.93. Consequently, median values are considered more suitable for comparing climatic groups for susceptability to micronutrient deficiency.

Median values for extractable Zn vary from 0.43 mg/l for the Mediterranean zone to 1.85 for the cool, subhumid tropics. Figure 4 shows the

Table 1. Mean and median values of extractable Zn and B for all sites as well as various climatic zones

Climate	No.	Zn Mean (mg/l)	Zn Median (mg/l)	B Mean (mg/l)	B Median (mg/l)
All sites	2094	1.69	0.72	0.70	0.49
Mediterranean	708	0.74	0.43	1.12	0.87
Semiarid, warm	498	1.35	0.85	0.49	0.35
Semiarid, cool	61	2.79	1.08	1.45	0.75
Subhumid, warm	393	2.46	0.73	0.39	0.32
Subhumid, cool	171	3.61	1.85	0.55	0.48
Humid, warm	244	2.28	0.96	0.33	0.30
Humid, cool	19	1.29	1.05	0.61	0.36

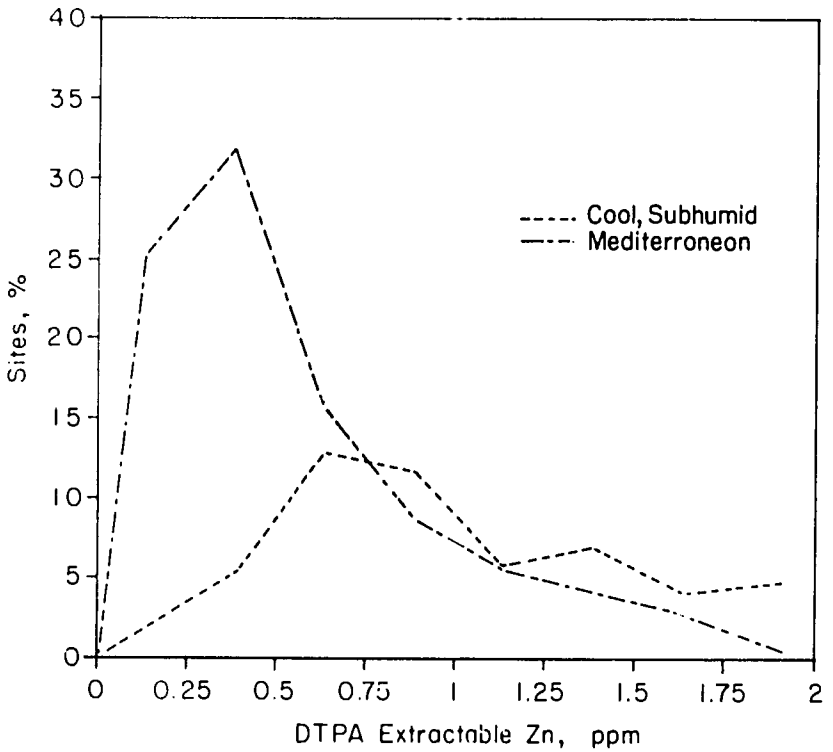

Figure 4. The percentage of cool, subhumid tropical sites, and Mediterranean sites, testing in various classes of DTPA-extractable Zn

distribution of sites (as a percentage of the various populations) that occur in different extractable zinc classes between 0 and 2 mg/l Zn, for these climatic zones. From this graph it seems reasonable to suspect a disproportionately high number of zinc deficiency cases in North Africa and the Near East and few cases in the cool subhumid region.

Results from this study are in agreement with those reported by Prasad and Pagel [19] who compared levels of Zn extractable in acid-ammonium acetate; those from humid zones were found to be 4.5 times higher, on the average, than those from arid (Mediterranean) zones. However, other factors, such as soil type and parent material, can override climatic considerations. On the basis of results in Table 1, one would not suspect major Zn problems in an area such as the Brazilian Cerrado (warm, subhumid), although this region is actually notoriously low in Zn [15].

Another example of climatic influence on available micronutrients is found in boron. The major shift in median values among climatic zones seems to be between cool and warm climates, and deficiency in boron seems to be associated with the warm (tropical) climates. The cool Mediterranean and cool tropical climates are generally well endowed with B. The humid climates are slightly lower in available B than are their drier counterparts. However, irrigation practices may confound the true climatic effects of humidity on B content in soil. Sillanpaa [22] found that soils from the traditionally irrigated Mesopotamian plains were fourfold to fivefold higher in extractable B than the soils from Northern Iraq where rainfed agriculture is predominant. Figure 5 shows the distribution of sites by class of hot water-extractable boron for the Mediterranean zone and the warm, subhumid tropics. Although more than 90% of the soils in the warm, subhumid tropics contain less than 0.75 mg/l B, this value is only 40% for the Mediterranean region.

The ability of soils from the Meditterranean region to provide B to plants was recognized by Prasad and Pagel [20] and was reflected in an average hot water-extractable B content of 0.83 ppm for that region as compared with 0.52 ppm for the warm tropics. There have been numerous reports from the tropics of boron deficiency in the field, particularly in sub-Sahara Africa and South America (see Chapters 4 and 5), whereas reports of boron deficiency from North Africa and the Near East are rare. In fact, soils of the drier region can accumulate boron in the topsoil as they accumulate salts [21].

Soils and micronutrients

Soils are formed as a result of certain processes that react on parent materials. Several of these soil-forming processes are related to ecological factors, such as climate, topography, and vegetation. The abundance of micronutrients in various rocks may vary in their orders of magnitude, depending on their origin. Krauskopf [10] summarized some published data, which are presented in Table 2. The range in micronutrient abundance in soils is somewhat similar to that in rocks, although soil-forming processes generally cause soils to be enriched or depleted with respect to the parent rock. Soil classification systems have taken these ecological factors into consideration to different extents. The U.S.S.R. classification system is largely based on information

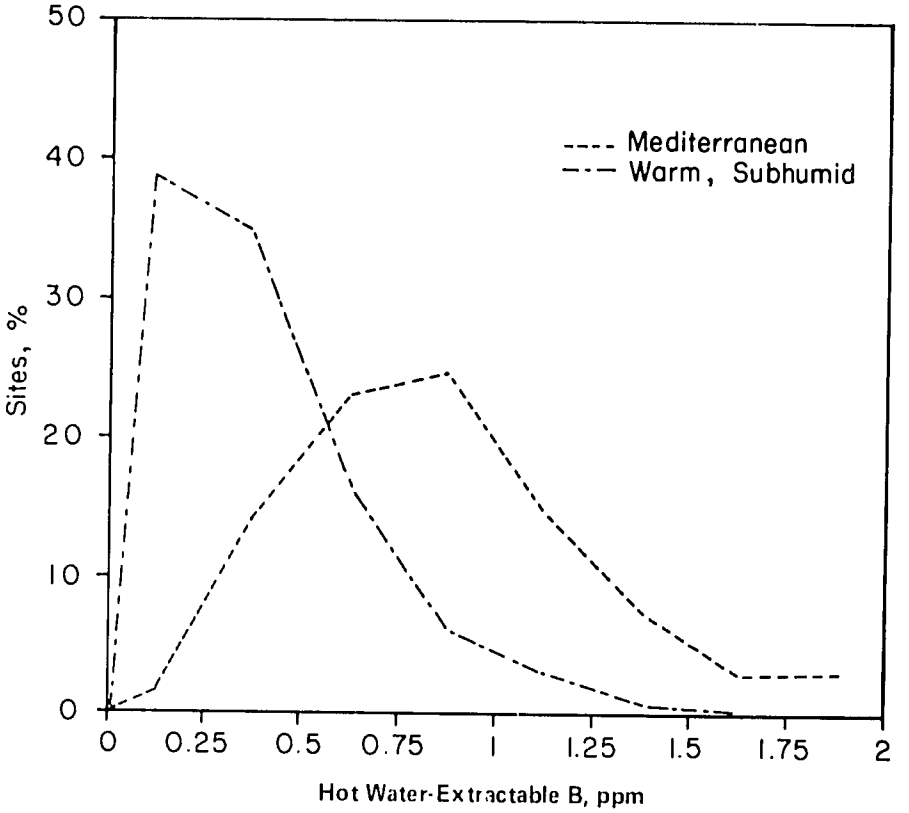

Figure 5. The percentage of sites in the Mediterranean and warm, subhumid tropical climates, testing in various classes of hot water-extractable B

concerning soil genetics and incorporates such information at relatively high levels of the classification system. The USDA classification is largely morphometric and incorporates ecological information at the subgroup and family level. The legend of the Soil Map of the World [5] takes an intermediate approach.

In an effort to relate the micronutrient status to an ecological parameter, Sillanpaa [22] used the UNESCO/FAO soil classification to group the sites across the entire sample population. Only 2265 of the 3538 sites sampled were properly classified by the collaborators. The data sets, averaged for soil groups, are plotted in Figure 6. The plots show a great deal of clustering in the intermediate zone (III), particularly for Cu, B, and Fe. Data set averages for soil groups never fall in the very low (I) and low (II) zones, a fact which reflects poor segregation among soil groups.

The best segregations are obtained with Mo, Mn, and Zn. For Mo and Mn, segregation is largely the result of including pH in the soil test, which forces the separation of inherently acid and alkaline soil groups, e.g., Halosols versus

Table 2. Abundances of micronutrient elements[a]

Element	Crust (ppm)	Igneous rocks		Sedimentary rocks			
		Granite (ppm)	Basalt (ppm)	Limestone (ppm)	Sandstone (ppm)	Shale (ppm)	Soils (ppm)
Fe	56 000	27 000	86000	3800	9800	47 000	10 000–100 000
Mn	950	400	1500	1100	10–100	850	20–3000
Cu	55	10	100	4	30	45	10–80
Zn	70	40	100	20	16	95	10–300
Mo	1.5	2	1	0.4	0.2	2.6	0.2–10
B	10	15	5	20	35	100	7–80

[a]Sources of data: For crust and igneous rocks, Taylor [25]. For sedimentary rocks, Turekian and Wedepohl [28]. For soils, compilation from many sources

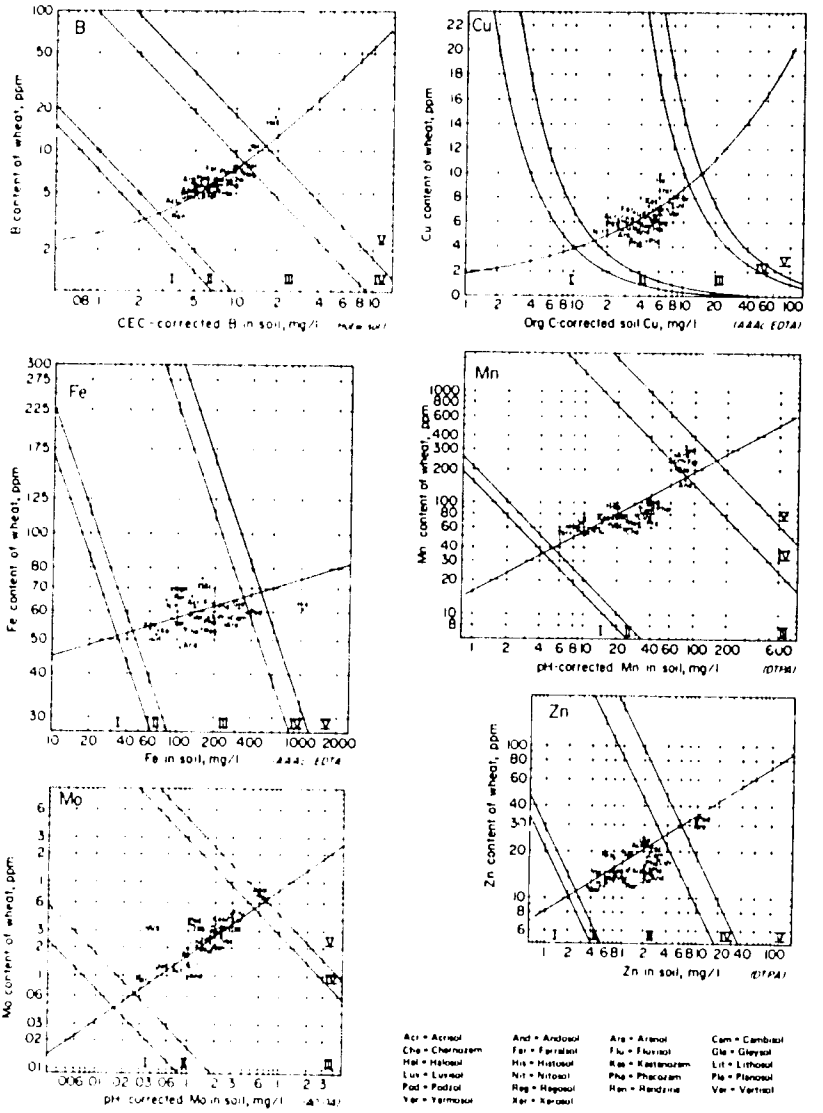

Figure 6. Regression of soil group-averaged micronutrient contents of pot-grown wheat (Y) on extractable soil test values (X). Global study

Ferralsols. This effect is demonstrated in Table 3 where uncorrected mean and median Mo levels in soils show little difference between those soil groups. Corrected soil Mo levels show a nearly 10-fold difference between Halosols and Ferralsols, due entirely to the correction factor k (pH). As a result, Halosols and Ferralsols appear at opposite extremes of the Mo plot in Figure 6. This distribution is similar to that of the original segregation found in plant values. Inclusion of pH in the Mo soil test (extraction by ammonium

Table 3. Effect of pH on Mo soil test value (mg/l)

	Halosols		Ferralsols	
	Mean	Median	Mean	Median
Uncorrected Mo	0.15	0.13	0.13	0.09
Corrected Mo	0.36	0.28	0.04	0.02
k (pH)	2.33	2.29	0.31	0.23

Note: Corrected Mo = k (pH) × uncorrected Mo.

oxalate-oxalic acid) is a necessity because pH is a dominating regulator of Mo availability to plants; the chemical extraction method, however, fails to properly reflect this effect of pH.

The data presented in Figure 6 show that soils of the arid and semiarid region (Halosols, Yermosols, Xerosols) are the least susceptible to B and Mo deficiencies; they are most susceptible to Zn and Mn deficiencies. Together with Vertisols, Kastanozems, Lithosols, and Histosols these soil groups contain less than 1 mg/l DTPA-extractable Zn on the average. Low B (< 0.5 mg/l) soil groups are Acrisols, Rendzinas, Gleysols, Andosols, and Arenosols. However, these data should be interpreted with caution because the sample population of several soil groups is extremely small (e.g., Andosols, Histosols, and Planosols).

As was the case with country averages, the use of soil group averages does not provide information regarding the probability of micronutrient deficiencies in a particular soil group. This information is obtained more readily from the frequency distribution of soil test values within a soil group. To further demonstrate soil group differences in extractable B, frequency distributions for this element for two contrasting soil groups (Ferralsols and Fluvisols) are depicted in Figure 7 using sites located in the tropics, North Africa, and the Middle East (n = 2096). The median value for all sites was 0.49 mg/l B, and the mean value was 0.70. As many as 50% of the Ferralsols contain less than 0.34 mg/l hot water extractable B, and approximately 90% less than 0.5 mg/l. In contrast, the median B level for Fluvisols is 0.84 mg/l, and only 30% contain less than 0.5 mg/l B. Similarly, in the case of Zn, the median of the total sample (n = 2096) from these tropical and subtropical countries is 0.72, with a mean of 1.69 mg/l Zn, which reflects the inclusion of some high Zn (polluted) sites. The median level of extractable Zn for Ferralsols was 0.79 mg/l (near average), whereas for Halosols the average was 0.20 mg/l Zn.

Information regarding Zn and B derived from the soil group analysis of the Global Study is generally consistent with reported field observations (Chapters 3–5). For instance, the light-textured soils of sub-Sahara Africa (derived from Voltaic sandstone) and the Andosols of Colombia are reportedly low in B. Zn problems have frequently been reported in soils with pH values of 7.5 or higher. Thus, in the case of some well-defined soil groups, general conclusions can be drawn regarding their micronutrient status. A

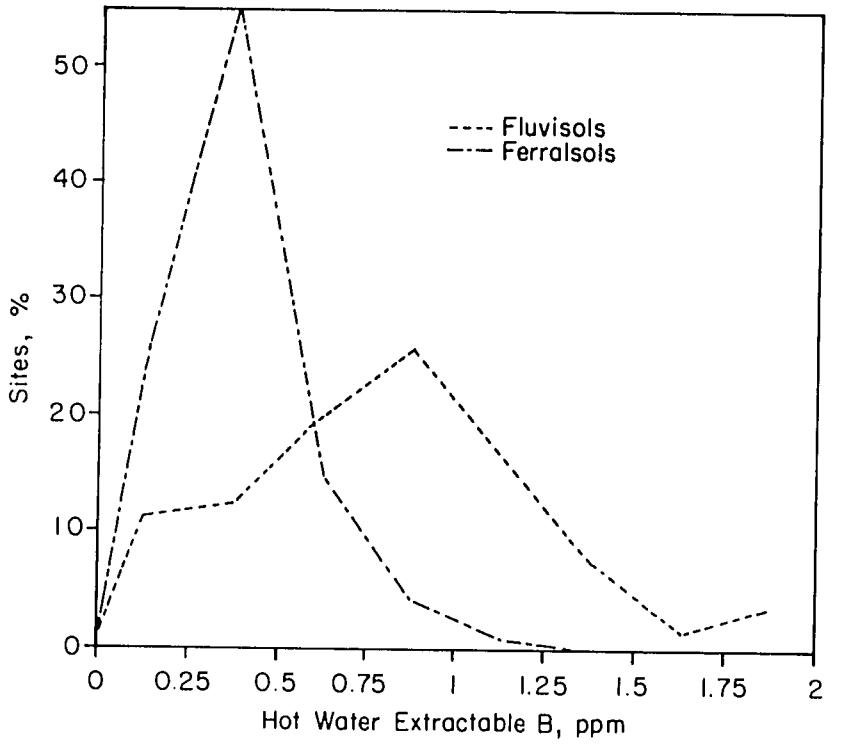

Figure 7. The percentage of Ferralsols and Fluvisols from the tropics, North Africa and Middle East testing in various classes of hot water-extractable B.

systematic research effort, testing various classification systems to verify their usefulness in delineating micronutrient problem areas, seems warranted.

Conclusions and recommendations

Micronutrients in agriculture have only gradually gained the recognition they deserve. Over 120 years ago iron was identified by Sachs as essential for plant growth. Subsequently, Mn [3], Zn and B [16], Cu [23], and Mo [1] were added to this list. The difficulty of firmly establishing the essentiality of these nutrients is reflected in their group name – micronutrients – which indicates that the requirements of these nutrients for healthy growth are extremely low.

Over 400 references were reviewed for the preceding chapters on deficiencies of micronutrients in the tropics. The most prominent areas with documented micronutrient deficiencies are shown in Table 4. However, some large areas in the tropics have hardly been studied: the Amazon basin and the Llanos in Latin America, the Congo basin in Africa, and the Indo-Chinese Peninsula in Asia. In general, these areas have only limited agricultural importance, but they may have great productive potential.

Table 4. Major areas with micronutrient deficiencies in the tropics

Continent	Country	Deficient Micronutrient	Physiography	Geology	Major crop
Latin America	Colombia	Boron	Andes mountain	Volcanic deposits	Beans/cereals
	Brazil	Zinc	Brazilian shield	Granite and gneiss	Cereals
Africa	Nigeria/Zambia	Boron	African plateau	Voltaic sandstone	Cotton
	Chad/Nigeria	Zinc	Chad basin	Sedimentary deposits	Cereals
	Kenya/Zimbabwe	Copper	Rift valley	Volcanic deposits	Wheat
Asia	India	Zinc (iron)	Indian shield	Granite and gneiss	Rice
	Malaysia/Indonesia	Copper	Coastal plains	Peat	Rice/palm
	Philippines	Zinc	Complex-volcanic	Wetlands	Rice

The study of micronutrient deficiency problems has rarely been approached in a systematic fashion, particularly in the tropics. The information brought together in Chapters 3–5, although fairly comprehensive, rarely permits the reader to draw conclusions that can be transferred to regions of similar agroecology. In many studies relevant information regarding parent material, soil, and climate is not provided or is incomplete. Moreover, cross-referencing of information is hampered by lack of uniformity in methodology, including treatment of such factors as crop type, genetic material, and experimental design, as well as soil test procedures and analytical methods.

One of the major problems in assessing the micronutrient situation in tropical and subtropical crop production is the diversity in soil testing procedures. As many as 15 different extraction techniques are presently in use (see Chapter 7). Within a continent, and even within a country, researchers often select soil test methods on the basis of analytical tools and/or personal preference, sometimes based on recommendations by specialists from abroad. Lack of proper calibration of these soil tests within the region makes for difficulty in interpreting the data. Moreover, cross-referencing of information based on different soil tests is impossible. Worldwide coordination appears to be needed in establishing unified methodologies for soil testing.

The Global Study represents the first effort in assessing problems with micronutrients on such a large scale [22]. Thirty countries collaborated in the effort with samples submitted from over 3500 sites. Since site selection was left to the collaborating scientists, however, there were great differences in the sampling approach. Some countries submitted samples from a wide range of agroecological zones, whereas others restricted their samples to the region most accessible to them.

Samples collected in the Global Study were all analyzed in the laboratory of the Institute of Soil Science, Finland, to assure uniformity in soil testing procedures. Similarly, samples of wheat grown on these soils in the greenhouse in Finland were analyzed in this laboratory. Thus, results from different countries could be compared with confidence. A limited number of soil extractants were tested in this study. DTPA (for Zn, Mn), AAAC-EDTA (for Fe, Cu), hot water (for B), and AO-OA (for Mo) were eventually selected as providing the best correlations with plant-available micronutrients. However, correction factors involving soil pH were required to obtain satisfactory correlations for Mo and Mn, while correlations for Cu and B were significantly improved by including a factor for organic C and CEC, respectively. The poor performance of the soil test alone in the case of Mo and Mn indicates the need for the development and testing of better soil test methods for these elements. The samples collected in the Global Study (or a subsample thereof) provide a unique opportunity for attaining this end.

Country-averaged soil test values provided limited insight into the geographical distribution of micronutrient problems in the tropics and subtropics. Some countries appeared exceptionally low in B, and low Zn status

seemed common in subtropical countries. For a national program to set priorities for research, the individual country reports that make up of the Global Study are more helpful. If combined with the indigenous knowledge of the environment from which the samples were taken, the country reports may identify regions within the country where additional research seems warranted.

The use of climatic criteria to differentiate among sites was only slightly more successful than the use of soil tests. The Mediterranean region with low (winter) rainfall was properly identified as low Zn; low B seemed typical for warm climates aggravated by high humidity. Although useful as an indicator of broad areas where deficiency problems are likely, climate does not take into consideration any of the other soil-forming and ecological factors that determine the availability of micronutrients to plants.

To assess the likelihood of identifying agroecological regions deficient in micronutrients, the Global Study requested that soils be classified according to the FAO/UNESCO legend at the soil group level. Unfortunately, only two-thirds of the soils were so classified. Soil group averages were calculated from widely different sample populations, ranging from 7 to 470. Soil group averages for soil test values provided an inconclusive picture, except for soils with widely different characteristics, e.g., Halosols versus Ferralsols. More information was obtained by comparing soil group frequency distributions for soil tests, which show distinctly different patterns for some selected soil groups. Apparently, a limited number of sites with excessively high levels of extractable micronutrients may cause strong bias in the mean value for that soil group. Consequently, it appears that median values may provide a better basis for soil group comparison.

The lack of segregation among most soil groups in the Global Study may be due to inaccurate classification and poor representation in several soil groups. The potential value of identifying soil types susceptible to micronutrient deficiency was demonstrated in some cases, such as with Ferralsols, susceptible to B deficiency, and Halosols, susceptible to Zn deficiency. Further research in this area, using various classification systems at various levels, may eventually provide the necessary guidance for compiling soil maps.

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7. Micronutrient soil testing for the tropics

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[1] Joint contribution from the Colorado Agricultural Experiment Station at Fort Collins and the North Carolina Agricultural Research Service at Raleigh. Scientific Paper No. 2901

Introduction

The purpose of soil testing is to determine which nutrients are deficient in a given field and, if possible, to estimate how much fertilizer is needed. Soil testing for micronutrients is particularly difficult because plant requirements for these elements are relatively low and even slight contamination of a sample or modification of a procedure may seriously affect soil test results.

The following micronutrient soil tests are considered in this chapter: iron, manganese, zinc, copper, boron, and molybdenum. Although chlorine is an essential micronutrient, its deficiency is so rare that soil testing is not necessary. Emphasis in this chapter will be placed on micronutrient testing for soils in the tropics in so far as this is possible. A survey is included of the soil test methods and the critical nutrient levels currently being used for several major crops in the tropics.

There are no unique problems associated with the use of soil tests for tropical soils. Many of the soil tests in use today, however, were developed for soils of the temperate region. In many cases such tests have not been fully evaluated for soils of the tropics. Because the age of parent material, temperature, and rainfall may vary more in tropical than in temperate regions, nutrient reserves also may be more variable. If micronutrient reserves are more highly depleted, a higher percentage of them may be tied up in biomass.

It is difficult to devise a soil test that will assess during a few minutes of extraction in the laboratory the amount of nutrient that becomes available over an entire growing season in the field. Ideally, a soil test should extract nutrients from the same labile pool that the plants do. Although it is not necessary for a soil test to extract exactly the same quantity of nutrient as the plant does, the amount extracted must be meaningfully related to the amount taken up by plants. A useful soil test should identify as nearly as possible the critical level of an extractable nutrient below which plants will be deficient and above which no deficiency occurs. Soil tests should also provide some guide as to how much fertilizer is needed to correct a given deficiency. In addition, soil tests should help to detect toxic or potentially toxic levels of micronutrients that might occur.

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A soil test should be inexpensive, reproducible in different laboratories, and easily adaptable to routine laboratory procedures. If an extractant can be used for more than one nutrient, it has a decided advantage.

Chemical basis for soil testing

Intensity and capacity factors

Most soil tests consist of shaking a sample of soil with an extracting solution for a specified period of time. The suspension is then filtered and the quantity of nutrient that comes into solution is measured. Both the intensity and capacity factors affect nutrient availability to plants, and these same factors must be reflected in a successful soil test. The concentration of nutrient maintained in the soil solution represents the intensity factor, while the quantity of nutrient that can readily come into solution to replace that removed is a measure of the capacity factor. An extractant that dissolves either too much or too little nutrient is not an ideal extractant.

The concentrations of micronutrients in the soil solution are very low and often below analytical detection limits. Exchangeable cations and anions in soils constitute a ready reserve (capacity factor) of available plant nutrients. Many soil tests contain salts that displace exchangeable ions and bring them into solution during the extraction process. In the case of micronutrients, however, their levels in the soil solution are generally very low, and the amounts held on exchange sites are also very low. For this reason, most micronutrient extractants contain either acid, base, complexing agents, or chelating agents that also dissolve some of the labile solids. Such extractants provide a more useful measure of the capacity of a soil to supply micronutrients than do solutions with ion exchange properties only.

Most soil test extractants remain in contact with the soil for only a few minutes, whereas plants' roots in the field are in contact with the soil for an entire growing season. Laboratory attempts to simulate actual conditions that may change during the growing season are extremely difficult to duplicate in the laboratory. Ultimately soil test extractants must be shown to be effective in identifying micronutrient responses in the field.

Acid or base extractions

Soil test extractants often make use of acids or bases to partially dissolve the more labile solids. Dilute acids have been widely used on acid soils, while bases such as carbonates and bicarbonates are often used for alkaline soils.

Concentrated acids or bases generally are too severe and remove nutrients from soils that normally are not available to growing plants. For these reasons, dilute acids are generally more successful as soil test extractants. Dilute acids generally are more successful on kaolinitic soils than on young soils where abundant bases are still present. It is anticipated that, in order to provide a measure of the soil's capacity to supply nutrients, kaolinitic soils

may require slightly stronger acids than would be required on soils with a good supply of primary minerals.

Chelating and complexing agents

Chelating and complexing agents have been widely used as extractants for assessing the availability of micronutrient cations. Extracting solutions have been carefully selected to simulate rather closely the chemical environment of absorbing plant roots in neutral and calcareous soils [17]. The use of such extractants should be successful on similar soils in the tropics. In kaolinitic soils of lower pH, however, the advantage of such extractants may be nullified. Perhaps a more severe extractant buffered at a lower pH, designed to simulate the chemical environment of plants growing in more acid soils, would be more successful. Most of the extractants used on acid soils have been dilute acids and the inclusion of complexes has not been particularly beneficial. There is need for further research on soil test methods that better simulate the chemical and nutritional environments of acid soils.

The ability of chelates to extract micronutrients from submerged soils is often modified by redox relationships. Time of sampling may be of utmost importance since redox relationships change considerably during submergence compared to the more oxidized conditions of drained paddy fields. Thus, critical levels of certain nutrients may change with time of sampling. It is unlikely that a soil test designed for oxidized conditions will also be equally effective when the soils are reduced.

Simultaneous extractions

Lakanen and Ervio [14] compared eight different extractants for the determination of plant-available micronutrients. They concluded that the acid ammonium acetate-EDTA (ethylenediamine tetraacetic acid) procedure could be used for macronutrients (potassium, calcium, magnesium, phosphorus); micronutrients (iron, manganese, zinc, copper, and molybdenum); and for cobalt. They pointed out that compromises were necessary since single micronutrient extractants may be better for a given micronutrient.

Lindsay and Norvell [16, 17] developed the DTPA (diethylenetriaminepentaacetic acid) micronutrient soil test for simultaneous extraction of zinc, iron, manganese, and copper. In their development they emphasized the simulation of the chemical environments expected in neutral and calcareous soils. The extraction procedure may not be as effective in highly weathered acid soils.

Soltanpour and Schwab [38] combined the DTPA soil test with the bicarbonate soil test for phosphorus into what they term the ammonium bicarbonate DTPA (AB-DTPA) soil test. They later recommended deletion of carbon black [39] and adapted their method of rapid analysis using inductively coupled plasma (ICP) spectrophotometry [40]. Havlin and Soltanpour [11] examined 40 soils and showed the AB-DTPA soil test to be about as

effective in separating zinc- and iron-deficient soils as the DTPA method. They have also examined grinding variables as they affect the extraction of micronutrients [37]. In addition to the four micronutrient cations, the AB-DTPA method is also used routinely for assessing available phosphorus and potassium. Again, the AB-DTPA soil test may not be an ideal soil test for acid soils in the tropics because it was developed to simulate the chemical environments of alkaline soils.

A bicarbonate plus EDTA method has been in use for some time in a number of Latin American countries. The extraction of phosphorus with bicarbonate is used over a broader range of soil conditions in the tropics than in the temperate region. Dilute acids, especially the double acid or Mehlich I extractant, have been used extensively for multinutrient analysis. As with many other extractants, the soil pH should be considered in the interpretation for several of the micronutrients.

Importance of physical factors

Soil test results are no more reliable than the soil samples on which the test is made. For this reason, a soil sample must be representative of the field for which the soil test results are to be used. Needless to say, it is imperative that sound soil sampling procedures be adopted and followed consistently.

Samples collected from the field must be properly handled or changes may occur that would seriously affect the level of extractable nutrients. If care is not taken, critical levels have no meaning. Of particular importance in the tropics are the wider ranges in temperature, moisture, and age of parent material. These factors affect microbiological activity, but how they affect micronutrient extractability is not well understood.

Lindsay and Norvell [17] showed that increasing the soil temperature from 15°C to 35°C during extraction of soils by DTPA greatly increased extractable zinc, iron, manganese, and copper. Drastic changes in soil temperature must be avoided during extraction if critical soil test levels are to be comparable.

Soltanpour et al. [36] and [37] showed that the force of grinding, type of extracting vessel, type of shaker, speed of shaking, time of shaking, soil-to-solution ration, and other factors affect micronutrient extraction. Their results clearly demonstrate the importance of standardizing methods of preparation and extraction of soils used for the DTPA micronutrient soil test. Detailed standardized methods should be developed for all routine procedures.

Combs and Dowdy [5] studied the effects of soil-to-solution ratio and time of extraction on DTPA-extractable copper and zinc from dredged materials. They concluded that the best estimates of plant-available copper and zinc occurred when the sediments were equilibrated for 24 hours in 1 : 10 soil : solution suspensions.

Leggett and Argyle [15] studied the effects of drying temperature on the micronutrients released. Generally DTPA-extractable zinc, iron, manganese, and copper all increased as the temperature was increased from 22 °C to 100 °C during drying, but the various elements were affected slightly differently. These findings again confirm the fact that sample preparation must be standardized if critical levels are to be useful.

Shuman [30] studied the effects of temperature and moisture conditions on DTPA-extractable micronutrient concentrations. He found that varying the temperature and moisture conditions caused significant changes in the extractability of manganese, iron, copper, and zinc. His studies stressed the importance of correctly handling samples intended for micronutrient analysis. In particular, his findings showed that soil moisture content, especially waterlogging prior to air drying, may influence extractable levels of soil micronutrients. These findings signal a warning in using the same micronutrient soil test for paddy soils as for well-drained soils unless the tests have been critically examined for both types of soils.

Tiller et al. [42] incubated soils under different conditions to simulate flooding and then extracted them with DTPA. Good correlations between the amount of zinc extracted from the simulated flooded soils and zinc uptake by rice from flooded soils in pots suggest that this approach to soil testing may be more useful for paddy soils than are existing tests on air-dried soils.

Severson et al. [28] examined the effect of different degrees of disaggregation, grinding, and sieving during sample preparation on the DTPA-extractable micronutrient as well as other trace elements. They found that both grinding and sieving increased the concentration of iron, manganese, and zinc in the extract by a factor of 2 to 4, but had little effect on copper. Sieving alone, however, increased copper concentration by 2 to 3 times that in the disaggregated soil. The importance of sample preparation is again emphasized.

Survey of micronutrient soil tests being used in the tropics

An important aspect of understanding soil testing in the tropics is to recognize which soil tests are being used. To obtain this information, a questionnaire was prepared and sent to several of the major micronutrient soil testing laboratories of the tropics. The results of this survey are summarized for each micronutrient in Tables 1–6.

Iron

Soil test extractants for iron used by tropical laboratories surveyed in this study are summarized in Table 1. Extractants for available iron include various concentrations and combinations of DTPA, NH_4OAc, HCl, $NaHCO_3$,

Table 1. Soil tests for iron being used by various tropical laboratories

Continent	Country	Source	Extractant	Soil/extr.	Shaking time	Critical level	Crop recommendation	Soil property limitations
Africa	Malawi	Chickonda	DTPA	1/2 (w/v)	2 hours	2.6 ppm	–	O.M.
Africa	Botswana	Stewart-Jones	$NH_4C_2H_3O_2$, 3 *M* + $C_2H_4O_2$, pH 4.7; or NH_4EDTA, 0.08 *N*, pH 4.0	2/5 (w/v)	30 minutes	–	–	Wide range
Africa	Botswana	Stewart-Jones	DTPA	1/2 (w/v)	2 hours	–	–	Calcareous soils
Africa	Kenya	Qureshi	HCl, 0.1 *N*	1/5 (w/v)	60 minutes	10 ppm	Foliar spray	–
Africa	Netherlands	van der Pol	DTPA	1/2 (w/v)	2 hours	4.5 ppm	–	–
Americas	Bolivia	Angulo	$NaHCO_3$, 0.5 *M*, + EDTA, 0.01 *M*, + Superfloc 127, pH 8.5	1/10 (w/v)	10 minutes	10 ppm	–	–
Americas	Mexico	Moncada	$NH_4C_2H_3O_2$, pH 4.8	1/4 (w/v)	30 minutes	0.4 ppm	Rice; 2.5 ton $CaSO_4$/ha	Very high pH (8.8)
Americas	Mexico	Cajuste	DTPA	1/2 (w/v)	2 hours	Toxic at > 20 ppm double acid	Maize	pH < 6, OM < 0.8%
Americas	Peru	Villagarcia	$NH_4C_2H_3O_2$, 1 *N*	1/10	30 minutes	–	–	–
Americas	Peru	Neyra	$NH_4C_2H_3O_2$, 1 *N*	1/10	30 minutes	–	–	–
Americas	Costa Rica	Ramirez	$NaHCO_3$, 0.5 *N* + EDTA, 0.01 *M*, + Superfloc, 25 ppm	1/10	15 minutes	10 ppm	–	–
Americas	Dominican Republic	Perez	$NaHCO_3$, 0.5 *N* + EDTA, 0.01 *M*, + Superfloc, 50 ppm	1/10 (v/v)	10 minutes	16 μg/ml	All crops	–
Americas	Chile	Subercaseaux	$NH_4C_2H_3O_2$, 1 *N*, pH 4.8	1/4 (w/v)	30 minutes	–	–	–
Americas	Jamaica	Thompson	HCl, 0.1 *N*	1/10	Shake once each 15 minutes for 1 hour	0.3–0.5 ppm	Corn, vegetables, root crops; 22–600 lb/acre	High pH, soil depth, moisture content

Americas	Guyana	Granger	$NaHCO_3$, 0.25 *N*, + EDTA, 0.01 *M*, + NH_4F, 0.01 *N*	1/10 (v/v)	10 minutes	–	–	–
Americas	Nicaragua	Quintana	$NaHCO_3$, 0.5 *N*, + EDTA, 0.01 *M* + Superfloc, 50 ppm	1/10 (v/v)	10 minutes	–	–	–
Americas	Colombia	Lora	$NaHCO_3$, 0.5 *N*, + EDTA, 0.01 *M*, pH 8.5	1/10 (v/v)	10 minutes	10 μg/ml	General	–
Americas	United States	Hunter	$NaHCO_3$, 0.25 *N*, + EDTA, 0.01 *M*, + NH_4F, 0.01 *N*, + Superfloc 127, 50 ppm	1/10 (v/v)	10 minutes	30 μg/ml	By crop	Texture, OM, CEC, ratios
Asia	Pakistan	Soomro	DTPA	1/2 (w/v)	2 hours	–	–	High pH, calcareous
Asia	Thailand	Kurmarohita	DTPA	1/2 (w/v)	2 hours	10 ppm	Foliar, 0.5% $FeSO_4 \cdot 7 H_2O$	–
Asia	Malaysia	Law	Na citrate/$NaHCO_3$/ Na dithizonate at 75 °C	1/40/5/1	15 minutes	–	–	–
Asia	Thailand	Lian	HCl, 0.1 *N*	1/10 (w/v)	5 minutes	–	Peanuts: 100 kg $FeSO_4$ or 10 ton compost/ ha	–
Asia	Hawaii	Bosshart	$NH_4C_2H_3O_2$, 1 *N*,	1/20 (w/w)	1.5 hours	–	–	–
Australia	Australia	Price	DTPA	1/10 (w/v)	30 minutes	–	Pastures	Deficiency rare on low pH soils
Australia	Australia	Price	DTPA	1/10 (w/v)	30 minutes	2 ppm	Wheat: 0.5% $FeSO_4$ spray at 3–5 weeks	–
Australia	Australia	Price	DTPA	1/10 (w/v)	30 minutes	Toxic at > 50 ppm	–	pH < 5.0–5.5

EDTA, Superfloc 127,[1] NH_4F, Na-Citrate, and Na-Dithionate. The ratio of soil to extractant varied from 1:2 to 1:40, and the time of extraction varied from 10 minutes to 2 hours. The critical levels of iron suggested for several crops varied from 0.3 to 10.0 ppm.

In most cases iron deficiency is restricted mainly to soils of high pH. There is no way to tell from the compiled data the reliability of various procedures for detecting iron-deficient soils. Independent studies are necessary to evaluate the effectiveness of the various methods and the reliability of the critical levels being used.

Manganese

The soil test extractions for manganese in this survey include various concentrations and combinations of DTPA, NH_4OAc, EDTA, HCl, $NaHCO_3$, H_2SO_4, Superfloc 127, water, and NH_4F (Table 2). The ratio of soil to extractant varied from 1:2 to 1:20, and shaking time varied from 5 minutes to 2 hours. The critical levels of manganese used to distinguish deficient from nondeficient soils varied widely from 1 to 28 ppm for the various extractants and crops.

Zinc

Soil test extractants for zinc used by the tropical laboratories include various concentrations and combinations of DTPA, EDTA, HCl, $NaHCO_3$, Superfloc 127, KCl, H_2SO_4, NH_4OAc, NH_4F, and dithizone (Table 3). The soil-to-extractant ratios varied from 1:1 to 1:20, while the shaking time varied from 5 minutes to 3 hours. Critical levels ranged from 0.5 to 10.0 ppm for extractable zinc.

Copper

Soil test extractants for copper include various concentrations and combinations of DTPA, EDTA, HCl, $NaHCO_3$, Superfloc 127, NH_4OAc, and NH_4F (Table 4). The ratios of soil to extractant varied from 1:1 to 1:20, and shaking time varied from 5 minutes to 2 hours. The critical levels for copper varied from 0.2 to 10.0 ppm.

Boron

Soil test extractants for boron include various concentrations and combinations of $Ca(H_2PO_4)_2 \cdot H_2O$, hot water, boiling water, saturation extract, H_2SO_4, HF, and HCl (Table 5). Soil-to-solution ratios varied from 1:1 to 1:2, while the shaking time varied from 5 minutes to 16 hours. The critical levels varied from 0.2 to 2.0 ppm of extractable boron.

[1] 'Superfloc 127' is an organic flocculating agent to assist in filtration of high pH extracts. It is a nonionic, very high-molecular-weight polyacrylamide. The term is a trademark of American Cyanamid Company.

Table 2. Soil tests for manganese being used by tropical laboratories

Continent	Country	Source	Extractant	Soil/extr.	Shaking time	Critical level	Crop recommendation	Soil property limitations
Africa	Malawi	Chickonda	DTPA	1/2 (w/v)	2 hours	1.0 ppm	–	pH, O.M.
Africa	Botswana	Stewart-Jones	$NH_4C_2H_3O_2$, 3 *M* + $C_2H_4O_2$, pH 4.7; or NH_4EDTA, 0.08 *N*, pH 4.0	1/10 (w/v)	16 hours standing + 45 minutes shaking	–	–	
Africa	Botswana	Stewart-Jones	DTPA	1/2 (w/v)	2 hours	–	–	Calcareous soils
Africa	Kenya	Quershi	HCl, 0.1 *N*	1/5 (w/v)	60 minutes	20 ppm	Foliar spary	–
Africa	Netherlands	van der Pol	DTPA	1/2 (w/v)	2 hours	1.0 ppm	–	–
Americas	Bolivia	Angulo	$NaHCO_3$, 0.5 *M*, + EDTA, 0.01 *M*	1/10 (w/v)	10 minutes	5 ppm	–	pH > 6.5
Americas	Mexico	Moncada	NH_4Ac, pH 7.0	1/20 (w/v)	1 hour	–	–	–
Americas	Mexico	Cajuste	DTPA	1/2 (w/v)	2 hours	Toxic at > 5 ppm	Maize	Sandy loams
Americas	Peru	Villagarcia	H_2SO_4, 0.1 *N*	1/5	60 minutes	–	0.3% $MnSO_4$	–
Americas	Peru	Olazabel	$NaHCO_3$, 0.5 *N*, + EDTA, 0.01 *M*	1/4.4	15 minutes	Low = 1 – 2 ppm	Foliar on vegetables, cereals, tubers, etc., not exceeding 1 – 2 kg/ha	Alkaline pH, high Ca, Zn, Cu, Fe
Americas	Peru	Neyra	H_2SO_4, 0.1 *N*	1/5	60 minutes	–	Citrus, 0.3% $MnSO_4$	–
Americas	Costa Rica	Ramirez	$NaHCO_3$, 0.5 *N* + EDTA, 0.01 *M*, + Superfloc, 25 ppm	1/10	15 minutes	5 ppm	–	–
Americas	Cuba	Muniz	H_2SO_4	1/10	1 hour	28 ppm	–	–
Americas	Dominican Republic	Perez	$NaHCO_3$, 0.5 *N* + EDTA, 0.01 *M*, + Superfloc, 50 ppm	1/10 (v/v)	10 minutes	5 μg/ml	All crops	$CaCO_3$, salts
Americas	Chile	Subercaseaux	Water	1/10 (w/v)	30 minutes	–	–	–

Table 2 (*continued*)

Continent	Country	Source	Extractant	Soil/extr.	Shaking time	Critical level	Crop recommendation	Soil property limitations
Americas	Chile	Subercaseaux	NH_4C_2H [illegible]$_2$, 1 *N*, pH 7.0	1/10 (w/v)	30 minutes	–	–	–
Americas	Jamaica	Thompson	HCl, 0.1 *N*	1/10	Shake once each 15 minutes for 1 hour	1–4 ppm	Sugarcane, coconut, banana, vegetables: 30–60 lb/acre	Soil depth, water holding capacity, high pH
Americas	Guyana	Granger	$NaHCO_3$, 0.25 *N*, + EDTA, 0.01 *M*, + NH_4F, 0.01 *N*	1/10 (v/v)	10 minutes	5 μg/ml	–	–
Americas	Nicaragua	Quintana	$NaHCO_3$, 0.5 *N*, + EDTA, 0.01 *M*, + Superfloc, 50 ppm	1/10 (v/v)	10 minutes	5 μg/ml	–	–
Americas	Colombia	Lora	$NaHCO_3$, 0.5 *N*, + EDTA, 0.01 *M*, pH 8.5	1/10 (w/v)	10 minutes	5 μg/ml	General	–
Americas	Colombia	Lora	HCl, 0.05 *N*, + H_2SO_4, 0.025 *N*	1/5	5 minutes	5 ppm	Beans	–
Americas	United States	Hunter	$NaHCO_3$, 0.25 *N*, + EDTA, 0.01 *M*, + NH_4F, 0.01 *N*, + Superfloc 127, 50 ppm	1/10 (v/v)	10 minutes	5 μg/ml	By crop	Texture, OM, CEC, ratios
Asia	Pakistan	Soomro	DTPA	1/2 (w/v)	2 hours	–	–	Toxicity with submergence
Asia	Thailand	Kurmarohita	DTPA	1/2 (w/v)	2 hours	5 ppm	25–50 kg $MnSO_4$/ha	–
Asia	Bangladesh	Bhuiyan	HCl, 0.05 *N*	1/2 (w/v)	5 minutes	1 ppm	–	–
Asia	Taiwan	Lian	HCl, 0.1 *N*	1/10 (w/v)	5 minutes	–	Paddy rice; 100 kg $MnSO_4$ or 1–3 ton furnace slag/ha	–

Asia	Hawaii	Bosshart	$NH_4C_2H_3O_2$, 1 *N*, pH 4.8	1/20 (w/v)	1.5 hours	116	–	pH > 7
Australia	Australia	Price	DTPA	1/10 (w/v)	30 minutes	–	Pastures	Deficiency rare on low pH soils
Australia	Australia	Price	DTPA	1/10 (w/v)	30 minutes	2 ppm	Wheat: 0.5% $MnSO_4$ spray at 3–5 weeks	–
Australia	Australia	Price	DTPA	1/10 (w/v)	30 minutes	5 ppm	Strawberries: 100 g $MnSO_4$/ 100 liter water	–
Australia	Australia	Price	DTPA	1/10 (w/v)	30 minutes	Toxic at > 45–50 ppm	–	Low pH

Table 3. Soil tests for zinc being used by tropical laboratories

Continent	Country	Source	Extractant	Soil/extr.	Shaking time	Critical level	Crop recommendation	Soil property limitations
Africa	Malawi	Chickonda	DTPA	10 g/ 20 cm^3	2 hours	0.5 ppm	–	O.M.
Africa	Zimbabwe	Tanner	EDTA, 1%	1/1 (w/v)	1 hour	0.6 ppm	Maize: 3–4 kg Zn/ha incorporated into granular fertilizer: Applied for 2 seasons, then rested for 3 seasons	–
Africa	Nigeria	Kang	HCl, 0.1 *N*	10 g/ 50 cm^3	30 minutes	–	Maize: 1–2 kg Zn/ha	Sandy, low CEC
Africa	Botswana	Stewart-Jones	HCl, 0.1 *N*	1/5 (w/v)	60 minutes	–	–	–
Africa	Botswana	Stewart-Jones	DTPA	1/2 (w/v)	2 hours	–	–	Calcareous soils
Africa	Kenya	Qureshi	HCl, 0.1 *N*	1/5 (w/v)	60 minutes	5 ppm	20 g $ZnSO_4$/ 20L/tree	–
Africa	Netherlands	van der Pol	DTPA	1/2 (w/v)	2 hours	1.0 ppm	–	–
Americas	Bolivia	Angulo	$NaHCO_3$, + EDTA 0.01 *M* + Superfloc 127, pH 8.5	1/10 (w/v)	10 minutes	3 ppm	–	pH > 6.5, certain Ultisols
Americas	Mexico	Moncada	KCl, 1 *N*, pH 7.0	1/4 (w/v)	1 hour	0.85 ppm	Rice: 25 kg $ZnSO_4$ (36% Zn)/ha	High Ca parent material
Americas	Mexico	Cajuste	DTPA	1/2 (w/v)	2 hours	0.5 ppm	Maize	pH > 6.1, O.M. < 0.8%
Americas	Mexico	Cajuste	HCl, 0.5 *N* + H_2SO_4 0.025 *N*	1/10 (w/v)	3 × 5 minutes	4.0 ppm	Maize	pH > 6.1, O.M. < 0.8%
Americas	Peru	Villagarcia	$NH_4C_2H_3O_2$, 1 *N*	1/10	60 minutes	–	0.5% $ZnSO_4$	–

Americas	Peru	Olazabal	$NaHCO_3$, 0.5 *N* + EDTA, 0.01 *M*	1/4.4	15 minutes	Low = 5–10	Foliar on vegetables, cereals, tubers, etc., not exceeding 0.3–0.7 kg/ha	Alkaline pH, high Mn, Cu, Fe
Americas	Peru	Neyra	$NH_4C_2H_3O_2$, 1.0 *N*	1/10	60 minutes	–	Citrus, 0.5% $ZnSO_4$	–
Americas	Costa Rica	Ramirez	$NaHCO_3$, 0.5 *N*, + EDTA, 0.01 *M*, + Superfloc, 25 ppm	1/10	15 minutes	3	3 kg Zn/ha	–
Americas	Dominican	Perez	$NaHCO_3$, 0.5 *N*, + EDTA, 0.01 *M*, + Superfloc, 25 ppm	1/10 (v/v)	10 minutes	3 μg/ml	All crops	$CaCO_3$ salts
Americas	Chile	Subercaseaux	HCl, 0.1 *N*	1/10 (w/v)	5 mintutes	–	–	–
Americas	Jamaica	Thompson	HCl, 0.1 *N*	1/10	Shake once every 15 minutes for 1 hour	1.0–1.5 ppm	Vegetables, forage crops, coconut: 19–100 lb/acre	High pH
Americas	Guyana	Granger	$NaHCO_3$, 0.25 *N*, + EDTA, 0.01 *M*, + NH_4F, 0.01 *N*	1/10 (v/v)	10 minutes	2 μg/ml	–	–
Americas	Nicaragua	Quintana	$NaHCO_3$, 0.5 *N* + EDTA, 0.01 *M*, + Superfloc, 50 ppm	1/10 (v/v)	10 minutes	3 μg/ml	–	–
Americas	Colombia	Lora	$NaHCO_3$, 0.5 *N* + EDTA, 0.01 *M*, pH 8.5	1/10 (v/v)	10 minutes	1.5 μg/ml	Cotton	–

Table 3 (*continued*)

Continent	Country	Source	Extractant	Soil/extr.	Shaking time	Critical level	Crop recommendation	Soil property limitations
Americas	Colombia	Lora	$NaHCO_3$, 0.5 *N*, + EDTA, 0.01 *M*, + pH 8.5	1/10 (v/v)	10 minutes	2.0 μg/ml	General	–
Americas	Colombia	Lora	HCl, 0.05 *N*, H_2SO_4, 0.025 *N*	1/5	5 minutes	0.5 ppm	Pastures	–
Americas	Colombia	Lora	HCl, 0.05 *N*, H_2SO_4, 0.025 *N*	1/5	5 minutes	0.8 ppm	Beans	–
Americas	United States	Hunter	$NaHCO_3$, 0.25 *N*, + EDTA, 0.02 *M*, + NH_4F, 0.01 *N*, + Superfloc 127, 50 ppm	1/10 (v/v)	10 minutes	2 μg/ml	By crop	Texture, O.M., CEC, ratios
Asia	Pakistan	Soomro	DTPA	1/2 (w/v)	2 hours	–	–	Low O.M., eroded, submerged, high pH and P
Asia	Thailand	Kurmarohita	DTPA	1/2 (w/v)	2 hours	2 ppm	25–50 kg $ZnSO_4$/ha	–
Asia	India	Katyal	$NH_4C_2H_3O_2$, 1 *N*, (pH 7.0), + Dithizone, 0.1%	–	180 minutes	0.65 ppm	Wheat	Vertisol
Asia	India	Katyal	Dithizone	1/20 (w/v)	60 minutes	0.6 ppm	Pearl millet	Mixed, Alfisol and Vertisol
Asia	India	Katyal	DTPA	1/2 (w/v)	120 minutes	0.46 ppm	Wheat	Vertisol
Asia	India	Virmani	DTPA	1/2 (w/v)	2 hours	0.6 ppm	–	pH, waterlogging
Asia	Indonesia	Soepardi	HCl, 0.05 *N*	1/6 (w/v)	30 minutes	1 ppm	Paddy rice; 2.5–5 kg $ZnSO_4$/ha	pH < 6
Asia	Indonesia	Soepardi	HCl, 0.05 *N*	1/6 (w/v)	30 minutes	3 ppm		pH > 6
Asia	Indonesia	Soepardi	DTPA	1/6 (w/v)	30 minutes	1 ppm		pH < 5
Asia	Indonesia	Soepardi	DTPA	1/6 (w/v)	30 minutes	~3 ppm		pH > 6

Asia	Bangladesh	Bhuiyan	HCl, 0.05 *N*	1/2 (w/v);	5 minutes	1 ppm	Rice: 3 kg Zn/ha	pH > 7.5
Asia	Taiwan	Lian	HCl, 0.1 *N*	1/10 (w/v)			Rice: 40–60 kg by ZnO or $ZnSO_4$	2–3 year residual effect
Asia	Taiwan	Lian	HCl, 0.1 *N*	1/10 (w/v)	1 hour	5 ppm	Sugarcane: 70–100 kg ZnO or $ZnSO_4$/ha	–
Asia	Hawaii	Bosshart	HCl, 0.1 *N*	1/20 (w/v)	1.5 hour	6 lb/acre-foot	–	pH < 7.0
Asia	Sri Lanka	Nagarajah	HCl, 0.05 *N*	1/2 (w/v)	5 minutes	1 ppm	Rice	–
Asia	Philippines	Ponnamperuma	HCl, 0.05 *M*	1/2 (w/v)	5 minutes	1 ppm	–	–
Australia	Australia	Price	DTPA	1/10 (w/v)	30 minutes	0.3 ppm	Wheat: 0.5% $ZnSO_4$ spray at 3–5 weeks, or soil applications according to soil type (Clays-16, loams-6, and sands 3 kg Zn/ha)	pH < 7
Australia	Australia	Price	DTPA	1/10 (w/v)	30 minutes	0.3 ppm	–	pH < 7

Table 4. Soil tests for copper being used by tropical laboratories

Continent	Country	Source	Extractant	Soil/extr.	Shaking time	Critical level	Crop recommendation	Soil property limitations
Africa	Malawi	Chickonda	DTPA	1/2 (w/v)	2 hours	0.2 ppm	–	pH, O.M.
Africa	Zimbabwe	Tanner	EDTA, 1%	1/1 (w/v)	1 hour	0.4 ppm (0.6 μg/ml)	Wheat: $CuSO_4$ at 10 kg/ha soil applied, 1.5 kg/ha foliar	–
Africa	Botswana	Stewart-Jones	NH_4 EDTA, 0.08 *N*, pH 4.0	1/5 (w/v)	60 minutes	-	–	–
Africa	Botswana	Stewart-Jones	DTPA	1/2 (w/v)	2 hours	–	–	Calcareous soils
Africa	Kenya	Qureshi	HCl, 0.1 *N*	1/5 (w/v)	60 minutes	1 ppm	Wheat: 2 kg Cu/ha	Parent material
Africa	Kenya	Qureshi	HCl, 0.1 *N*	1/5 (w/v)	60 minutes	1 ppm	Citrus: 20 g Cu/2 L/tree	Parent material
Africa	Netherlands	van der Pol	DTPA	1/2 (w/v)	2 hours	0.2 ppm	–	–
Americas	Bolivia	Angulo	$NaHCO_3$, 0.5 M, + EDTA, 0.01 *M*, + Superfloc 127, pH 8.5	1/10 (w/v)	10 minutes	1 ppm	–	–
Americas	Mexico	Moncada	NH_4 Ac, pH 4.8	1/4 (w/v)	1 hour	–	Rice: 2.5 $CuSO_4$/ha	Very high pH (8.8)
Americas	Mexico	Cajuste	DTPA	1/2 (w/v)	2 hours	0.5 ppm (double acid)	Maize	–
Americas	Peru	Villagarcia	HCl, 20%	1/5	30 minutes	2 ppm	0.5% $CuSO_4$	–
Americas	Peru	Neyra	HCl, 20%	1/5	30 minutes	2 ppm	Citrus, 0.5% $CuSO_4$	–
Americas	Costa Rica	Ramirez	$NaHCO_3$, 0.5 *N* + EDTA, 0.01 *M*, + Superfloc, 25 ppm	1/10	15 minutes	1 ppm	–	–
Americas	Dominican Republic	Perez	$NaHCO_3$, 0.5 *N* + EDTA, 0.01 *M*, + Superfloc, 50 ppm	1/10 (v/v)	10 minutes	1 μg/ml	All crops	$CaCO_3$, salts

Americas	Chile	Subercaseaux	$NH_4C_2H_3O_2$, 1 *N* pH 4.8	1/2 (w/v)	1 hour	–		
Americas	Chile	Subercaseaux	HCl, 0.1 *N*	1/10 (w/w)	1 hour	–		
Americas	Jamaica	Thompson	HCl, 0.1 *N*	1/10	Shake once each 15 minutes for 1 hour	2–5 ppm	Corn, vegetable, potato, coconut; 12–60 lb/acre	High pH, CEC, O.M.
Americas	Guyana	Granger	$NaHCO_3$, 0.25 *N*, + EDTA, 0.01 *M*, + NH_4F, 0.01 *N*	1/10 (v/v)	10 minutes	1 μg/ml	–	–
Americas	Nicaragua	Quintana	$NaHCO_3$ 0.5 *N*, + EDTA, 0.01 *M*, + Superfloc, 50 ppm	1/10 (v/v)	10 minutes	1 μg/ml	–	–
Americas	Colombia	Lora	$NaHCO_3$ 0.5 *N*, + EDTA, 0.05 *M*, + pH 8.5	1/10 (v/v)	10 minutes	1 μg/ml	General	–
Americas	Colombia	Lora	HCl, 0.05 *N* H_2SO_4, 0.025 *N*	1/5	5 minutes	0.5 ppm	Pastures	–
Americas	United	Hunter	$NaHCO_3$, 0.25 *N*, + EDTA, 0.01 *M*, + NH_4F, 0.01 *N*, + Superfloc 127, 50 ppm	1/10 (v/v)	10 minutes	1 μg/ml	By crop	Texture, O.M., CEC, ratios
Asia	Pakistan	Soomro	DTPA	1/2 (w/v)	2 hours	–	–	Low O.M., eroded, submerged, high pH and P
Asia	Thailand	Kurmarohita	DTPA	1/2 (w/w)	2 hours	1 ppm	25–50 kg $CuSO_4$/ha	–
Asia	Bangladesh	Bhuiyan	HCl, 0.05 *N*	1/2 (w/v)	5 mintues	0.1 ppm	–	–
Asia	Malaysia	Law	Wet digestion	–	–		30 lb/acre	Peats only
Asia	Hawaii	Bosshart	HCl, 0.1 *N*	1/20 (w/v)	1.5 hour	10 lb/acre-foot	–	pH < 7.0
Asia	Philippines	Ponnamperuma	HCl, 0.05 *M*	1/2 (w/v)	5 minutes	0.1 ppm	–	–
Australia	Australia	Price	DTPA	1/10 (w/v)	30 minutes	0.3 ppm	Wheat; 1% $CuSO_4$ spray at 3–5 weeks	–
Australia	Australia	Price	DTPA	1/10 (w/v)	30 minutes	Toxic at > 20 ppm	–	pH < 7.0

Table 5. Soil tests for boron being used in tropical laboratories

Continent	Country	Source	Extractant	Soil/extr.	Shaking time	Critical level	Crop recommendation	Soil property limitations
Africa	Malawi	Chickonda	$CaH_4(PO_4)_2 \cdot H_2O$	1/2.5 (w/v)	10 minutes	–	–	–
Africa	Zimbabwe	Tanner	Hot water	1/2.5 (w/v)	5 min reflux	0.5 ppm	–	–
Africa	Botswana	Stewart-Jones	Hot water	1/2 (w/v)	5 min boiling	0.1 – 0.2 ppm	Legumes	–
Africa	Netherlands	van der Pol	Hot water	1/2 (w/v)	5 minutes	0.5 ppm	Farm crops	–
Africa	Netherlands	van der Pol	Hot water	1/2 (w/v)	5 minutes	1.5 ppm	Beets, cotton, alfalfa	–
Americas	Mexico	Moncada	Boiling water	1/10 (w/v)	1 hour	0.36 ppm	Potato; 15 kg boric acid/ha	–
Americas	Peru	Villagarcia	Hot water	1/2 (w/v)	–	1.0 ppm	0.1% borax	–
Americas	Peru	Olazabal	Water	1/2 (w/v)	15 minutes	0.8 ppm	4–9 kg borax/ha	Clay
Americas	Peru	Olazabal	Water	1/2 (w/v)	15 minutes	0.5 ppm	4–9 kg borax/ha	Loam
Americas	Peru	Olazabal	Water	1/2 (w/v)	15 minutes	0.3 ppm	4–9 kg borax/ha	Sand
Americas	Peru	Olazabal	Water	1/2 (w/v)	15 minutes	1.0 ppm	4–9 kg borax/ha	pH > 7
Americas	Peru	Neyra	Hot water	1/2 (w/v)	–	1.0 ppm	Citrus; 0.1% borax	–
Americas	Costa Rica	Ramirez	CaH_2PO_4, 0.08 *M*	1/2.5 (w/v)	10 minutes	0.2 ppm	0.5 kg B/ha	–
Americas	Dominican	Perez	$CaH_4(PO_4)_2 \cdot H_2O$	1/2.5 (w/v)	10 minutes	0.2 μg/ml	All crops	–
Americas	Chile	Subercaseaux	Hot water	1/2 (w/v)	5 minutes	–	–	–
Americas	Chile	Subercaseaux	Saturation extract	–	16 hours	–	–	–
Americas	Jamaica	Thompson	H_2SO_4, 1:7 by vol. HF, + 5%	1/15 (w/v)	Stand 2 hours	1.5 ppm	Forage, vegetable and root crops; 4–80 lb/acre	High pH, O.M.
Americas	Guyana	Granger	$CaH_4(PO_4)_2 \cdot H_2O$	1/5 (w/v)	10 minutes	0.2 μg/ml	–	–

Ameri as	Nicaragua	Quintana	$CaH_4(PO_4)_2 \cdot H_2O$	1/2.5 (v/v)	10 minutes	0.2 μg/ml	–	–
Americas	Colombia	Lora	Hot water	1/2 (v/v)	5 minutes	0.2 μg/ml	Vegetables	pH, O.M.
Americas	Colombia	Lora	Hot water	1/2 (v/v)	5 minutes	0.5 μg/ml	Beans, coffee, pastures	pH, O.M.
Americas	Colombia	Lora	Hot water	1/2 (v/v)	5 mintues	0.6 μg/ml	Potatoes	pH, O.M.
Americas	Colombia	Lora	CaH_2PO_4, 0.08 *M*	1/2.5 (v/v)	10 minutes	0.2 μg/ml	General	pH, O.M.
Americas	United States	Hunter	$CaH_4(PO_4)_2 \cdot H_2O$, 0.1 *M*	1/5 (v/v)	10 minutes	0.2 μg/ml	–	–
Asia	Pakistan	Soomro	Hot water	1/2 (w/v)	5 min reflux	–	–	High pH and salinity, low O.M.
Asia	Thailand	Kurmarohita	Hot water	1/2 (w/v)	5 min reflux	2 ppm	25 kg borax/ha	Sesquioxides
Asia	Malaysia	Law	Hot water	1/2	10 minutes	–	–	–
Asia	Taiwan	Lian	Hot water	1/2 (w/v)	5 min reflux	0.15 ppm	Papaya; 10 g borax/tree	About 4 years
Asia	Taiwan	Lian	Hot water	1/2 (w/v)	5 min reflux	0.15 ppm	Citrus; 40 g borax/tree	Residual effect
Asia	Hawaii	Bosshart	Hot water	1/2 (w/v)	5 min reflux	2.9 lb/acre-foot	–	pH > 7
Asia	Hawaii	Bosshart	Hot water	1/2 (w/v)	5 min reflux	1.5 lb/acre-foot	–	pH < 7
Asia	Philippines	Ponnamperuma	HCl, 0.05 *M*	1/2 (w/v)	5 minutes	Toxic at > 4 ppm	–	–

Molybdenum

Only a few laboratories conduct routine soil tests for molybdenum (Table 6). The two extractants being used are $(NH_4)_2C_2O_4$ and hot water. The ratios of soil to extractant varied from 1 : 1 to 1 : 10, while shaking time varied from 1 hour to overnight. Critical levels were between 0.1 and 0.3 ppm of extractable molybdenum.

Evaluation and discussion

General considerations

The fact that a soil test is used by several laboratories is no guarantee that it is effective. Calibration data are necessary to determine the effectiveness of a soil test. An attempt will be made in this section to examine some of the more commonly used soil test extractants for micronutrients to see if their use under the wider range of soil conditions that occur in the tropics can be justified.

Cox and Kamprath [6] made an extensive examination of soil test methods for diagnosing micronutrient deficiencies. They listed the most commonly used extractants for each micronutrient along with reported critical levels. Viets and Lindsay [45] reviewed soil test methods for zinc, copper, manganese, and iron. These reviews are rather extensive and will not be repeated here except as they may relate to soil testing in the tropics. Instead, the evaluation and discussion will be focused on recent studies that help to show the reliability of various soil testing procedures and methods.

Finland-FAO micronutrient studies

A comprehensive micronutrient investigation was conducted by Sillanpää [31] in cooperation with scientists from 30 countries. This study included many tropical countries, 8000 soil and plant samples, and over 170 000 analyses. It provides valuable data on the correlation between micronutrient concentrations in plants growing on these soils and extractable levels by several soil tests. Wheat and maize were sampled at the original sites where the soil samples were taken; then wheat was also grown on all soils under uniform greenhouse conditions.

The correlation coefficients for micronutrients in the plants grown in the field at the original sites were rather low; they reflect the great variability of field sampling, growing conditions, and handling of samples (Table 7). When the same soils were cropped with wheat under uniform conditions in the greenhouse, the correlation coefficients improved significantly.

Two extractants, acid ammonium acetate-EDTA (AAAc-EDTA) at pH 4.65 and DTPA at pH 7.30, were evaluated as soil test extractants for iron, zinc, manganese, and copper (Table 7). Neither extractant did well for iron in field-grown plants on the broad range of soils included in this study. This

Table 6. Soil tests for molybdenum being used by tropical laboratories

Continent	Country	Source	Extractant	Soil/extr.	Shaking time	Critical level	Crop recommendation	Soil property limitations
Africa	Botswana	Stewart-Jones	$(NH_4)_2C_2O_4$, pH 3.3	1/1 (w/v)	Overnight standing, then leach to make 1/5	–	–	–
Americas	Mexico	Moncada	$(NH_4)_2C_2O_4$	1/10 (w/v)	8 hours	–	–	–
Americas	Chile	Subercaseaux	$(NH_4)_2C_2O_4$	1/10 (w/v)	Overnight	–	–	–
Americas	Jamaica	Thompson	Hot water	1/5	Shake once every 30 sec for 6 min	0.2–0.3 ppm	–	Low pH
Americas	Colombia	Lora	$(NH_4)_2C_2O_4$, pH 3.3	1/10 (w/v)	10 hours	0.2 ppm	Cauliflower and other brassicas	–
Americas	Colombia	Lora	$(NH_4)_2C_2O_4$, pH 3.3	1/10 (w/v)	10 hours	0.1 ppm	Other crops	–
Asia	Thailand	Kurmarohita	$(NH_4)_2C_2O_4$, pH 3.3	1/10 (w/v)	1 hour	0.2 ppm	2.4 kg Na MoO_4/ha	–
Asia	Taiwan	Lian	$(NH_4)_2C_2O_4$, pH 3.3	–	–	–	Peanuts and soybeans: 0.3–0.6 kg NH_4 MoO_4/ha	–

Table 7. Correlation between the micronutrient concentration of three indicator plants and the soil concentration determined by several methods [31]

Micronutrient	Extraction method	Original maize (n = 1966)	Original wheat (n = 1968)	Pot-grown wheat (n = 3538)
Fe	AAAc-EDTA[a]	−0.007 n.s.	0.032 n.s.	0.325***
Fe	DTPA[b]	0.028 n.s.	−0.030 n.s.	0.263***
Mn	AAAc-EDTA	−0.108***	0.046*	0.039*
Mn	DTPA	0.161***	0.119***	0.552***
Zn	AAAc-EDTA	0.391***	0.405***	0.665***
Zn	DTPA	0.381***	0.473***	0.732***
Cu	AAAc-EDTA	0.344***	0.254***	0.664***
Cu	DTPA	0.114***	0.125***	0.518***
B	Hot water ext[c]	0.548***	0.694***	0.741***
Mo	AO-OA[d]	0.134***	0.117***	0.245***

[a] 1.0 *M* acid ammonium acetate and 0.02 *M* EDTA adjusted to pH 4.65 [14].
[b] 0.005 *M* DTPA, 0.01 *M* $CaCl_2$ and 0.1 *M* triethanolamine [17].
[c] Method of Berger and Truog [2] modified by Sippola and Ervio [35].
[d] Ammonium oxalate-oxalic acid and adjusted to pH 3.3 [41].

is not surprising since iron deficiencies are generally restricted to high pH soils regardless of mineralogy. The author also pointed out that contamination of plant samples with dust or soil could easily result in serious errors in iron concentration since soil and dust contain much more iron than the iron content of plants. The slightly higher correlations obtained with greenhouse-grown plants perhaps reflect less contamination of plant samples. The problem of contamination is less for the other micronutrients because their content in soil is much less.

The two extractants, AAAc-EDTA and DTPA, were equally effective for Zn and Cu concentrations in greenhouse-grown plants. However, DTPA was definitely superior to AAAc-EDTA for Mn.

With a few exceptions, inclusion of one other soil property with the soil micronutrient level improved the correlation with the plant concentration. There was no improvement for iron with either extractant, but there was slight improvement for Zn with DTPA. The latter, however, already had a coefficient of about 0.7. With one other soil property included, the correlation coefficients were all in the range of 0.6–0.8. The dominant second soil property was soil pH for manganese, zinc, and molybdenum; organic carbon for copper; and CEC for boron. Molybdenum was extracted with ammonium oxalate and oxalic acid, while boron was extracted with hot water.

Examination of the data in Table 8 is encouraging regarding the use of both micronutrient extractants. The results contain much data that will enhance our understanding of the merits and deficiencies of extractants for soils of different pH and other properties. A careful examination of the detailed results of this study should be helpful in devising new soil test extractants that may be of greater universal use than the extractants reported in this study. For a wide range in soil conditions, such as may be encountered in

Table 8. Correlation coefficients of soil extractable micronutrients content of pot-grown wheat plants with and without correction coefficients for 3536 soils [31]

Micronutrient	Extraction method[a]	r value without correction	Significant correction coefficients (k)[b]	r value with correction
Fe	AAAc-EDTA	0.325***	None	0.325***
Fe	DTPA	0.263***	None	0.263***
Mn	AAAc-EDTA	0.039***	k (pH)	0.588***
Mn	DTPA	0.552***	k (pH)	0.713***
Zn	AAAc-EDTA	0.665***	k (pH)	0.707***
Zn	DTPA	0.732***	None	0.732***
Cu	AAAc-EDTA	0.664***	k (Org. C)	0.731***
Cu	DTPA	0.518***		
B	Hot water	0.741***	k (CEC)	0.826***
Mo	OA-AC	0.245***	k (pH)	0.696***

[a]See footnotes Table 7.
[b]Correction coefficients:

B: k (CEC) $10^{[illegible]}$

where x = cation exchange capacity (me/100 g)

Cu (AAAc-EDTA): k (Org. C) $10^{[illegible] \log x + [illegible] (\log x)^2}$

where x = soil organic carbon content (%)

Mn(DTPA): k (pH) $10^{[illegible] pH + [illegible] pH^2}$

Mn(AAAc-EDTA): k (pH) $10^{[illegible] pH + [illegible] pH^2}$

Mo: k (pH) $10^{[illegible] pH}$

Zn: k (pH) $10^{[illegible] pH + [illegible] pH^2}$

the tropics, inclusion of other soil properties may be not only beneficial, but mandatory.

The tentative critical levels of micronutrients estimated for the various methods under greenhouse conditions are summarized in Table 9 [31]. In many cases these critical levels are only rough estimates, and they need to be examined for different crops and conditions in the field.

Iron, manganese, zinc, and copper extractants

The four micronutrient cations will be discussed together since the same extractant is often used to evaluate two or more of these elements simultaneously.

Korcak and Fanning [13] included a direct comparison between DTPA and double acid (0.05 *N* HCl, 0.025 *N* H_2SO_4) for soil copper and zinc from both metal sulfate salt and sewage sludge amendments to three soils at two different liming regimes. DTPA was found to be more reliable than double acid based on r^2 values relating extractable and plant tissue metal concentrations using maize. The DTPA extractant was also more effective in indicating reduced availability of copper and zinc upon liming.

Table 9. Tentative critical levels of micronutrients determined by various methods [31]

Micronutrient and method	Deficiency	Excess
B, hot water extraction	< 0.3 – 0.5	> 3 – 5
B, hot water extraction + CEC correction	< 0.3 – 0.5	> 3 – 5
Cu, AAAc-EDTA	< 0.8 – 1.0	> 17 – 25
Cu, AAAc-EDTA + org. C correction	< 0.8 – 1.0	> 17 – 25
Fe, AAAc-EDTA	< 30 – 35	–
Mn, DTPA	< 2 – 5	> 140 – 200
Mn, DTPA + pH correction	< 2 – 4	> 150 – 220
Mo, AO-OA + pH correction	< 0.01 – 0.02	> 0.5 – 1.0
Zn, DTPA	< 0.4 – 0.6	> 10 – 20
Zn, AAAc-EDTA + pH correction	< 1.0 – 1.5	> 20 – 30

Gupta and Mittal [10] conducted studies on 22 noncalcareous soils from India to evaluate various extractants to obtain critical levels of soil and plant zinc for green gram (*Phaseolus aureus* Roxb.). The order of extractability by the different extractants was 1 *N* HCl > 0.1 *N* HCl > EDTA-$(NH_4)_2CO_3$ > EDTA-NH_4OAc > DTPA + $CaCl_2$ > 1 *M* $MgCl_2$. Critical levels for these soils were estimated to be 0.48 ppm DTPA + CaCl extractable zinc, 0.80 ppm EDTA NH_4OAc extractable zinc, 0.70 ppm EDTA $(NH_4)_2CO_3$ extractable zinc, and 2.2 ppm 0.1 *N* HCl extractable zinc. The critical zinc concentration in 6-week old plants was found to be 19 ppm. The 0.1 *N* HCl method gave the best correlation ($r = 0.588^{**}$) between extractable zinc and Bray's percent yield, while the DTPA method gave the best correlation with zinc concentration. The 0.1 *N* HCl showed slightly higher correlation with zinc uptake ($r = 0.661^{**}$) than did DTPA ($r = 0.634^{**}$). Both 1 *N* HCl and 1 *M* $MgCl_2$ showed nonsignificant relationships.

Selvarajah et al. [27] conducted a pot experiment with two rice varieties under flooded conditions to evaluate five extractants for available zinc and copper. The extractants included: 1 *N* NH_4OAc (pH 4.6), 0.01 *M* EDTA-1 *M* $(NH_4)_2CO_3$ (pH 8.6), 0.05 *N* HCl, 0.01 *M* $CaCl_2$, and 0.2 *M* $MgSO_4$. Soil zinc and copper extracted from dry soils before puddling and from wet soils at 4 weeks and 8 weeks after transplanting were correlated with plant copper and zinc contents. All extractants gave significant correlations with plant zinc. Highest correlation was obtained with NH_4OAc, followed by HCl. Zinc extracted from the dry soils correlated significantly with that from wet soils. Ammonium acetate, HCl, and EDTA extracted about equal amounts of zinc. EDTA was most suitable for copper, followed by NH_4OAc and HCl. The generally low 'r' values obtained for copper suggest that more study is needed.

Trierweiler and Lindsay [44] developed an EDTA-ammonium carbonate extractant for assessing available zinc in high pH soils. They showed that the method was superior to 0.1 *N* HCl [22]. The method was equal to the dithizone procedure of Shaw and Dean [29] but was much easier to perform.

Osiname et al. [23] examined four soil tests for copper and zinc to evaluate their ability to predict the uptake of these micronutrients by oats grown

on 28 soils from western Nigeria. Their results showed that EDTA was better than DTPA, 0.1 *N* HCl or 1 *N* HCl in predicting uptake. Copper uptake was more strongly correlated with inorganic soil fractions than with organic matter and was not significantly affected by soil pH. The best prediction of zinc uptake was provided by a combination of 0.1 *N* HCl-extractable zinc, pH, organic matter, and the silt-plus-clay fraction in a multiple regression analysis. With all four extractants, the uptake of zinc was predicted better on soils of pH less than 6.0 than on those greater than 6.0.

Tiwari and Kumar [43] examined the relative efficiencies of five chemical extractants for assessing available copper to rice in pot culture. The correlation coefficients of copper uptake to extractable copper were as follows: 0.1 *N* HCl ($r = 0.847^{**}$), 0.05 *M* EDTA (0.788^{**}), 0.01 *M* EDTA in 1 *N* NH_4-acetate (0.441), NH_4-acetate pH 7.0 (0.417), and NH_4-acetate pH 4.8 (0.292). Thus, copper extracted by 0.1 *N* HCl was the best indicator of copper available to rice and that extracted by 0.05 *M* EDTA was second best. The other extractants did not have significant correlations.

Makarim and Cox [20] evaluated four extractants for Cu: double acid, Mehlich-Bowling, ammonium bicarbonate DTPA, and Mehlich-3. Three crops were grown in the greenhouse on 15 soils, primarily Ultisols and a few Histosols. Yield response was predicted equally well by each of the extractants, accounting for about 70% of the variation.

Singh et al. [33] evaluated 7 extractants for assessing zinc availability in 30 calcareous soils of India. The correlation coefficients between extractable zinc and zinc uptake by maize were: DTPA (0.927^{**}), 0.5 *M* KCl (0.021), 0.02 *M* EDTA (0.111), 1 *N* NH_4-acetate: pH 3 (0.084), pH 4.8 (0.382^{**}), pH 7 (0.049), and pH 7 + 0.2% hydroquinone (0.249). They rated the DTPA best and the 1 *N* NH_4OAc at pH 4.8 as second. None of the other tests were significant. The DTPA extractant showed the critical level of zinc to be 1.4 ppm.

Aboul-Roos and Abdel-Wabid [1] extracted available copper from 15 soils from various regions of Egypt and grew barley on these soils in the greenhouse. They found correlation coefficients of 0.85^{**} and 0.88^{**} between plant uptake of copper and that extracted by 0.1 *N* HCl + titratable alkalinity and by 0.01 *M* EDTA + ammonium carbonate, respectively. Critical levels were 3.0 and 2.6 ppm of copper extracted by these two methods, respectively.

Sakal et al. [26] conducted a pot experiment to determine the critical zinc concentration in rice and wheat plant tissues for predicting response to zinc application. DTPA-extractable zinc in soil was found to be significantly correlated with tissue zinc concentration in rice ($r = 0.717^{**}$) and wheat ($r = 0.851^{**}$). Also, the concentration of zinc in the tissue was significantly correlated with Bray's percent yield in rice ($r = 0.787^{*}$) and wheat ($r = 0.888^{**}$). The critical zinc concentrations in 52-day-old rice and wheat plants were 37 and 29 ppm, respectively.

Singh and Takkar [34] examined several soil test extractants for zinc in

soils planted to rice in India. There were significant correlations of zinc uptake and yield with 0.005 *M* DTPA, 0.05 *M* EDTA, and 0.01 *M* EDTA-ammonium carbonate-extractable zinc, whereas there were none with double acid-extractable and soil solution zinc. For 46 soils on two different salt associations, the critical levels of zinc were 0.86 ppm for DTPA with a predictive value of 89%, 1.42 ppm for EDTA with a predictive value of 91%, and 1.00 ppm for EDTA ammonium carbonate with a predictive value of 87%.

Madziva [19] examined the ability of six extractants to predict the occurrence of zinc deficiency symptoms and to assess the relation of soil zinc to plant zinc uptake in greenhouse trials. Efficiency of prediction for the extractants was in the order HCl > DTPA > EDTA-NH_4OAc > EDTA > NH_4OAc > 0.05 *N* HCl + 0.025 *N* H_2SO_4. Critical levels of soil zinc below which zinc deficiency symptoms occurred were 0.48, 0.25, 0.48, 0.59, 0.06, and 0.50 ppm, respectively. Closeness of fit of the correlation between plant zinc uptake and soil-extractable zinc was in the following order: HCl-H_2SO_4 > DTPA > HCl > EDTA-NH_4OAc > EDTA, with correlation coefficients (r) of 0.68, 0.64, 0.59, 0.48, 0.46, and 0.43, respectively. It was concluded that either the double acid or DTPA would be suitable extractants.

Singh et al. [32] examined the following extractants on 30 calcareous soils of India: 0.005 *M* DTPA, 0.5 *M* KCl, 0.02 *M* EDTA, 1 *N* NH_4OAc (pH 3.0, 4.8, 7.0), 1 *N* NH_4OAc + 0.2% hydroquinone. When the extractable nutrients were correlated with yield, concentration, and uptake of micronutrients by maize in pot trials, it was concluded that 1 *N* NH_4OAc (pH 7.0 and 4.8, respectively) was the most suitable extractant for copper and manganese, whereas DTPA was most suitable for iron.

Berrow et al. [3] have tested the possibility of using 2-ketogluconic acid as an extractant for micronutrients. Although they tested it on only three soils, it would appear that it may offer some promise of reflecting the uptake of copper, manganese, molybdenum, and zinc compared with uptake by pasture grasses and clovers growing on those soils.

El-Nennah et al. [8] examined four methods of measuring available soil zinc and ranked them according to their abilities to predict zinc uptake by barley from unfertilized soils of Egypt. They concluded the following: DTPA > EDTA $(NH_4)_2CO_3$ > laboratory E-value > biological A-value.

Ponnamperuma et al. [25] compared 0.05 *M* HCl with 0.1 *M* HCl, EDTA, and DTPA as an extractant for available zinc and copper on 33 wetland rice soils. Rice was grown on the flooded soils, scored visually for zinc deficiency, and the plants were analyzed for zinc and copper. Fourteen of the sixteen soils on which rice showed zinc deficiency contained < 1 ppm of 0.05 *N* HCl-extractable zinc but had values far in excess of the critical limits by the other methods. The correlation coefficients for available and plant zinc were: 0.05 *N* HCl (0.88^{**}), 0.1 *N* HCl (0.55^{**}), EDTA (0.43^{**}), and DTPA (0.31^{ns}). Twelve of the zinc-deficient soils gave < 0.1 ppm copper by the 0.05 *N* HCl method, but they gave values exceeding the critical limits by the

EDTA and DTPA methods. The r values for available and plant copper were 0.05 *N* HCl (0.74**), 0.1 *N* HCl (0.64**), EDTA (0.28^{ns}), and DTPA (0.20^{ns}). The critical limit of 1.0 ppm by the 0.05 *N* HCl extraction was confirmed for zinc deficiency and a tentative critical value of 0.1 ppm was proposed for copper.

Three extractants for zinc were evaluated in the southern region of the United States with corn and rice grown in the field [7]. Two of these were dilute acids (the double acid and 0.1 *N* HCl) and one was a chelate (DTPA). The soils were generally noncalcareous, mostly Ultisols that had been limed to pH 6–7. Although the critical level of zinc in the soil was greater with the acids than with the chelate, the extractants performed similarly in predicting responsive fields. The interpretation was limited to soils with a CEC less than 7.5 meq/100 g. No limitation due to pH was noted, but the range in pH was quite small.

Boron and molybdenum extractants

Ponnamperuma et al. [25] compared 0.05 *N* HCl extraction with the reflux method for boron on 53 soils. Rice was grown on the flooded soils, scored visually for boron toxicity, and the plants analyzed for boron content. The 0.05 *N* HCl method separated boron-toxic soils from nontoxic soils and gave a better correlation (r = 0.91**) between available and plant boron than did the reflux extraction (r = 0.84**). The toxic limit by the 0.05 *N* HCl method was provisionally set at 4 ppm.

Bhella and Dawson [4] showed that anion-exchangeable molybdenum (Dowex 1-X4) was a good indicator of available molybdenum in 30 soils from western Oregon. The correlation coefficients of anion exchangeable molybdenum versus pH was 0.803**; versus plant molybdenum it was 0.861**; and versus plant nitrogen content it was 0.875**. Although none of the laboratories surveyed in this study reported using the anion exchange method, perhaps some studies should be done to examine its merits in soils of the tropics.

Lowe and Massey [18] examined a soxhlet apparatus for extracting molybdenum by hot water over a period of 10 hours. They worked with some 43 soils from Kentucky and found that hot water-extractable molybdenum showed better correlations with plant molybdenum contents (r = 0.83) than did ammonium oxalate (r = 0.18) for cultivated soils. The corresponding correlation of molybdenum uptake by alfalfa versus soil pH was 0.65. They concluded that the hot water-soluble method of extraction for available molybdenum was considerably better.

Pathak et al. [24] grew alfalfa on 13 Indian soils and determined a correlation coefficient of 0.617** between uptake of molybdenum by alfalfa and the hot water-extractable molybdenum of Lowe and Massey [18] compared to a correlation coefficient of 0.257 for the ammonium oxalate method of Grigg [9]. They concluded that the hot water method was superior.

Mortvedt and Anderson [21] developed simple and multiple correlation coefficients for forage legumes grown in the southern states of the United States from 1977 through 1979. They obtained correlation coefficients for alfalfa yields versus soil Mo of 0.315**, versus soil pH of 0.641**, and versus soil Mo + soil pH of 0.714**. Similar correlations for clover were 0.399**, 0.578**, and 0.666**. Soil Mo in their study was that extractable by ammonium oxalate. They found that molybdenum uptake strongly increased with soil pH. Maximum yields were associated with plant molybdenum contents of greater than 0.5 ppm in the plants. No critical ammonium oxalate levels were obtained in their study.

Karimian and Cox [12] found that neither ammonium oxalate- nor resin-extractable Mo was of value in predicting a response of cauliflower to Mo fertilization. Responses were more related to soil pH and an estimate of the degree of crystallinity of iron minerals. This again emphasizes the importance of considering other soil properties.

Summary and conclusions

Many extractants have been used to diagnose micronutrient deficiencies throughout the world. So far no particular extractant has been found to be superior under all conditions. Nevertheless, many studies conducted during the past 10 years show that several soil text extractants may be used successfully to diagnose micronutrient deficiencies. The most common of these are the dilute acids and the chelates for the analyses of iron, manganese, copper, and zinc. The use of dilute acids is limited to acid soils. Chelates have been used most extensively on alkaline soils. The DPTA extractant was designed for use on calcareous soils, but studies on acid soils indicate it may be quite applicable on those as well. The current limitation on chelates may be one of lack of calibration more than anything else.

Calibration of micronutrient soil tests with various extractants has been difficult. Extractants that are most practical for routine application allow analyses of several elements, both macronutrients and micronutrients. If the soil-solution ratios are very high, dilution of the already low concentration of micronutrients aggravate the problem of getting an accurate reading. Also contamination becomes a greater factor at low concentrations. For these reasons detailed standardized procedures are essential.

Perhaps the greatest difficulty in calibration studies has been the lack of consistent yield responses under field conditions. Most of the comparisons among micronutrient soil test extractants have been conducted in the greenhouse with a few soils providing only a limited range of conditions.

Consideration of soil conditions is important in the temperate region and may be even more important in the tropics. Most soils in the tropics are similar to those in the temperate region but a few are not. There is a small percentage of Oxisols in the tropics, but these are not greatly different from

some of the Ultisols of the temperate region. In general, there is a wider range of soil conditions in the tropics than in the temperate region.

Inclusion of other soil properties has been shown to be worthwhile in the interpretation of a micronutrient soil test in many instances. In fact, for some tests such as molybdenum, the other properties are usually more important than the extractable soil concentration in predicting response. With acid extractants inclusion of soil pH is essential for manganese and, in some cases, for zinc.

Selection of an extractant for a micronutrient soil test may not be as critical as was previously thought when soil conditions are taken into account. That is, the prediction ability does not vary widely among extractants. Selection can be made on the basis of practicality and experience. Extractants designed for multiple nutrient analyses on a routine basis are advantageous. Detailed standardized procedures for these are essential. Experience with an extractant on similar soils should also be an advantage, even though calibration data have not been published for a given region.

Although many extractants have been used for the micronutrients iron, manganese, copper, and zinc in soil testing laboratories in the tropics, it appears that three are most common. Development of these can be traced to the temperate region, and most published calibration data are from there; nevertheless, considerable experience has been amassed with them in the tropics. Published calibration data are available for DTPA and those data are also considered applicable for the more recently developed ammonium bicarbonate DTPA extractant. Sodium carbonate with EDTA lacks extensive calibration data.

Dilute acids have been used extensively in the tropics for iron, manganese, copper, and zinc. Common concentrations are 0.050, 0.075, and 0.100*N*. Recently the trend has been toward the more dilute solutions, but there are more calibration data for 0.1 *N* and the double acid which is 0.075 *N*. Soil pH should also be included with the dilute acids methods.

Soil testing laboratories in the tropics have not made wide use of acid extractants with chelates, such as the ammonium acetate with EDTA at pH 4.65 used in the Finland-FAO study. This extractant was better for copper than was DTPA in that study but was not quite as good for manganese or zinc. Field calibration on a wide range of soils is needed for this extractant.

If one were to recommend an extractant for iron, manganese, zinc, and copper that should be applicable to routine laboratory analyses of soils of the tropics, it would likely be DTPA or ammonium bicarbonate-DTPA for alkaline (and possibly acid) soils and the double acid (0.05 *N* HCl + 0.025 *N* H_2SO_4) for acid soils with inclusion of other soil properties as appropriate. Unfortunately, there are no routine laboratory analyses for boron and molybdenum. Hot water is still the standard extractant for boron, although 0.05 *N* HCl has shown promise. Ammonium oxalate still remains the commonly used extractant for molybdenum.

In the future, advances in soil testing may not all be made by searching for an 'ideal' extractant suitable for all soils; they may be made by carefully standardizing a given procedure and improving its interpretation with the inclusion of important soil factors that affect extractability and availability of nutrients.

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8. Plant tissue testing for micronutrient deficiencies and toxicities

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Summary

The relationship between nutrient concentration and yield, when properly used, is a powerful tool for diagnosing the nutritional status of annual crops for B, Cu, Mn, Mo, Zn and occasionally Fe. Imbalance between P and Zn may affect interpretation of plant Zn data at high levels of P. Also, lack of adequate field calibration, especially that involving recently matured leaves, within geographical regions at various yield levels makes the interpretation of data for some crop-element situations difficult. Mobility of elements in plants during growth should be considered when selecting tissues for analysis. Although there undoubtedly will be exceptions, fertilization of most annual crops in the year of diagnosis is unlikely to be based on plant analysis. Successful use of plant analysis for diagnosing the micronutrient status of plants demands careful attention to plant sampling, processing of samples, and laboratory techniques. These aspects and problems with calibration and interpretation of data are discussed in detail. Sap tests would appear to have only a small role to play in diagnosis of field micronutrient problems, but they may be of assistance in studying Mn toxicity and deficiency.

Introduction

Plant analysis is a procedure by which the nutritional requirement or status of an element, an inorganic fraction of the element, or some related organic of an element, an inoragnic fraction of the element, or some related organic compound or enzyme activity that is associated with the metabolism of the plant. Plant analysis involving the micronutrients B, Cu, Fe, Mn, Mo and Zn is generally believed to be more useful for orchard or perennial crops than for annual crops [89].

In this review general principles and methodology will be discussed, but the agronomic emphasis will be placed on micronutrient analyses for B, Cu,

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Fe, Mn, Mo and Zn and the production of annual crops. Analytical data for micronutrients are usually expressed in terms of ppm or micrograms of element per gram of oven-dried tissue ($\mu g/g$).

Traditionally, plant analysis is used: (1) to make fertilizer recommendations for the current crop; (2) to identify causes of poor growth, due to either deficiencies or toxicities, under field conditions; (3) to identify possible problems associated with introduction of new crops into an area; (4) to evaluate the effectiveness of fertilizer programs; (5) to survey the nutrient status of a crop within a region; (6) to complement soil test programs; and (7) to gain an understanding of interactions among elements. Plant analysis also has an important role to play in comparing nutrient utilization by different cultivars and species. Siddiqi and Glass [94] proposed that a utilization quotient, defined as biomass per unit amount of nutrient present in biomass, should be used in such comparisons.

Because of the shortness of the growing season for annual crops, the value of plant-analysis programs for fertilizing the current crop is often questioned. However, several successful uses of the technique with micronutrients have been reported [28, 29, 32].

Goodall and Gregory's classical treatise [33] on plant analysis and a number of other general reviews provide useful background reading about this technique for evaluating plant health [2, 9, 17, 18, 20, 44, 48, 55, 56, 62, 89, 98, 105, 106, 107, 112, 113].

Theory of plant analysis

The underlying assumption behind the use of plant analysis as a diagnostic tool is that there is some relationship between levels of chemical constituents in the plant and the health of plants. The literature is not always unequivocal as to the desirable constituent to determine, the plant part and time to sample, and the meaning of the analytical data obtained. This uncertainty reflects partly the complexity of the problem and partly, for many plant species, the lack of data from suitable designed experiments.

Relevant chemical constituents

Total concentrations of B, Cu, Fe, Mn, Mo and Zn in plant tissue are normally used for diagnostic purposes. However, "active" Fe fractions, enzyme activities associated with an element, and ratios of elements are also used.

The concept and literature concerning an "active" Fe fraction and the uncertainty about the effectiveness of using total Fe for diagnostic purposes were discussed by Goodall and Gregory [33] over 35 years ago, but the issues are not yet resolved [81, 111]. A new technique (see Table 1) based on the quantity of Fe^{2+} which reacts with O-phenanthroline was found, unlike total Fe, to differentiate between the chlorotic and green leaves of rice and

Table 1. Comparison of total and O-phenanthroline-extractable Fe as criteria for separating healthy (green) and iron-deficient (chlorotic) rice plants at five sites [50]

Site	Total		O-Phenanthroline	
	Green	Chlorotic	Green	Chlorotic
	Fe, ppm			
1	135	260	51	27
2	170	200	55	29
3	140	220	53	29
4	130	270	50	34
5	160	260	52	30

possibly other crops [50]. An attractive feature of this test is that washing of leaves prior to analysis is not needed. Hydrochloric acid was previously reported to remove "active" Fe fractions from various plants, including soybeans [23, 33]. Peroxidase activity, rather than total Fe, has also been employed to diagnose Fe deficiency [7]. Iron deficiency in corn reportedly can be diagnosed by a rapid field test for peroxidase activity [8].

Many cases of Zn deficiency in the field are associated with high levels of soil P. Phosphorus-induced Zn deficiencies in plants are usually attributed to plant-dilution effects, to restricted translocation of Zn, or to an imbalance of P and Zn [82], but they may also involve a P toxicity [61]. Inactivation of Zn due to an imbalance of P and Zn could affect the efficacy of total Zn analyses in plants with high levels of P. Andrew et al. [3] concluded that normal response curves can be used for the determination of critical Zn concentrations provided samples with high P values are discarded. Gibson and Leece [31] found that total Zn in corn plants well supplied with P fertilizer was similar in both Zn-deficient and healthy plants. They proposed use of leaf carbonic anhydrase, but not ribonuclease or adolase activities, as an index of "active" Zn in corn. Various measurements of enzyme activities have been proposed for measuring the Fe, Cu, Mn, Zn and Mo status of plants [56]. Under certain conditions ratios such as P/Zn [12] and Fe/Zn [71] were found to be more effective than total Zn for diagnosing Zn deficiency in beans and corn, respectively. Shaw [93] suggested that the formation of red zinc dithizonate in nodal tissue of corn offered promise as a rapid field test for Zn.

For Mn, quick sap tests, which involve rapid semiquantitative analysis of petiole or stem sap under field conditions, were described by Nicholas [72]; these tests can be used for determining both deficiency and toxicity levels of Mn in selected horticultural crops. Syltie et al. [102] subsequently found that the sap of the midrib from a corn leaf below and opposite the ear leaf at early tassel and the sap of the petiole of the youngest mature leaf of soybean at the early pod stage can be analyzed for Mn to diagnose Mn adequacy. The possibility of using sap analysis, including that for Mn, to select plant material for regular foliar analysis has also been advocated [63]. With intensification of agriculture in tropical regions with acid soils, a suitable

sap test for Mn toxicity may prove to be an effective screening tool. Scaife and Bray [92] reviewed the role of quick sap tests for controlling the nutrient status of plants.

Nutrient level and plant growth

Knowledge of the relationship between nutrient concentration and yield is essential for interpretative purposes and for selection of the most suitable tissue for analysis. A schematic representation, based on that given by Smith [98] and Ulrich [107], for such a relationship is given in Figure 1. AB is a zone in which yield increases as nutrient concentration decreases at severe levels of deficiency. The problem of the so-called Steenbjerg or Piper-Steenbjerg effects occurs in this zone [58, 100]. Bates [9] referred to curves with AB zones as being "C-shaped." BC is a zone of large increases in dry matter with small increases in nutrient concentration and is equivalent to Ulrich's [107] "deficient" zone or Macy's [64] "minimum percentage." CD is a zone in which the nutrient concentration increases as yield increases at a proportionately slower rate; this zone corresponds to Macy's "poverty adjustment" [64] or Ulrich's [107] "transition" zone. DE is a zone in which no increase in yield is observed in spite of large increases in nutrient concentration; it corresponds to Macy's region of "luxury consumption" [64] or Ulrich's "adequate" zone [107]. EF is the "toxic" zone in which yield progressively decreases as nutrient concentration increases.

C-shaped curves [9] cause problems in interpretation of plant analysis

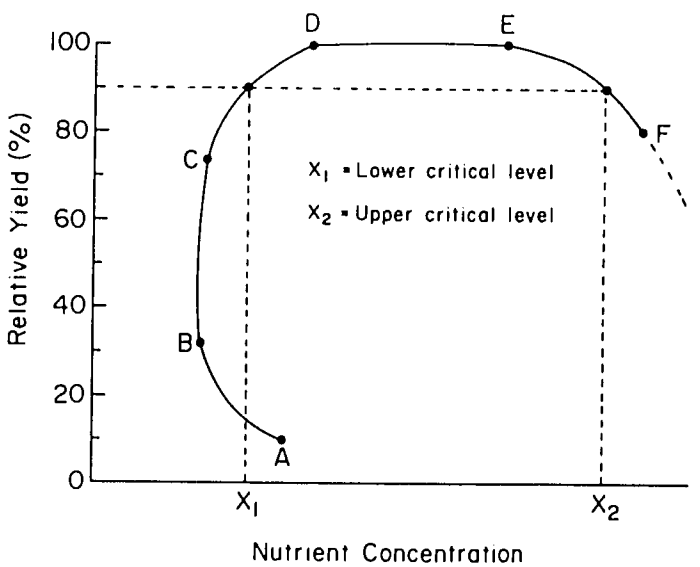

Figure 1. Schematic representation of the relationship between yield and nutrient concentration and of critical value concepts based on reports of Smith [98] and Ulrich [107].

data. Two distinctly different types of these curves have been reported: (1) those associated with low yields due to a deficiency of the element required [100]; and (2) those associated with an element not present in minimum amount required when another element causes a "Liebig Law of the Minimum" effect [104]. Problems due to the first type may be identified by sampling recently matured leaves or plant tissue soon after the appearance of symptoms [9]. Reported causes of this anomaly may be delayed senescence [87], stimulation of carbohydrate production which causes a dilution effect [95, 100], accumulation of a toxic level of another element at a low level of the element in question [70], and reduction in number of plant sinks such as tillers or grains in cereals [25]. The second type of situation is associated with growth responses caused by application of a second deficient element [104]. The possibility of complications arising from multinutrient deficiency must always be suspected with analytical data from severely deficient plants.

The ideal plant analysis situation is to arrange sampling procedures to eliminate the possibility of working in zone AB. Sharp breaks in the "transition" zone CD and in the "toxic" zone EF with reproducible critical values little affected by sampling time make diagnosis easier. Plant analysis is of limited value unless adequate research is done to provide a basis for interpretation and for selection of suitable sampling techniques, preferably with the genotypes of interest. Cultivars of many species differ greatly in their susceptibility to micronutrient deficiencies and toxicities [120], but information on intraspecific variability in critical values is limited. Corn genotypes vary in the critical level indicating Zn deficiency [65], and cultivars of wheat, cotton, and soybeans display different critical levels for Mn in the toxicity range [27].

Various terms are employed to describe quantitative or semiquantitative relationships in plant analysis. Lower and upper critical values represent nutrient composition levels in zones CD and EF, respectively. Ulrich and Hills [106, 107, 108] and Ohki [74] associate these lower and upper values with yield reductions of 10%. Other researchers define the lower critical level as being that nutrient concentration at which the element is barely above the point of limiting growth [98], the level at which a growth stress may be expected to occur [67], the level corresponding to maximum growth under a given set of conditions [70], or the nutrient concentration which is just deficient for maximum growth [105].

Dow and Roberts [21] in agreement with Smith [98] favored the use of a critical nutrient range, rather than a single critical nutrient concentration, since it is difficult to establish a single point experimentally and a single value may vary under different conditions. Although Ulrich and his associates [108] frequently give a point in zone CD (see Figure 1) as the critical value, that school of researchers recognizes that a narrow range more truly represents the situation [105]. Leaf composition values are also expressed as a series of ranges such as deficient or showing deficiency symptoms, low,

normal or sufficient, high, and excess or showing toxicity symptoms [18, 56, 89, 114]. Concentration values within ranges established under different conditions may vary considerably.

The methodology for determining critical values for annual crops is now well established, but each element/crop situation must normally be studied separately. Such studies evaluate the extent to which the plant part analyzed, the time of sampling, and the genotype affect the critical values. Crops are first grown under greenhouse conditions in nutrient solutions or in a suitable soil with different levels of the nutrient under study [75, 106]. Critical tissue data are determined at this stage by relating yield of dry matter, often expressed as percentages of maximum yield, to nutrient concentration. Specific values may be obtained by drawing curves to fit multiple data points in the "transition" and "toxic" zones [75], or by use of regression [10] or the Cate and Nelson overlay techniques [16, 91] on the experimental data.

As a followup to the greenhouse work, the critical values should be checked in field experiments suitably designed to determine the responses of the portion of the plant that is of economic value to the element in question. The part of the plant sampled in the field study is normally selected on the basis of the greenhouse study. Determination of critical values in the "transition" zone is usually stressed in the field study.

Selection of homogeneous field sites is much more difficult for micronutrient work than for P and N studied. Consequently, field data from many experiments often show no response to the micronutrient or have a high coefficient of variability. The heterogeneity also presents a problem with using unknown plant samples for routine analysis; inadvertent mixing of samples with variable composition in a composite sample may result in masking of a possible deficiency. To overcome this effect, Gartrell et al. [29] suggested that the bulk sample for diagnosing Cu deficiency in wheat should be taken from 10 identical plants from the smallest, most uniform patch of soil possible. Such a sampling technique is probably appropriate for the diagnosis of a specific problem, but it makes extrapolation of findings to entire fields difficult.

An excellent series of studies by Ohki [75, 77, 78, 79], in which critical values for Mn in soybean production were determined, can be consulted for additional insight into calibration for plant analysis. Another useful study illustrates greenhouse techniques for determining critical tissue concentrations of B, Cu, Fe, Mn, and Zn in cassava [39]. Data pertaining to critical nutrient levels have also been developed by analysis of plants showing characteristic deficiency symptoms; this approach is not as satisfactory as the previously described experimental approach [105], but for an element such as Mo it may be of some value.

Tissue selection and time of sampling

When plant analysis is used for making diagnoses or fertilizer recommendations, a part of the plant, usually recently matured leaves, is preferred for

determining B, Cu, Fe, Mn, Mo, and Zn [17, 105]. However, a few researchers favor whole-plant analysis at the boot stage for crops like wheat, oats, and barley [67, 114]. Some criteria that should be considered in the choice of type of tissue are as follows:

1. The breaks in the yield-nutrient concentration curve between the "adequate" zone and the "deficient" and toxic" zones should be sharp. Few definitive studies have been made which justify the choice of tissue for micronutrient analysis in tropical annual crops.

   Loneragan et al. [59] concluded that younger and older leaves would be clearly superior for diagnosing the nutrient status of immobile and mobile elements, respectively. Thus young tissue, rather than old leaves or whole plants, should be used for diagnosing the B status of plants. However, for the elements Fe, Mn, Zn, Cu, and Mo, classed under certain circumstances as being intermediate in mobility [15], the problem is more complex.

   Young blade tissue was efficacious for indicating both conditions of deficiency and toxicity for Mn in soybeans [75] and Zn in cotton [74], even though the toxic accumulations of the elements were much larger in older leaves. However, in a subsequent field study, Ohki et al. [78] found that the transition zone for Mn deficiency in soybeans broadened with a delay in sampling; the critical value also increased late in the season and sampling blade 2 at 9 weeks was favored for diagnosis.

   The youngest fully expanded leaf of sorghum at the boot stage [73] and of wheat from the seedling stage to senescence [29, 30] were superior to older leaves for diagnosing Mn and Cu deficiencies, respectively. The B level in the youngest mature leaf of sunflower at flowering was closely related to the percentage of deformed heads suffering from B deficiency [10]. Iron is generally considered relatively immobile in plants, and young tissue must be analyzed for diagnostic purposes [111].

   Some micronutrient deficiencies such as Zn deficiency in corn [83] and Fe deficiency in flax (*Linum usitatissimum* L.) [80] are often associated with cool or excessively wet conditions early in the season, but subsequently the plant grows out of the deficiencies as availability of soil micronutrients increases late in the season. Calibration studies using plant analysis data from such experiments are difficult, and the likelihood of a response to a micronutrient fertilizer is probably dependent on the yield potential and the length of the deficiency period.

2. The likelihood of Steenbjerg effects [100] developing and resulting in tissue concentration values greater than those associated with a deficiency must be minimized. Bates [9] considered that this problem could be reduced if sampling were restricted to plants with newly

developed symptoms.

3. The part of the plant that is sampled should preferably be one for which the critical concentration value is little affected by sampling time. Such a requirement is more difficult to attain with a fast-growing annual plant than with a perennial plant [98]. Critical concentration levels for whole plants, however, change during growth of cereals [60, 104]. Grain formation and lack of production of young, recently matured leaves in determinate crops with sexual stages present a sampling problem late in the growing season.

   Melsted et al. [67] provided data showing how leaf position and time of sampling of corn around tasseling influenced the levels of Mn, Fe, B, Zn and Cu. The effects, which probably were measured in the zone of "adequacy," varied according to the element.

4. Ease of sampling should be another factor considered in tissue selection. The corn ear leaf, or an adjacent one, which is customarily and easily sampled at silking or tasseling, is frequently analyzed for micronutrients [47, 68, 85]. The efficacy of this leaf for diagnosing micronutrient deficiencies, especially when a deficiency of Zn occurs early in the season, is questionable. Ohki et al. [76] suggested that leaf 3 or 4 might be superior to the ear leaf for diagnosing the Zn status of corn. From an analytical point of view the analysis of one tissue for most essential macro- and micronutrients is advantageous. Selection of whole plant samples for analysis of small grains also seems to be partly related to ease of sampling and convenience.

Preparation of samples for analysis

Attention must be paid to the following points during sample preparation: (1) respiration losses must be avoided during transportation of tissue to the processing center, (2) adequate subsampling techniques must be used both before and after grinding, (3) samples must be effectively ground to the required particle size, and (4) effective drying and storage techniques must be employed. Contamination must be guarded against at all stages. Sample preparation has been frequently discussed [17, 43, 44, 48, 69, 89, 96, 98, 101].

1. Any samples showing evidence of rotting at the time of processing should be discarded [57]. Most samples that cannot be processed within approximately 4 hours generally should be loosely placed in polyethylene bags, transported in an ice chest, and kept refrigerated until cleaning and oven drying can be done [17].

2. Not more than about 100 g of tissue can be finely ground conveniently. Subsampling of dried tissue before grinding tends to increase greatly the subsampling errors because of separation of veinal and interveinal tissue. If necessary, fresh samples can be cut

with stainless steel scissors or knives, uniformly mixed, and then subsampled by quartering. The ground, dried material must also be mixed uniformly before taking subsamples.

3. Many currently recommended methods of analysis require from 0.5 to 3 g of ground plant material. Material for analysis should be ground to pass sieves with either 0.8-mm or 0.4-mm openings (20- or 40-mesh, respectively); the finer material is preferable with samples in the 0.5 to 1 g range. Stainless steel Wiley mills are often used [36], and care must be taken to ensure that all the plant tissue passes through the screen. Plant material is heterogeneous, and considerable time is sometimes required to comminute the fibrous tissue. In one study, fractions of different particle sizes from ground samples contained different nutrient concentrations, but the effects differed among species [97]; this indicates that both fine grinding and careful mixing are essential.
4. Enzyme activity is usually stopped in fresh plant tissue by heating in forced-air drying cabinets, preferably supplied with filters to remove dust and maintained at 60° 70°C for 24 to 48 hours. Samples should not be packed tightly in containers or within dryers or allowed to become scorched [88]. Blades normally dry much easier than stems or petiole tissue which frequently must be cut into small pieces. Plant tissue is hygroscopic, and the finely ground powder must be redried after grinding. Drying most ground plant samples at 85°C for 12 hours would appear to be adequate for most analytical purposes.

Chemical analysis of plant tissue

Contamination problems

An understanding of likely causes of contamination is essential for increasing the efficacy of any plant analysis program, particularly one involving micronutrients. Great care must be taken to (1) remove any surface contamination; (2) avoid contamination during the collection, drying, grinding, and storage of plant tissue; and (3) avoid contamination during the analysis.

1. Any surface contamination likely to interfere with the analyses must be removed soon after the relevant tissue has been collected and before it is dried or wilted. Washing tissue requires the ready availability of distilled and/or deionized water. If a knowledge of total concentration of Fe in the plant is required, washing of plant tissue is essential. Many researchers have shown that inflated Fe values are obtained if tissues are not washed [4, 26, 37, 41, 51, 52, 99, 103, 110]. However, results of one recent study with nonsprayed soybeans grown both out-of-doors and in a greenhouse suggest that measurement of the "true" Fe content of leaves is difficult even with washing

[110]. According to Mitchell [69], an effective test for soil contamination of plant samples is to analyze for Ti, which is not normally absorbed in appreciable amounts by plants.

Soil contamination is removed much more easily than are micronutrient sprays adhering to tissue [4, 99]. Detergent alone appears to be as effective as HCl or HCl-detergent mixtures for removing soil (14), but HCl-detergent washes are recommended if plants have received alkaline sprays containing micronutrients [111]. However, such sprays are difficult to remove even with acid-detergent [4, 99] or EDTA-detergent washings [103]. If detergents are used for washing, care must be taken to avoid contamination with any element of interest.

Small or negligible losses occur from many tissues during washing procedures of short duration [4, 5, 13, 37, 52]. However, when apple leaves were soaked in 1 *N* HCl for 10 minutes to remove strongly held Zn-spray material, elements such as K, Mg and Mn were apparently lost in the wash water [84]. An effective washing procedure was proposed by Chapman [17] to remove soil.

Most research has shown that, provided reasonable care is taken to brush off any adhering soil from plant tissue, washing has little effect on unsprayed plant tissue values for Cu, Zn, Mo, and B [5, 13, 14, 26, 37, 52]. However, washing occasionally has slightly reduced the Mn concentrations in plant tissue, presumable by removing contamination [14, 26]. Experience, knowledge of the local situation, and the value of Fe data are factors influencing the decision of whether to wash tissue or not.

2. Care should be taken that utensils used for harvesting and preparing samples for analysis do not introduce contamination. Some paper bags contain B and could cause contamination [117]. Drying ovens should preferably be of stainless steel construction or painted with a high quality epoxy paint; galvanized trays must not be used because of likely Zn contamination. Mechanical chrome-plated [53, 111], agate [43, 86], and stainless steel mills [5, 36] are recommended for grinding; brass and ordinary steel parts must not be allowed to come in contact with plant material. Also, storage of ground plant material in polyethylene bags or glassine-lined bags, rather than in glass containers, is occasionally preferred to decrease contamination [86, 95]; glass bottles, however, are commonly used.
3. Extreme care is needed to avoid accidental or systematic introduction of foreign elements in the course of various analytical operations [86]. As far as possible reagents should be stored in polyethylene containers. Acid washing of glassware followed by rinsing in distilled or deionized water is essential. Johnson and Ulrich [43] recommended washing glassware in warm 3 *N* HCl, rinsing in succession with

several small portions of redistilled water and 10% (w/v) $(NH_4)_3$ EDTA (pH 8), and finally washing with redistilled water. Washing glassware used in micronutrient studies with 20% (v/v) HNO_3 [49] and 0.5 *N* acetic acid or 0.5 *N* HCl [88] followed by rinsing with tap water and successive portions of distilled and/or deionized water has also been reported.

Rubber used in tubing, stoppers, clamps of shakers, etc., can cause Zn contamination, and its use should be avoided [69, 86]. Rubber bulbs attached to transfer pipettes can cause contamination with Zn, Cu, and Fe [5]. Pyrex or Kimax glassware contains B, and any solutions used in analyses for this element should be stored in polyethylene bottles [86]. In separate studies, dust from linings of furnaces used in dry-ash digestions was found to cause both B [116] and Zn and Al [5] contamination. Lining the inside of the furnace with stainless steel sheeting eliminated the problem for Zn and Al [5]. Corrosion of metal surfaces within the laboratory can be particularly troublesome. Copper or brass fittings should be replaced or coated with an epoxy paint or resin; basic salts formed on copper surfaces can be readily diffused as a fine dust [88]. Pinta [86] suggests that all personnel working with trace elements should be warned of all the risks of contamination. Glassware used for trace element analyses should be reserved for that purpose. Colorimetric analysis for phosphorus frequently contaminates laboratories with Mo, and such work should be done away from a micronutrient laboratory doing Mo analyses. Every effort should be made to control dust in the laboratory.

Careful attention should be paid to the distilled-deionized water system [24]. Rubber, brass, bronze, or copper surfaces should not come in contact with purified water, and polyethylene storage containers should be used.

Precision and accuracy

Considerable effort is needed to ensure that good precision and accuracy are obtained during chemical analysis. Precision, representing operator or random laboratory errors, can be easily calculated as a coefficient of variation by doing analyses on subsamples of a relevant sample. However, this gives no estimate of method bias or accuracy [66].

Measurement of accuracy is best obtained by including a "standard" control sample in each batch of unknown samples. This task is simplified by the availability of plant samples as Standard Reference Materials (SRM) from the U.S. National Bureau of Standards. SRM 1570 (spinach), SRM 1571 (orchard leaves), SRM 1573 (tomato leaves), and SRM 1575 (pine needles) have been extensively used, and data of interest for the first three samples are given in Table 2. The SRM plant tissues described in Table 2 contain more than 10 times the reported critical amounts of Cu in young wheat leaves at

Table 2. Analytical data provided by the U.S. National Bureau of Standards for Fe, Mn, Zn, Cu, Mo and B for three plant standards.

Material	SRM No.*	Element†					
		Fe	Mn	Zn	Cu	Mo	B
		μg/g					
Spinach	1570	555 ± 20	165 ± 6	50 ± 2	12 ± 2	a	(30)
Orchard leaves	1571	300 ± 20	91 ± 4	25 ± 3	12 ± 1	0.3 (± .1)	33 ± 3
Tomato leaves	1573	690 ± 25	238 ± 7	62 ± 6	11 ± 1	b	(30)

*The supply of SRM 1571 has unfortunately become exhausted but a new citrus leaf sample, SRM 1572, became available during 1982.
†"a" and "b" indicate that no information from National Bureau of Standards (NBS) was provided; however, data reported in the literature [49] give values of 0.3 ± 0.1 and 0.65 ± 0.10 and 0.62 ± 0.04 μg/g, respectively. Numbers in parenthesis were noncertified NBS values.

tillering [29] and of Fe in corn leaves at silking [67]. Cost of SRMs is now exceeding $100/75 g, and this may limit their use on a routine basis in some laboratories.

Several laboratories or groups of analysts may conveniently pool their resources for preparation and standardization of a suitable plant standard. Use of a carefully analyzed control, such as an SRM sample, is efficacious in the calibration of secondary standards. Interlaboratory exchanges of suitable samples have a valuable role to play in the evaluation of new methods and in quality control [40, 45, 54, 115].

Method of analysis

Chemical methods for determination of total elements based on emission spectroscopy, atomic absorption spectrophotometry (AAS), inductively coupled argon plasma emission spectroscopy (ICAP), and colorimetry require that the organic matter be removed and the elements be solubilized before analysis. Both wet and dry digestion techniques are commonly used. However, Baker and Greweling [6] reported that Cu and Zn analyses made on 0.1*M* EDTA extracts of sorghum and other crops yielded values comparable to those obtained after dry ashing. Choice of methods depends on such factors as convenience, safety, available equipment, and elements to be analyzed.

Where large numbers of plant samples are analyzed for diagnostic purposes, there is a tendency to favor dry-ashing techniques. One advantage of the dry-ashing technique is that a separate digestion is not required for B, which is difficult to analyze by wet-digestion methods because of possible contamination associated with use of Pyrex glassware [30] and volatilization during digestion [43].

Recommended dry-ashing techniques for plant tissue have been extensively discussed by Piper [88] and Gorsuch [34, 35]. Volatilization losses and reactions of micronutrients with surfaces of crucibles and with silica from

plants are possible causes of low recoveries with this method of organic matter removal. Gorsuch [34] concluded that considerable experience is needed in using this technique to solubilize effectively the elements in plant tissue; its application to unknown samples without first discovering its suitability is questionable. Overheating in furnaces must be avoided [34, 88]. Jones [46] recommended that the crucibles used, 15-ml high and made of porcelain, should not come in contact with walls or floors of furnaces heated to 500°C.

The availability of Al-heating blocks, which allow many 75-ml digestion tubes to be heated in a small area, has popularized wet-digestion techniques in the past decade [11]. Addition of one or two drops of kerosene and use of blocks thermostatically controlled at suitable temperatures greatly aid digestion [1]. Some digestion mixtures, discussed by Gorsuch [35], that have been used for plant decomposition are HNO_3-$HClO_4$ [1, 40, 49, 121], HNO_3-$HClO_4$-H_2SO_4 [43, 50], and H_2SO_4-H_2O_2 [119]. Nitric acid alone [38] was recently reported to be nearly as efficacious as HNO_3-$HClO_4$, the most commonly used digestion mixture for plant analysis.

Wet-digestion methods involving use of HNO_3-$HClO_4$ to destroy organic matter appear reasonably efficacious for recovery of Cu, Zn, Mn, and possible Mo, but not for recovery of Fe [49] or B [43]. Wolf [118] described a wet-digestion method for B determination involving heating of plant tissue with H_2SO_4-H_2O_2 in Vycor tubes. Gestring and Soltanpour [30] also concluded that B was not lost from HNO_3 digests heated at 90°C in Nalgene bottles.

The exact method of analysis will depend upon available equipment, number of samples to be anayzed, and cost considerations. Where large numbers of samples must be analyzed for essential micronutrients as well as for Al, P, Ca, Mg, Na, and K, ICAP techniques and dry ashing appear attractive for Cu, Mn, Zn, and B [46, 49]. However, sensitivity of ICAP techniques is poor [49] for Mo determinations at plant levels near 0.3 μg/g, a level well above that found in some Mo-deficient plants. Colorimetric techniques [22, 43] appear to be superior in such cases. Colorimetric techniques [42, 43, 118] probably are also to be preferred for plant B analyses if the AAS method, instead of ICAP or emission spectroscopy, is used for Cu, Zn, and Mn analyses. Because of difficulties with contamination and analysis, and the often-noted poor relationship of total Fe with plant Fe stress [33, 50, 110], it is questionable whether much emphasis should be placed on total Fe analysis for routine diagnostic purposes.

Difficulties with plant analysis

Both theoretical and practical difficulties restrict the applicability of plant analysis for diagnosing micronutrient problems in annual crops over wide regions. Special attention must be given to time of sampling and plant part

selected for analysis. Additional research is needed on the efficacy of using the same part for diagnosing both nutrient deficiencies and toxicities.

Although there undoubtedly will be exceptions, the prime use of plant analysis will probably be as an aid in the interpretation of field problems rather than as a routine means of making fertilizer recommendations. Micronutrient deficiencies in most areas of the world are secondary to deficiencies of N and P. This together with the cost of any routine plant analysis program, relative to the value of most annual field crops, places restrictions on the use of this technique.

If yields are extremely low because of a particular deficiency, only limited information about other elements can be gained from plant analysis. This situation is often encountered with plants growing on soils where micronutrient deficiencies are only obvious when deficiencies of N and P are rectified. Such situations are related to Liebig's Law of the Minimum [90]. For instance, Chaudhry and Loneragan [19] found that wheat when grown on a particular soil responded to Cu and Zn fertilizers only if nitrogen fertilizer was applied; the increased growth resulting from the response to N diluted the quantities of Cu and Zn to deficiency levels. Andrew [2] considered that, if a legume was not well supplied with symbiotic or mineral N, plant analysis for other elements served little purpose.

Multiple nutrient deficiencies at levels where plants respond to two or more elements, both individually and in combination, also present interpretation difficulties. Only limited research is available with annual crops showing how critical levels or ranges change in such circumstances.

Interactions between plant nutrients undoubtedly complicate interpretation of plant analysis data, and blind acceptance of individual critical values or ranges must be viewed with caution. Regression techniques have been used to refine relationships between critical values and yield [85, 109]. Bates [9] concluded that interactions become more important in the vicinity of the optimum yield. Adequate field research with specific crops in given environments is needed to evaluate the importance of interactions among nutrients and between nutrients and the environment.

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9. Micronutrient fertilizers and fertilization practices

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Introduction

Increased knowledge acquired during the past 25 years about plant requirements, sources, and most effective methods of applying micronutrients has increased their use in many regions. Higher crop yields, usually resulting from higher rates of NPK fertilizers, also may have increased needs for micronutrients. In addition, the dramatic shift in the tropics to higher analysis fertilizers such as urea, triple superphosphate, and diammonium phosphate, has decreased the amounts of some micronutrients applied to the soil as fertilizer contaminants.

Micronutrients are sold in forms which vary in physical state, chemical reactivity, cost, and relative agronomic effectiveness. Therefore, it is important to select the most effective and economical source for each particular crop and specific soil condition.

Micronutrient fertilization practices

There are two general philosophies to micronutrient fertilization – insurance or prescription applications. The insurance or "shotgun" philosophy has been used to add low amounts of more than one, and sometimes all, micronutrients to the soil. This method, designed to supply all micronutrients removed by a crop, also could be considered as a maintenance program. Premium fertilizers containing all micronutrients were promoted in this manner; usually this program did not consider specific crop needs nor levels of available micronutrients in the soil. Many of the micronutrients applied with this philosophy may not be needed by the crop, so this method may be wasteful of resources.

Maintenance applications may be economical on high-value crops, such as coffee, vegetables, and some tree crops. The fertilizer cost for this program usually is low in comparison with the possible decrease in income due to loss in yields and/or quality of these high-value crops. This philosophy also may be used for other crops where the nutrient status of the soil or nutrient needs of the crop have not been determined in a given region. After soil tests

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and crop needs of these lower value crops have been determined, the growers then could change to the prescription approach for micronutrient fertilization.

The prescription philosophy uses results of plant and soil analyses to assess the micronutrient status of crops and soils. It is recommended that only those nutrients which are required should be applied at rates necessary to obtain a specified yield goal for a crop in a given field. This practice helps prevent application of excessive amounts of needed micronutrients and eliminates application of those nutrients already present in adequate amounts. More precise recommendations also protect against antagonisms encountered among nutrients in plant nutrition due to unbalanced ratios in the soil.

Ideally, the prescription philosophy should be used for micronutrient fertilization of all field crops. Economic returns per unit area generally are lower with most field crops than with specialty crops. Therefore, fertilizer costs should be minimized but still give maximum economic yields. This can be best accomplished by determining the micronutrient status of the soil and then applying only those nutrients that will be needed by the crop. Use of the prescription philosophy requires soil testing and knowledge of crop needs in a given region, so it is a more intense program than the insurance philosophy.

The prescription philosophy requires formulation of different fertilizer grades for almost every field. Such formulations are possible with bulk-blended fertilizers or with certain fluid fertilizers but not with bagged products containing incorporated micronutrients. Therefore, premium fertilizers have been formulated to meet the general micronutrient requirements for a specific crop over a wide geographic area. For example, a premium fertilizer for maize may contain 1%–2% Zn, 0.5% Mn, and possibly very low amounts of the other micronutrients. Premium fertilizers for soybeans contain higher levels of Mn than Zn, while those for cotton contain mainly B and Mn. Because large tonnages of a specific grade are needed for profitable production the demand for such a grade must be estimated beforehand and integrated into the normal fertilizer production schedule.

Micronutrient sources

Inorganic sources Naturally occurring ores, manufactured oxides, carbonates, and metallic salts such as sulfates, chlorides, and nitrates are the main inorganic sources. Some oxides, such as Cu_2O, may be used as mined, but plant availability of other naturally occurring oxides, such as MnO_2, is so low their use is not recommended. Sulfates are by far the most common of the metallic micronutrient salts and have physical properties that make them suitable for use with mixed fertilizers. These sources also add plant-available S to soils, but the amount of S applied at most recommended micronutrient rates is low. Crystalline sulfate materials usually are converted to granular form for easier handling. Oxysulfates are produced by partial acidulation of oxides so that the product contains micronutrients, especially of Zn and Mn, in both

oxide and sulfate forms. Oxysulfates are sold in powder or granular form. Inorganic sources usually are the least expensive per unit of micronutrient, but they are not always the most effective for soil application.

Sulfates of Cu, Fe, Mn, and Zn are widely used for soil and foliar application, although $FeSO_4$ is not recommended as a soil application. Oxides generally cost less per unit of micronutrient than sulfates; most oxides are available to plants if they are in powder form and are mixed with the soil. Oxides are not water soluble so they are not effective for crops in granular form since their specific surface area is greatly reduced. Effectiveness of granular oxysulfates for crops is related to the level of water-soluble micronutrient in a product. At least one-third of the total micronutrient should be water soluble to be effective as a granular fertilizer.

Borax, $Na_2B_4O_7 \cdot 10H_2O$, has been the most common B source, but products containing fewer waters of hydration now are used more widely. Granular borates now can be made for applications with granular NPK fertilizers [21], and finely ground borates are produced for foliar sprays. Boric acid, H_3BO_3, also is used but it is more expensive per unit of B. Colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$, is a product of low water solubility. The most common sources of Mo are Na_2MoO_4, $(NH_4)_6Mo_7O_{24}$, and MoO_3. The molybdates are completely water soluble but MoO_3 is less soluble.

Organic sources Synthetic or natural chelates, natural organic complexes, and various combinations constitute the organic micronutrient sources. Chelates are formed by combining a chelating agent with a metal through coordinate bonds. Chelates may be synthetic (manufactured) or natural (from sugars or other natural products). A chelating agent is a compound containing donor atoms that can combine with a single metal ion to form a cyclic structure called a chelation complex, or more simply, a chelate. The word "chelate" is derived from the Greek "chela" or "claw" which describes the type of chemical structure. The stability of the metal-chelate bond generally determines the availability of the applied nutrient to plants. An effective chelate is one in which the substitution rate of the chelated micronutrient for soil cations is low, thus maintaining the applied nutrient in chelate form for sufficient time to be absorbed by plant roots.

Some chelating agents used for production of micronutrient chelates are: ethylenediaminetetracetic acid (EDTA), N(hydroxyethyl) ethylene diamine triacetic acid (HEDTA), diethylene triamine pentaacetic acid (DTPA), ethylene diamine di(o-hydroxyphenylacetic) acid (EDDHA), nitrilo triacetic acid (NTA), glucoheptonic acid, and citric acid. The most common chelating agent used with micronutrients is EDTA. Many chelates are sold in liquid form because production costs per unit of micronutrient are lower than those of the powdered form which requires drying. These liquid chelates are used mainly for mixing with fluid fertilizers. Dry chelates are incorporated in some granular NPK fertilizers, but their use generally is restricted to specialty products.

Natural organic complexes, such as lignosulfonates, phenols, and polyflavonoids, are produced commercially by reacting metallic salts with organic byproducts of the wood pulp industry. The type of chemical bonding of the metals to organic components in the above products is not well understood. Some of the bonds may be similar to those in chelates but the remainder are not well defined, hence, the term complexes. The most popular complexes are of Zn and Fe, although limited amounts of Cu and Mn complexes are produced. Products containing more than one micronutrient are made for foliar sprays or for application with irrigation water. Effectiveness of organic sources for plants varies widely. Synthetic chelates usually are more expensive than natural organic complexes, but they also may be more effective under certain soil conditions.

Fritted micronutrients Frits are glassy products whose solubility is controlled by particle size and variations in matrix composition. Frits generally are used only on sandy soils in regions of high rainfall where leaching occurs. Some producers mix frits with NPK fertilizers, but availability to plants of incorporated frits is not very high. Frits are more appropriate for maintenance programs than for correcting severe micronutrient deficiencies. Since government regulations now restrict indiscriminate disposal of industrial wastes, many industrial byproducts may be marketed as micronutrient fertilizers. Flue and baghouse dusts from galvanizing, pigment, rubber, battery, and other industries are used widely as Zn sources. Several processes are used to remove impurities from these materials, but some ZnO products are used without purification. Byproduct Zn chlorides, nitrates, sulfates and oxysulfates, and Mn sulfates and oxysulfates also are marketed as micronutrient fertilizers.

Some of these byproducts also may contain appreciable amounts of other heavy metals such as Cd, Cr, Ni, and Pb. The availability of these heavy metals to plants has not been clearly determined, but their effects should be minimal because the soil application rate is very low. For example, applying ZnO (60% Zn) containing 500 ppm Pb to soil at a rate of 5 kg of Zn/ha would result in a rate of only 0.004 kg of Pb/ha. These heavy metals are relatively immobile in the soil, so they will accumulate in the surface layer. If such byproducts are applied to the same field for a number of years, the levels of heavy metals in the surface layer of the soil could become significant.

Agronomic effectiveness

Relative agronomic effectiveness of two or more fertilizers is defined as the ratio of crop responses per unit of nutrient applied. For example, if maximum yields were obtained with soil application of 1 kg of Zn/ha as ZnEDTA and 5 kg of Zn/ha as $ZnSO_4$, the relative agronomic effectiveness of ZnEDTA would be five when compared with $ZnSO_4$. Determination of the relative agronomic effectiveness of several micronutrient sources requires

that several rates including the zero rate be used to develop crop response curves. Multiple regression analyses can be used to give relative agronomic effectiveness of various sources in multirate fertilizer experiments [12, 13]. Band application of several Zn sources with a 10-34-0 fluid fertilizer for maize at rates of 0, 0.11, 0.33, 1.1, and 3.3 kg of Zn/ha resulted in different orders of effectiveness for the Zn sources with each Zn rate [23]. The order of effectiveness at the lowest Zn rate was ZnEDTA > $ZnSO_4$ > ZnO. In contrast, yields were lower with ZnEDTA than with $ZnSO_4$ and ZnO at the highest Zn rate because Fe nutrition was adversely affected. Therefore, relative effectiveness of Zn sources depends on the rate at which they are compared. Obviously, the entire response curve must be considered when making such comparisons.

Boron: Crop response to B sources in tropical soils will be affected by rainfall distribution, soil texture, and B sorption by the soil. Borax is completely water soluble and subject to leaching, so more than one application per growing season may be required under such conditions. Colemanite, which has moderate water solubility, may be more suitable than borax for use in tropical or subtropical soil and climatic conditions. Colemanite and fertilizer borate were found equally effective for cotton and sunflower when incorporated with NPK fertilizers in Zimbabwe [47]. Both colemanite and B frits (low water solubility) were superior to borax for cotton on sandy soils in South Carolina under relatively high rainfall conditions [44]. Use of high initial rates of borax to offset leaching losses may result in B toxicity. Yield of hairy indigo was severely reduced with about 4 kg/ha of B applied as borax in Florida (Table 1), but yield was not affected by equal or higher B rates as colemanite or a powdered borosilicate [56].

Table 1. Effect of B sources varying in water solubility on yields kg plot^{-1} of hairy indigo on a sandy Florida soil [56]

B source	B solubility	B applied, kg ha^{-1} 0	1.25	2.50	5.00
		2.84			
Borax	high		2.86	1.84	0.64
Colemanite	moderate		2.72	1.84	2.14
Borosilicate[a]	low		2.91	3.55	2.36

a. Application rates were 2.25, 4.5, and 9.0 kg ha^{-1} of B, respectively.

Molybdenum Many tropical soils are very acid and probably are low in available Mo, especially for legumes. Both Na_2MoO_4 and MoO_3 were equally effective for several tropical legumes, including Siratro and Desmodium grown in association with panic grass in Queensland, Australia [28]. Both Mo sources were surface applied with NPK fertilizers but at rates up to 200 g of Mo/ha. Results also showed that incorporating MoO_3 in the seed pellet was

equally effective and assured a uniform application of Mo (Table 2). Differential response to applied Mo among legume species also was noted.

Table 2. Effects of molybdenum source and rate on yield and nitrogen concentrations in legume and grass species in Queensland [28]

Molybdenum applied (g ha^{-1})	Mo source	Siratro		Panic grass	
		yield (mt ha^{-1})	% N	yield (mt ha^{-1})	% N
0	-	1.0	2.56	1.5	1.93
25	MoO_3	1.4	2.85	1.8	1.98
100	MoO_3	1.6	3.12	1.3	2.06
200	MoO_3	2.0	3.19	2.0	2.14
100	Na_2MoO_4	1.8	3.12	1.8	2.10
100	MoO_3[a]	1.8	3.23	2.2	2.11
L.S.D. (0.05)		0.7		0.7	

a. Included in seed pellet.

Zinc More research has been conducted with Zn sources than with other micronutrients because Zn deficiencies are more widespread. There are several Zn sources which are widely used. Response of rice to Zn has been shown in many countries, and there are more reports of Zn deficiency with the development of improved varieties. Results of a 5-year study comparing Zn sources and methods of application for rice in nine countries showed that 5 kg of Zn/ha as $ZnSO_4$ supplied the Zn requirement of at least two crops [26]. Lower rates of application (1 or 2 kg/ha) were sufficient in greenhouse trials; chelated ZnEDTA was equal to $ZnSO_4$ at usual Zn rates in these studies but was ineffective at low Zn rates. These results were confirmed in another study [17]; apparently, the highly mobile ZnEDTA may move from the root zone during flooding. In contrast, several chelates were equally effective with $ZnSO_4$ for dry matter production of rice in the greenhouse [9]. Uptake of Zn was higher from the chelates than from $ZnSO_4$.

Zinc oxide was more effective than $ZnSO_4$ with mixed application to rice in two field experiments on a flooded calcareous soil in Egypt [3]. Effectiveness was related to the effects of these sources on Zn in soil solution; $ZnSO_4$ dissolved soon after application, which caused a sharp increase in solution Zn followed by a rapid decline. Zinc oxide dissolved more slowly and maintained soluble Zn at intermediate levels for at least 9 weeks. Suspensions of ZnO were more effective than ZnS suspensions, and inclusion of attapulgite clay in ZnO suspensions increased adherence to the roots but decreased Zn availability to rice [19].

Maize has a relatively high Zn requirement and numerous experiments have been conducted to determine the most effective Zn sources and rates. Maximum grain yields resulted from 1 to 2 kg of Zn/ha as ZnEDTA in Nigeria [43] and from 3 to 9 kg of Zn/ha as $ZnSO_4$ in Cerrado soils of central Brazil [41]. Lime applications decreased grain yields on these Cerrado soils even at high Zn rates; these soils are very low in available Zn, which then decreased

upon liming. Zinc sulfate, ZnO, and fritted Zn were equally effective for maize in Brazil [15]. Application of $ZnSO_4$ to an exposed subsoil resulted in increased yields on an Oxisol in Puerto Rico [4]. Chelated Zn sources were more effective than $ZnSO_4$ for maize in Indian soils [45].

Several other crops also have shown response to Zn. Zinc oxide was twice as effective as a granular ZnO-based byproduct for wheat in South Africa [11]. Zinc deficiencies in improved cultivars of potatoes in India have been corrected with $ZnSO_4$ application [20]. Cassava appears to have a high Zn requirement; Zn rates up to 20 kg/ha of $ZnSO_4$ were required for maximum yields in Colombia [24]. Responses to sources of Zn and other micronutrients for tropical crops, such as coffee, pineapple, and rubber, are summarized by deGeus [16].

Other micronutrients Agronomic effectiveness of Mn sources is closely related to the application method because available divalent Mn is easily oxidized to unavailable forms in neutral and calcareous soils. Maximum soybean yields from $MnSO_4$ were obtained with Mn rates of 2.2 kg/ha foliar, 5.6 kg/ha banded, and 11 to 22 kg/ha broadcast depending on soil pH [2]. Both $MnSO_4$ and MnO usually are equally effective for crops, but only if MnO is applied as a fine powder [36]. Similar results are reported for $CuSO_4$ and CuO. Because inorganic Fe sources are rapidly oxidized to unavailable forms in soil, foliar applications are much more effective per unit of applied Fe [38, 50]. Effects of micronutrient sources and rates of application on correction of micronutrient deficiencies have been reviewed elsewhere [8, 30, 31, 32, 36, 38].

Residual effectiveness The magnitude of crop response to a given micronutrient for succeeding crops is defined as its residual effectiveness. Both Cu and Zn have significant residual effects, so it may not be necessary to apply these micronutrients every year [50]. Three kilograms of Zn/ha as $ZnSO_4$ applied 4 years before cropping was adequate for maize in the Cerrado soil of central Brazil, but maximum soybean yields resulted with the 9 kg/ha rate of Zn (Table 3). Wheat yields were increased by Zn application to the

Table 3. Residual effectiveness of $ZnSO_4$ applied 4 years prior to cropping by maize and soybeans in central Brazil [42]

Zn applied (kg/ha)	Grain production: Maize (mt ha^{-1})	Grain production: Soybeans (mt ha^{-1})
0	3.28a[a]	1.08a
1	4.99b	1.57b
3	6.90c	2.13c
9	6.29bc	2.60d
27	6.25bc	2.81d

a. Values followed by the same letter in each column are not significantly different at the 95 % probability level by DMRT.

previous crop of rice but there were no residual effects in subsequent rice and wheat crops [5]. Broadcast $ZnSO_4$ applications or ZnO applied as a suspension for roots of rice transplants supplied Zn to a succeeding wheat crop on calcareous soils in India [54]. Neither Fe nor Mn sources have significant residual effects in neutral or calcareous soils because these micronutrients are oxidized to unavailable forms.

Methods of application

Seed treatment and root dipping Amounts which may be applied as a seed treatment are very limited; Mo is the only micronutrient that is usually applied in this manner. Seed coatings of ZnO provided sufficient Zn for rice on an alkaline soil and did not affect seed germination [19]. Dipping roots of rice transplants in a 1% ZnO suspension provided sufficient Zn at a lower cost than foliar or soil application [55]. Higher dry matter yields and Zn uptake resulted with soaking rice seed in a fritted Zn suspension than in a ZnEDTA solution in Nigeria [29]. Application of $ZnSO_4$ by seed treatment, foliar spray, or soil application was equally effective for potatoes in India [20].

Seed application of B and Mo resulted in increased yields, nodulation, and N content of beans in Brazil [48]. Seed dressing of Mo was very effective in preventing Mo deficiency of maize in Zimbabwe [51], although maximum crop yields were not attained with coatings to seed that was very low in Mo (<0.04 ppm). Soaking wheat seed in solutions of $CuSO_4$ or $MnSO_4$ for 12 hours just prior to planting resulted in increased yields and also Cu and Mn content of grain in Pakistan [33].

Foliar sprays Solutions containing one or more micronutrients are used widely as foliar sprays. Some advantages of foliar sprays are:

1. Application rates are much lower than for soil application.
2. Uniform distribution is easily obtained.
3. Response to the applied nutrient is almost immediate; therefore, deficiencies can be corrected during the growing season.
4. Suspected deficiencies can be more easily diagnosed with spray trials.

Some disadvantages are:

1. Nutrient demand often is high when plants are small and leaf surface is insufficient for foliar absorption.
2. Leaf burn may result if salt concentrations are excessive.
3. It may be too late to correct the deficiency and still obtain maximum yields.
4. There is little residual effect from foliar sprays.
5. Extra application costs may be required because more than one spray application may be needed.

Foliar sprays may not always be more effective than soil applications. Foliar B sprays to cotton were less effective than preplant soil applications on severely B-deficient soils in Nigeria [22]. Foliar sprays of B are recommended

for beans in Colombia on moderately deficient soils, but soil applications are recommended where B deficiency limits early growth [25]. Foliar Mo sprays did not result in increased rice yields in one location [40], but indirect effects of foliar Mo sprays on soil populations of N-fixing bacteria and blue-green algae increased yields and N content of rice at another location in India [10].

Soil application The most common method is applying micronutrients to the soil either as a broadcast (mixed) treatment prior to tillage or as a band application at planting. Broadcast applications allow a greater proportion of the soil in the root zone to be affected by the fertilizer. However, this also results in greater reaction of the soil with the applied micronutrient which may reduce its agronomic effectiveness. Surface broadcast applications of inorganic micronutrient sources without subsequent tillage usually are less effective for crops because the metallic micronutrients do not move into the root zone. However, topdressing $ZnSO_4$ after observing Zn-deficiency symptoms in rice was as effective as preplant broadcast $ZnSO_4$ applications in Pakistan [55]. Chelated micronutrients will leach into the root zone after surface application because chelates are not tightly sorbed by soil colloids.

Preplant or broadcast applications of $ZnSO_4$ (10 kg of Zn/ha) after puddling of soil were as effective as dipping roots of rice plants in a 1% ZnO suspension at transplanting from nurseries (Table 4). The latter method in widely used and is one of the least expensive methods for supplying Zn to transplanted rice [6]. Applying Zn sources to rice seedbeds also provides sufficient Zn for rice transplants in the Philippines and requires much less Zn than Zn application to the entire paddy [8].

Table 4. Effect of zinc sources and methods of application on rice yields, West Pakistan [55]

Zn source	Zn rate (kg ha^{-1})	Method of application	Grain yield (mt ha^{-1})[a]
			4.32 a
$ZnSO_4$	10	Preplant	5.98 bcd
$ZnSO_4$	100	Preplant	6.52 cd
$ZnSO_4$	10	Broadcast after puddling	6.01 bcd
$ZnSO_4$	100	Broadcast after puddling	6.92 d
$ZnSO_4$	10	Broadcast after first symptoms	5.69 bcd
$ZnSO_4$	100	Broadcast after first symptoms	6.17 bcd
ZnO	0.1[b]	Dip seedlings in 1% ZnO suspension	5.86 bcd

a. Values followed by the same letter are not significantly different at the 95% probability level by DMRT.
b. Approximate Zn rate.

Band applications of Mn sources generally are more effective than broadcast applications because Mn reacts with the soil to become unavailable to crops more rapidly with broadcast applications. Higher rates of Mn are required for broadcast than band applications for soybeans. Band application

of Mn sources is more effective with acid-forming than with neutral fertilizers because acid conditions in the fertilizer band delay the rate of Mn oxidation to less available forms [2]. Improvements in agronomic efficiency with band over broadcast applications are not as marked with Cu and Zn as with Mn and Fe applications. Inorganic Mn and Fe sources oxidize to unavailable forms in the soil, but Cu and Zn sources do not. Care should be taken to place starter fertilizers containing B at the recommended distances away from the seed row because B can be toxic to seedlings of some crops, even at low rates.

Application with NPK fertilizers It is difficult to apply micronutrient sources separately and uniformly in the field at recommended rates, which usually are < 10 kg/ha. Applying micronutrients in combination with NPK fertilizers is convenient and allows more uniform distribution with conventional application equipment. Costs also are reduced by eliminating the separate application of micronutrients.

During incorporation of micronutrients with NPK fertilizers, the micronutrient source is in intimate contact with components of the mixed fertilizer under conditions of high temperature and moisture. This enhances the rate of chemical reactions which may decrease the availability to plants of some micronutrient sources [18]. For example, when ZnEDTA was mixed with superphosphate before ammoniation, acid decomposition of the chelate molecule resulted in decreased availability of the applied Zn for navy beans [14]. When the process was changed by adding the ZnEDTA after partial ammoniation, availability of Zn was increased [7]. Incorporating $ZnSO_4$ with superphosphates before ammoniation decreases water solubility of Zn [27] which results in decreased plant availability of the applied Zn [34]. Maize yields were slightly higher with the application of ZnO incorporated with a granular NPK fertilizer (to contain 1% Zn) than with granular dolomite at rates up to 4.4 kg of Zn/ha in Zimbabwe [53]. Zincated urea (containing 2% - 3% Zn as $ZnSO_4$) was as effective as broadcast $ZnSO_4$ for wheat in India [39]. Zincated superphosphates also are being evaluated in India [46].

Agronomic effectiveness of micronutrients coated onto soluble granular fertilizers should be similar to that with incorporation during the manufacture. Navy bean yields were similar with either $ZnSO_4$ or ZnO incorporated during the manufacture or coated onto a granular NPK fertilizer, but Zn uptake was higher with $ZnSO_4$ (Table 5). Also, ZnEDTA remained completely water soluble when coated onto a NPK fertilizer in conjunction with $MnSO_4$, while it was only 40% water soluble when coated with MnO onto the same fertilizer. Yields of navy beans also were lower with the latter product [14]. The relative effectiveness of Zn sources for maize was ZnO coated > $ZnSO_4$ incorporated > ZnO incorporated with granular NPK fertilizer [52]; $ZnSO_4$ coated onto this fertilizer was not tested.

When bulk blending micronutrients with granular fertilizers, using granular

Table 5. Yield and zinc concentration of navy beans as affected by Zn source and method of inclusion with a granular NPK fertilizer in Michigan [14]

Zn source[a]	Method of inclusion	Yield (mt ha^{-1})	Zn in plants (mg kg^{-1})
		12.3	20
$ZnSO_4$	Blended	16.6	40
$ZnSO_4$	Incorporated	16.4	31
$ZnSO_4$	Coated	17.0	34
ZnO	Incorporated	16.2	23
ZnO	Coated	16.7	26
L.S.D. (0.05)		1.7	3

a. Fertilizers banded at planting to supply 3 kg of Zn/ha.

micronutrient sources helps prevent segregation from the NPK fertilizer because of more equal particle sizes. However, the granular size of micronutrient sources reduces the number of application sites in the soil. For example, the number of granule sites may be less than 20/m^2 when granular $ZnSO_4$ is applied at a rate of 1 kg of Zn/ha. In contrast, if $ZnSO_4$ was incorporated with a mixed fertilizer to contain 2% Zn, the number of granule sites would be about 350/m^2 at the same Zn rate. Application of granular $Na_2B_4O_7$ also results in high B concentrations in the soil near the granule site that could be toxic to nearby roots of some sensitive crop species [37]. Granular micronutrient oxides may not be available to plants because they are relatively water insoluble and their specific surface area is greatly reduced in granule form. Granular ZnO was ineffective in providing Zn for maize [1] and granular MnO did not provide available Mn for oats [35] in greenhouse tests. Therefore, granular oxides may not be satisfactory for use in bulk blends, especially to correct micronutrient deficiencies in young plants.

Economics When determining optimum micronutrient rates for a given crop and soil condition, soil scientists sometimes use maximum crop yields as the main criterion. However, maximum crop yields are not always the maximum economic yields. Input costs to produce the last increments of yield may be very costly in relation to the return for those increments. Other inputs, such as NPK fertilizers, other agricultural chemicals, and irrigation water, also must be considered in the economic analyses. Crop prices affect the optimum fertilizer rates so they must be considered. It is suggested that economists be consulted in designing experiments to determine the most economical rate of micronutrients to apply.

In a study of this type, it was shown that net income from maize and wheat was highly associated with rate of Zn application to a Zn-deficient soil in India [49]. Use of seed coating rice with ZnO or applying $ZnSO_4$ to seedbeds of transplant rice resulted in considerable cost savings in the Philippines [8]. Foliar sprays generally are more economical than soil applications of most micronutrients because the required rates are much lower. However,

added costs of the extra applications needed for foliar sprays may offset the savings in micronutrient costs.

Summary and suggested research needs

Micronutrient sources vary widely in price and agronomic effectiveness. The most effective source of a given micronutrient depends on the method of application, crop species, availability to farmers, price, and availability to plants. There have been relatively few studies in the tropics which included comparisons of micronutrient sources. However, the most economic source and rate of application for each crop can be determined under field conditions by traditional small-plot field experimentation. More than one nonzero micronutrient rate should be included in these experiments. Choice of micronutrient source may be dictated by availability to farmers but demand for an improved source could change marketing practices.

Method of application also influences effectiveness of some micronutrient sources for crops. For example, banding Mn sources generally is more effective than broadcasting. Application methods must be compatible with cultural practices for a particular crop. Foliar applications generally are used for tree crops while soil applications may be most satisfactory for field crops. Time of application also affects efficiency of micronutrient use by the crop. Experiments to compare sources also should include more than one method and/or time of application where applicable.

Residual effectiveness of micronutrients varies widely, ranging from none with Fe sources to perhaps 10 years or more with Cu and Zn sources. Selection of Cu and Zn sources should consider their residual effectiveness; it may be preferable to apply larger rates of a less expensive source so that available Cu or Zn levels are adequate for several years. Because toxicities can result from high levels, especially with B and Cu, available levels in soils should be monitored with soil tests. Residual studies on B, Cu, and Zn applications should be concluded to determine the most economical rate and how often to apply.

The prescription philosophy of micronutrient fertilization generally is the recommended practice, but it requires knowledge of crop needs, available levels in the soil, and most effective sources and methods of application. Experiments should be conducted to gain the above knowledge so that crop yields are not limited by improper micronutrient fertilization.

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Common and Scientific Names of Crops

Bean, navy	*Phaseolus vulgaris* L.
Coffee	*Coffea arabica* L.
Cotton	*Gossypium hirsutum* L.
Desmodium	*Desmodium intortum*
Hairy indigo	*Indigofera hirsuita* L.
Maize	*Zea mays* L.
Oats	*Avena sativa* L.
Panic grass	*Panicum maximum*
Pineapple	*Ananas sativus*
Rice	*Oryza sativa* L.
Rubber	*Hevea braziliensis*
Rutabaga	*Brassica napobrassica* L.
Siratro	*Macroptilium atropurpureum*
Soybean	*Glycine max* L.
Wheat	*Triticum aestivum* L.

10. Sources and production of micronutrient fertilizers

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Chemically, the six micronutrient elements are an odd assortment: a light nonmetal (B), four metals of the first transition group (Mn, Fe, Cu, and Zn) and one heavy metal of the second transition group (Mo). These elements range in earth's crustal abundance from the fourth most abundant (Fe) to the very scarce metal Mo. In at least one of their valence states, these elements all form compounds that are fairly soluble under conditions at the earth's surface and are designated by geologists as mobile. Mobile elements often move from the site of the source mineral as a result of weathering.

A comparison of the distribution of these micronutrient elements in various geologic environments (Table 1) shows that micronutrient elements are more abundant in igneous basalts and sedimentary shales than in other types of rock. Basalts tend to concentrate dark-colored (ferromagnesian) silicates and sulfides that are high in Fe, Cu, Mn, and Zn. Shales are the most common sediment and represent debris from all other rocks.

The most common minerals containing the micronutrient elements (Table 2) occur as oxysalts, sulfides, oxides, carbonates, and silicates. The list includes the principal ore minerals in their approximate order of importance. A comprehensive lost of all the minerals that contain these selected elements would be very long and beyond the scope of a review chapter (see Appendix B of *Dana's Textbook of Mineralogy*, W.E. Ford, 4th edition, John Wiley and Sons, New York, New York, 1932, for details).

Use of micronutrients in agriculture accounts for only small percentages of the total use of these elements. Although there are no worldwide statistics on micronutrient use, the U.S. Department of Agriculture annually reports the amount of micronutrients sold for fertilizer in the United States. The largest tonnage use is for zinc; in 1979/80 139,000 short tons of zinc compounds was consumed and in 1980/81 consumption increased to 196,000 tons [34]. The 1979/80 use corresponds to about 40,000 metric tons of Zn. This micronutrient use of Zn corresponds to about 14% of the U.S. mine production or 4% of the total U.S. consumption of zinc in all forms.

Use of boron compounds in agriculture in the United States amounts to about 5% of the total consumption, but most of the agricultural use is for

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Table 1. Average abundance of selected micronutrient elements in geologic environments (all values ppm except those for river water which are ppb) [25, 21]

Element	Earth's crust	Basalt	Granite	Shale	Limestone	Soil	River water
B	10	5	15	100	10	2–100	10
Mn	950	2,200	500	850	1,100	850	7
Zn	70	100	40	100	25	10–300	20
Fe	56,000	86,000	27,000	47,000	3,800	10,000–100,000	–
Mo	1.5	1	2	3	1	2	1
Cu	55	100	10	50	15	2–100	7

Table 2. Micronutrient ore minerals

Boron
Hydrous borates: borax $Na_2B_4O_7 \cdot 10H_2O$, kernite $Na_2B_4O_7 \cdot 4H_2O$, colemanite $Ca_2B_6O_{11} \cdot 5H_2O$, ulexite $NaCaB_5O_9 \cdot 8H_2O$
Anhydrous borates: ludwigite Mg_2FeBO_5, kotoite $Mg_3(BO_3)_2$
Complex borosilicates: tourmaline,[a] $R_2Al_3(B,OH)_2Si_4O_{18}$
Complex chloride borate: boracite $Mg_4Cl_2B_{14}O_{30}$

Copper
Complex sulfides: chalcopyrite $CuFeS_2$, bornite Cu_5FeS_4, enargite Cu_3AsS_4, tetrahedrite $(Cu, Fe)_{12}Sb_4S_{13}$
Simple sulfides: chalcocite Cu_2S, covellite CuS
Oxides: cuprite Cu_2O
Carbonates: malachite $Cu_2(OH)_2CO_3$, azurite $Cu_3(OH)_2(CO_3)_2$

Iron
Oxides: hematite Fe_2O_3, magnetite Fe_3O_4, goethite $FeOOH$
Sulfides: pyrite FeS_2
Carbonate: siderite $FeCO_3$

Manganese
Simple oxides: pyrolusite MnO_2, hausmannite Mn_3O_4, manganite $MnOOH$
Complex oxides: braunite $(Mn, Si)_2O_3$, psilomelane
Carbonate: rhodochrosite $MnCO_3$
Silicate: rhodonite $MnSiO_3$

Molybdenum
Sulfide: molybdenite MoS_2
Oxide: molybdite MoO_3

Zinc
Sulfide: sphalerite ZnS
Carbonate: smithsonite $ZnCO_3$
Silicate: willemite, Zn_2SiO_4, hemimorphite $Zn_4(OH)_2Si_2O_7 \cdot H_2O$

a Variable composition: R may be Li, Na, K, H, Ca, Fe, or Mg.

nonselective herbicides; micronutrient use of boron was about 7,000 tons of boron compounds in 1980/81. Assuming an average B_2O_3 content of 50%, this use would be about 1% of the total U.S. consumption. All other micronutrients are used in amounts of less than 1% of total use. Table 3 shows the total mine production of the six elements that are used for micronutrients. The small percentage use of micronutrients contrasts sharply with that for the primary nutrients: fertilizer use represents roughly 80%, 85%, and 95% of the total N, P, and K consumption.

The existence of a large-scale industrial demand for the compounds of elements that are also used for micronutrient fertilizers has a favorable effect on the supply and cost of these materials. Economies of scale are realized in mining, beneficiation, and processing the ores that would not be possible for agricultural use alone. Consequently, manufacture of micronutrient materials is commonly based on some intermediate product, byproduct, or final product of industries whose main market is not in agriculture.

Table 3. Mine production of micronutrient ores in 1981[a]

Element	Units	Mine production U.S.	World
Boron	1,000 mt of B_2O_3	680	1,038
Copper	1,000 mt of Cu	1,520	7,800
Iron	1,000 mt of Fe	75,184	866,648
Manganese	1,000 mt of ore (35% -54% Mn)	0	26,300
Molybdenum	___ mt of Mo	658	101,130
Zinc	1,000 mt of Zn	281	5,306

a Derived from Mineral Commodity Summaries, 1982, U.S. Bureau of Mines.

However, most of the processing is done in developed countries. Developing countries often supply the raw materials, but in only a few developing countries are these raw materials processed to a stage that they can be considered for use as a basis for a micronutrient industry. Consequently, when micronutrients are needed in developing countries, the only source may be importation, which is often expensive. On the other hand, some natural minerals are known to be suitable for use as micronutrient fertilizers without processing, and many other minerals that may be suitable have not been tried.

Geochemical distribution of micronutrient elements

The earth may be thought of as a large chemical system, and geochemistry considers the study of the reactions by which components of the earth approach equilibrium. Considered on a grand scale, the geochemical cycle recurs countless times. Igneous rock-forming magma is generated within the crust of the earth and erupts on the surface or is emplaced within existing rocks. In time, these rocks are worn away by interaction with the hydrosphere and atmosphere. The reactions proceed through diagenesis, lithification, and orogenesis to metamorphism which, in its highest grade, regenerates a magma [10]. This simplified cycle almost never proceeds according to the ideal plan. At various steps, components are lost or gained, and this results in deviations in magma composition, crystallization, and rock weathering. Through the cycle, the chemical elements obey certain laws that determine the individual geochemical cycles. Study of the individual cycles is a manageable activity that reveals many subtleties of the systems and helps to give a fuller understanding of the chemical forces at work on the earth.

Data from the study of the micronutrient element cycles might indicate the kinds of minerals that would be stable or soluble in soils. Solubility products and stability fields, in turn, might indicate how minerals will perform in contact with soil solutions. Although this is an important area of study, the identification of mineral reaction products ("new" minerals) remains difficult because of the complicated mixtures encountered. In many cases the products are poorly crystalline or may even be chemically adsorbed as an organic or inorganic complex on the surfaces of soil constituents. The

reaction products often are described by vague generalities when detailed data are needed to help in understanding the behaviour of micronutrients in soils.

Boron

In chemical compounds boron is always trivalent and has properties analogous to those of carbon and silicon. Boron forms nonionic bonds with oxygen resulting in two types of oxyions (BO_3^{3-} and BO_4^{5-}). The four-coordinated boron occurs extensively in the boron-silicon diadochy of borosilicates, the most important of which is tourmaline. The BO_3^{3-} occurs as the economically important alkali and alkaline earth borates and volcanic exhalations (gases and liquid) including boric acid (H_3BO_3). In sedimentary processes, undissociated boric acid and associated sodium borate are the second most important buffers in marine waters (carbonates are the most important). Boron is extracted from marine waters by the formation of tourmaline in sediments and substitution for silicon in clay minerals.

The economic deposits of boron occur in the evaporite salts of marine origin or in desert playas. Weathering of volcanic rocks is assumed to be the source of boron in continental evaporites. The borates of commercial interest are borax, kernite, colemanite, and ulexite. Boracite occurs as an accessory mineral in some potash mines and has been used as a source of boron in granular compound fertilizers [31].

Molybdenum

The most common valence of this metal is Mo^{6+}; less common valences range from Mo^{5+} to Mo^{2+}. During hydrothermal crystallization (crystallization from very hot water at high pressures), molybdenite (MoS_2), the most common molybdenum mineral, forms before all other sulfides. Molybdite, MoO_3, can form from molybdenite in late-stage igneous deposits and hydrothermal veins. At much lower temperatures, molybdenum occurs with calcium (powellite, $CaMoO_4$) and lead (wulfenite, $PbMoO_4$). In weathering zones and sediments, molybdenum often occurs as iron-containing hydrated complexes.

Molybdenite is mined as a primary ore and recovered as a byproduct, mostly from copper mining operations. In general, molybdenum ores are associated with igneous activity or high-temperature metamorphism.

Some alloys are a scrap source of molybdenum although data concerning this source are incomplete. Very little molybdenum-containing scrap metal is processed for its molybdenum content. Spent catalysts and chemical residues are potential sources of an indeterminate quantity of recyclable molybdenum.

Manganese

At or near the earth's surface, oxides consitute the most important manganese ore minerals. Geochemically manganese is a member of the iron

family, and the elements are closely associated. Pyrolusite is one of the specifically identified forms of manganese dioxide. Rhodochrosite is the manganese carbonate and is part of a series of carbonates (Fe^{2+}, Mg^{2+}, Zn^{2+}, Ca^{2+}, and Co^{2+}). Braunite ($Mn_4Mn_3SiO_{12}$) is the only silicate ore of manganese although rhodonite ($MnSiO_3$) is a more common silicate. Manganese nodules occur as ocean floor deposits over wide areas. These nodules contain cryptocrystalline ferromanganese oxides and also contain significant amounts of nickel, cobalt, and copper. Manganese often is a coproduct or a byproduct of iron and zinc processing.

Iron

Iron is a common metal in the earth's crust and occurs in almost all major mineral classes. In igneous rocks, it is important in silicates, sulfides, and oxides. In sedimentary deposits, it occurs as oxides, hydroxides, carbonates, sulfides, and silicates. The action of air and water oxidizes iron to rather insoluble ferric oxide; this results in a separation of the iron from more mobile constituents (Ca^{2+}, Na^{1+}, Mg^{2+}, K^{1+}, etc). Magnetite, hematite, geothite/limonite, siderite, pyrite, and chamosite are the principal ore minerals of iron. Many of the large, massive occurrences of magnetite and hematite are thought to be related to igneous origins, whereas sedimentary iron ores derive their iron from the chemical and physical weathering of rocks of all types. Although there are some detrital iron ores, iron is mainly transported in solution. Iron solutions may react with aluminous sediment to form chamosite which may be carbonated to siderite. Decaying vegetation may deposit iron as siderite which may be oxidized to limonite. Weathering often leaches accessory minerals and elements to give a very high grade ore.

The presence of ferric oxide as the principal form of iron in oxidized soil is expected from the geochemistry of the element. Iron oxide minerals (for example, magnetite) persist in soils because they weather more slowly than the silicates or carbonates. The fact that iron has more than one valence state allows it to be reduced by organic matter. This may allow iron to enter the soil solution or to be adsorbed on soil surfaces as Fe^{2+} or as complexes of this ion.

Copper

Man's knowledge of copper dates from the Bronze Age nearly 6,000 years ago. In nature it occurs both in the free state and combined with other elements in a host of minerals. Copper usually occurs as the metal or associated with sulfur is most rock types. In the primary rocks of the earth's crust, copper invariably occurs as sulfides. Two distinct assemblages of sulfides are recognized. The magnetic sulfides include the Cu-Fe sulfides and are represented by chalcopyrite ($CuFeS_2$), the most important mineral of this group. The second assemblage is characterized by the complex sulfides and sulfo-salts and is the source of up to 70% of the world's copper production. Elemental copper is found in association with basic extrusives.

Very large copper deposits occur in basic to acidic igneous intrusives at various sites around the world. Sedimentary copper deposits are known to occur in black shales and ground water zones where secondary sulfides occur. Although copper occurs in approximately 150 minerals, only about 15 are considered important ore minerals (Table 2).

Copper in soils is probably present as adsorbed Cu^{2+} ions and solution complexes. Geochemical data suggest that copper remains close to its source when it occurs in the soil.

Zinc

Although zinc occurs uniformly distributed in silicate, iron, and sulfide phases in meteorites, concentrations as ores in the earth's crust are almost exclusively as sulfide bodies [10]. Geochemically, zinc often occurs dispersed in igneous rocks because of its similarity in behavior to ferrous iron. Economic deposits of zinc minerals occur in late-stage hydrothermal deposits and often are associated with copper and lead sulfides.

During oxidative weathering of sulfide ores, the highly mobile divalent ion is formed and transported in sulfate solution. Zinc may be immobilized by reaction with carbonate or reduction to sulfide. Much zinc reaches the sea where concentrations in deep-sea clays often are well over the mean crustal abundance.

The major zinc deposits of the world contain the sulfide mineral sphalerite (ZnS). A few important deposits contain oxide, zincite; carbonate, smithsonite; or silicate, willemite (Table 2).

In soils, Zn^{2+} ions are probably adsorbed on the fine-grained constituents, particularly iron oxides and clay minerals. Mobile Zn^{2+} ions in the soil solution may react to form local minerals such as carbonates and silicates. Zinc is a useful geochemical indicator element, but its high mobility in surface and ground water limits its correlation with local soil and rock compositions.

Zinc from various scrap sources represents about 5% of the total supply [6]. In some cases it is possible to recover the zinc alone, but in others the zinc is reprocessed into brass and bronze.

Geographic distribution of micronutrient elements

These six elements are known to occur in reserves or resources in 47 countries (Table 4) including a number of developing countries in South America, Africa, and Asia. In many cases, the mineral resources of the latter countries have not been adequately investigated to actually determine the presence of any but the largest deposits. Therefore, the absence of a country from this particular list may indicate a lack of knowledge rather than the lack of a mineral occurrence that might be of local significance. Also, the compilation of such data emphasizes deposits of suitable size and quality with a favorable location for large-scale commercial development. The requirements to meet a local or regional supply of these elements may be less demanding.

Table 4. Geographic distribution of mineral deposits of micronutrient elements[a]

	Boron	Molybdenum	Manganese	Iron	Copper	Zinc
North America						
Canada		X	X	X	X	X
Mexico		X	X	X	X	X
United States	X	X	X	X	X	X
South America						
Argentina	X					
Bolivia						X
Brazil			X			
Chile			X	X		X
Peru	X	X		X	X	
Venezuela	X	X		X	X	X
				X		
Europe						
Bulgaria		X	X			
Greece			X			X
Hungary			X			
Italy	X					X
Norway		X	X			
U.S.S.R.	X	X	X	X		X
France				X		
Spain						X
Sweden				X		X
Yugoslavia					X	X
Finland						X
Germany						X
Greenland						X
Poland						X
Oceania						
Australia		X	X	X	X	X
Fiji			X			
New Hebrides			X			X
New Zealand						
Asia						
China	X	X	X	X		X
India	X		X	X		
Iran		X				X
Japan		X	X		X	X
Korea		X		X		X
Philippines		X			X	
Thailand			X			
Turkey	X					
Papua New Guinea					X	
Africa						
Angola				X		
Gabon			X			
Ghana			X			
Ivory Coast			X			
Morocco			X			
South Africa			X	X	X	X
Upper Volta			X			
Zaire			X		X	X

Table 4. Cont.

	Boron	Molybdenum	Manganese	Iron	Copper	Zinc
Africa Cont.						
Liberia				X		
Mauritania				X		
Zambia					X	X

a. Sources are various U.S. Bureau of Mines Mineral Commodity Profiles (see Bibliography)

Of the six elements considered, boron has the fewest occurrences reported (nine) with only six in developing countries and none on the continent of Africa. Zinc has the most reported occurrences (25) with about half in developing countries but only three in Africa. There also are no reported occurrences of molybdenum in Africa. Thus, large areas with soils that are subjected to tropical and subtropical weathering processes apparently have no immediate mineral sources of the micronutrient elements.

Processing micronutrient ores

At least part of the processing of micronutrient ores is not specifically intended to produce materials for agriculture, so this section will outline very briefly the main methods for processing the ores for industrial use with particular emphasis on products that can be used for micronutrient fertilizers.

Boron Sodium borates are the main commercial boron ores; they are mined by open pit methods in arid regions. The ore contains insoluble impurities such as clay; it is refined by dissolving the borax in hot water and removing the insoluble material by settling. The solution is then cooled to crystalline borax $Na_2B_4O_7 \cdot 10H_2O$, which is dried. Much of the borax is dehydrated to the pentahydrate, $Na_2B_4O_7 \cdot 5H_2O$ by heating at moderate temperature. Complete dehydration requires heating to about 700°C; the product is molten at this temperature and forms a water-soluble glass on cooling.

Borax and boric acid, along with several other salts, are also recovered from alkali brines by fractional crystallization.

Colemanite (calcium borate, $Ca_2B_6O_{11} \cdot 5H_2O$) may occur in shale. The shale is heated, which causes the colemanite to distintegrate to a powder. It is then separated from the shale by screening and calcined to the anhydrous form. A flotation process for beneficiating colemanite has been developed [1].

Although boron compounds have many uses, probably the highest volume use is in glass manufacture. For this purpose either sodium or calcium borate can be used for most grades of glass.

Sodium borate ($Na_2B_4O_7$) is widely used as a micronutrient material, both as the decahydrate (borax) and the pentahydrate, and in the anhydrous form. It is available in various particle sizes: fine, coarse, and granular. Also a

product made by granulating borax with sulfuric acid is available. Sodium borates containing a higher ratio of boron to sodium than $Na_2B_4O_7$ also are available. One such product is sodium pentaborate, $Na_2B_{10}O_{18} \cdot 10H_2O$.

Calcium borate also is used as a micronutrient material, particularly in locations where it is less expensive than sodium borate. Calcinated colemanite from Turkey contains about 14% B. It is available in various particle sizes, but it is not known to be used for fertilizer purposes in granular form.

Boron frit is essentially a borosilicate glass made by fusing boron materials with silica, quenching the melt, and grinding to the desired fineness. A typical material contains 10% B.

Copper Although there are many copper minerals, chalcopyrite, $CuFeS_2$, is the most abundant [30]. Most copper ores contain only a small percentage of copper, often less than 1%. However ores containing chalcopyrite are readily enriched by flotation to yield a concentrate containing about 30% each of copper, iron, and sulfur. Some ores contain copper in both sulfide and oxidized forms. The oxidized forms include oxides, carbonates, and silicates. Such ores usually are first leached with dilute sulfuric acid to dissolve the oxidized copper as copper sulfate. Metallic copper is recovered from the solution by electrolysis or by precipitation with iron. The leached ore is then beneficiated to produce the copper concentrates containing sulfides. The concentrates are roasted in air to remove part of the sulfur, then melted in a reverberatory furnace. The melt is transferred to a converter and blown with air to produce an iron silicate slag and metallic copper called "blister copper" which is then refined electrolytically. All of these pyrometallurgical operations emit gases containing SO_2, most of which must be recovered as sulfuric acid to control air pollution. Ores that contain mainly sulfide copper may be concentrated first by flotation, and the copper remaining in the tailing may then be recovered by acid leaching.

Hydrometallurgical processes can be an alternative method [13]. In such processes, sulfide-containing ores or concentrates are leached with sulfuric or hydrochloric acid under oxidizing conditions. Some leaching processes permit recovery of the sulfur in elemental form.

The most popular copper materials for use as micronutrients are the copper sulfates: they are available in all sizes from fine powder to granular. These materials are prepared by crystallization from solutions. The various particle sizes are produced by control of the crystal size or by crushing and screening larger crystals. Copper sulfate solutions are often intermediates from copper leaching or refining operations, but they also can be made by dissolving copper metal or oxide in sulfuric acid. A granular product containing both copper oxide and copper sulfate can be made by granulating copper oxide with sulfuric acid.

In a few mines, copper is present mainly in the elemental form called "native copper." Such copper usually is in veins in the rock, and it is freed by

crushing the rock. The metallic copper recovered from such ore is in various shapes and sizes; the finer material is called flake copper.

The principal copper materials that are used for micronutrient fertilization are as follows:

Material	Formula	% Cu[a]
Copper sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	25
Copper sulfate monohydrate	$CuSO_4 \cdot H_2O$	35
Basic copper sulfate	$Cu_4(OH)_6SO_4$	53
Copper carbonate	$CuCO_3$	55
Copper oxide	CuO	50–75

a. The percentage copper listed is that of the usual grade marketed, not necessarily that of the pure compound.

In addition to the materials listed above, various compositions of frits and chelates are marketed. Of the various copper minerals that might be used without processing, many apparently have not been tried. Kretschmer and Forsee [22] reported greenhouse tests in which metallic copper flakes (98% Cu) and several copper concentrates containing 11%–50% Cu were used with good results. Unfortunately the authors did not state the chemical compounds in the concentrates.

Iron — About 98% of the iron ore mined goes into the iron and steel industry [19]. Many of the iron ore deposits are pure enough to require no beneficiation; some deposits do require beneficiation. Most of the iron ore is ferric oxide (Fe_2O_3). Because the ferrous form is preferred for micronutrient use, iron ore is seldom used directly to make micronutrient materials. Ferrous oxide is available as "mill scale," a by product from the steel industry. Ferrous sulfate may be produced by dissolving ferrous oxide or metallic iron in sulfuric acid. One source of ferrous sulfate is "pickle liquor," which is produced when steel is dipped into sulfuric acid for cleaning preparatory to galvanizing [28]. Ferrous sulfate is recovered from solution by crystallization as the heptahydrate ($FeSO_4 \cdot 7H_2O$), and it may be sold as such or calcined to the monohydrate. Also a granular product may be made by granulating ferrous oxide with sulfuric acid. The product contains both ferrous oxide and sulfate.

Ferrous ammonium sulfate ($FeSO_4 \cdot [NH_4]_2SO_4 \cdot 6H_2O$) is also used as a micronutrient source. It is made either by dissolving ferrous oxide (or iron) in an excess of sulfuric acid and then adding ammonia, or by ammoniating pickle liquor.

Inorganic sources of iron are not always effective in supplying iron to crops through soil application, so iron chelates often are used. This method will be discussed later.

Manganese The principal manganese ores are the oxides, as mentioned in a previous section of this chapter. Metallurgical grade manganese ore contains 35% 54% Mn [9]. The ore is used to produce ferromanganese or silicomanganese by reduction with coke in an electric furnace or blast furnace. These alloys are added to molten iron or steel to produce various grades or cast iron or steel. Lower grade ores containing manganese oxide, carbonate, or silicate can be used to make manganese salts by leaching with acids or ammoniacal liquor. There are several leaching processes; selection depends on the character of the ore and the desired salt [28]. Manganese carbonate ore has been used as a micronutrient source. Basic open-hearth slag may contain 5% 20% Mn depending on the manganese content of the iron ore. It can be used as a micronutrient source for direct application or for leaching. Manganese oxide (MnO) is often used as a micronutrient source, usually as a powder for incorporation in fertilizers. Manganous sulfate ($MnSO_4 \cdot 4H_2O$) may be produced by dissolving manganous oxide in sulfuric acid and recovering the crystals from solution by evaporation. The tetrahydrate may be used as such or after dehydration. Both granular and powdered forms are available. Also a granular product may be made by granulating manganous oxide with sulfuric acid. Manganous chloride is also available in the form of flakes.

Molybdenum The main ore is molybdenite, MoS_2, which often occurs in association with other sulfide minerals. The ore is beneficiated to produce a concentrate which is then converted to the oxide MoO_3 by roasting in air or by other methods. Coproducts or byproducts include copper, tungsten, tin, and pyrite. The molybdenum oxide is available to the fertilizer industry in various degrees of purity. Also the water-soluble salts, sodium or ammonium molybdate, are used as micronutrient sources. They are produced by treating molybdenum oxide with solutions of sodium hydroxide or ammonium hydroxide, respectively.

Forms of micronutrient materials

Most of the micronutrient materials in common use fall into one of several general classes:

1. Soluble salts, including sodium borates, sodium or ammonium molybdate, and sulfates or copper, manganese, iron, or zinc.
2. Insoluble compounds, mainly copper, manganese, or zinc oxides or carbonates.
3. Partially soluble combinations of oxides and sulfates.
4. Liquids that may be solutions or inorganic salts, including chlorides, nitrates, and sulfates, or solutions of chelates. Liquid materials are convenient for addition to liquid fertilizers or for foliar application after dilution.
5. Chelates that are soluble complex organic materials. They are available in both solid and solution form. Inorganic chelates are also possible

but are usually produced in making liquid fertilizers based on ammonium polyphosphates.

6. Frits that are glasses of silicate or phosphate composition. Fritted materials are slow-release materials made by fusion of one or more micronutrients with a glass-forming composition. The melt is quenched, cooled, and ground to about 90% minus 200-mesh [5]. The release rate depends on the particle size, the glass composition, and soil conditions. The finely ground frits may be granulated by roll compaction if desired.
7. Metals that have been used for micronutrients are mainly copper or zinc or their alloys, brasses. Fine metal particles such as filings or turnings may be incorporated in granular fertilizers.
8. Adventitious sources include manganese and some other micronutrients in basic slag. Some phosphate fertilizers contain significant amounts of micronutrients originating from phosphate rock. Organic fertilizers usually contain some micronutrients; heavy applications of sewage sludge may even contain excessive amounts.
9. Mixtures of two or more micronutrients are available in all of the above classifications. Usually the mixtures are compounded for incorporation in mixed fertilizers to produce premium fertilizers or to serve regional needs. Custom mixes are available. In some cases byproduct solutions, available from metallurgical operations, are processed into a mixture containing two or more micronutrients plus primary and secondary elements. One such product contains 15% Zn, 1.5% Mn, 20% S, and 9% N (as ammonium sulfate).

Preparation of fertilizers containing micronutrients

As mentioned in the previous chapter, micronutrients can be applied in many ways including foliar application, seed treatment, root dipping of transplanted seedlings, and application with pesticides. However the most popular method is to apply the micronutrients in admixture with the primary nutrient fertilizer that the farmer regularly uses. The first reason for this popularity is convenience, the farmer does not have to devote extra labor to micronutrient application if the micronutrient carrier is a fertilizer that he is already using. A second reason is that uniformity of application is much easier when the micronutrient material is mixed with a much larger volume of fertilizer. The purpose of this section is to describe some of the methods that are used to produce fertilizer mixtures containing micronutrients and to discuss their advantages and disadvantages.

Reaction of micronutrient materials with fertilizers It should be recognized that when micronutrient materials are mixed with other fertilizers, chemical reactions are likely to occur. Lehr [24] has described many of the numerous chemical reactions. The effect of these chemical reactions may or may not be important. A water-soluble micronutrient source may be partially or

wholly converted to a water-insoluble compound. Conversely, water-insoluble sources may be converted to water-soluble forms. The gain or loss of water solubility may or may not be important. Some examples follow.

Soluble salts of copper, manganese, iron, and zinc are likely to become insoluble when incorporated in ammonium phosphates or ammoniated mixed fertilizers. The reaction forms one of several metal ammonium phosphates such as $ZnNH_4PO_4$. In general the water solubility decreases with increase in pH of the fertilizer product. Loss of water solubility does not necessarily imply loss of effectiveness but may delay it. Sodium borate when incorporated in ammoniated fertilizers containing calcium may become partially or wholly insoluble presumably because of formation of calcium borate. (The boron in calcium borate is insoluble in cold water but soluble in boiling water). This effect has been noted with nitrophosphate fertilizers and may occur with other formulations.

Many water-insoluble micronutrients (oxides, carbonates, and silicates) become at least partially soluble when incorporated in superphosphates or mixed fertilizers containing unammoniated superphosphate.

Some insoluble oxides become soluble when incorporated in ammonium polyphosphate fertilizers. In practice the ammonium polyphosphate liquid fertilizers are widely used in some countries, and zinc oxide often is added and dissolved in them. However, solid fertilizers containing ammonium polyphosphate also will convert zinc oxide (or carbonate) to a soluble form.

Zinc oxide and cuprous oxide (Cu_2O) become partially soluble when incorporated in ammonium nitrate or nitrogen solutions such as urea ammonium nitrate solutions. The solubility can be increased by adding enough ammonia to keep the solution pH at 7 or 8. The soluble compounds formed are presumed to be zinc nitrate amine and copper nitrate amine. Because the addition of copper compounds to ammonium nitrate is said to sensitize its decomposition, copper is not used in some countries for solid fertilizers containing a high percentage of both ammonium nitrate and chloride [20]. In TVA tests, the addition of zinc to ammonium nitrate did not cause any increase in explosibility.

Coating of micronutrient materials on granular fertilizers would be expected to result in less reaction than would incorporation, but even so, substantial gain or loss of water solubility of the micronutrient has been found to occur with coated materials.

When chelated micronutrients are incorporated in fertilizers, there is less likelihood of reactions that cause loss of water solubility. Some granulation processes, however, involve high temperature and use of ammonia and acids which can cause decomposition of the organic chelant and consequent loss of availability. Frits are ordinarily insoluble and remain so when incorporated in neutral fertilizers, but an increase in solubility was observed when frits were incorporated in triple superphosphate.

Dry mixing Perhaps the simplest method for producing mixtures containing micronutrients is to dry-mix the micronutrient material with the primary nutrient materials. This method works well with nongranular materials. Segregation usually is not serious when all materials are fine, such as less than 1 mm in particle size. Fine materials, however, are likely to cake, and some micronutrient materials may promote caking. Caro et al. [7] noted increased caking of some formulations of dry-mixed fertilizer when zinc sulfate was added.

Nongranular dry-mixed fertilizers are not popular in most areas but are still used in some. One of these areas is in Florida where there are multiple micronutrient deficiencies. Hundreds of formulations are used, often custom mixed, so granulation is impractical.

Dry mixing by farmers may be practical in some countries. Bautista et al. [3] reported that in the Philippines farmers were supplied with fine granular zinc sulfate heptahydrate (22% Zn) in 5-kg bags and were instructed to mix it with the fertilizer used for basal application for rice to provide about 1 kg of Zn per hectare. The paper did not say what the primary nutrient fertilizer was, but prilled urea is the most popular fertilizer in the Philippines.

Bulk blending Bulk blending is a form of dry mixing in which all of the nutrients are granular (e.g., 1.0–3.3 or 2–4 mm). Micronutrient materials are available in granular form for use in bulk blends. One problem is segregation; unless all materials are closely matched in particle size, segregation will occur in piles, in bins, in spreader trucks, or during mechanical spreading. If the blends are bagged from a bin, disparity in particle size will lead to wide variation in micronutrient content from one bag to another. This variation can cause poor results because of oversupply in some spots and undersupply in others.

Hoffmeister [18] has outlined some methods for preventing segregation of blends. A blending system that is used in Ireland effectively minimizes segregation. The materials for blending are fed continuously from separate hoppers by weigh belts to a collecting belt where the materials form layers. The collecting belt discharged into a continuous mixer which discharges to a small hopper over the bagging machine. Since the bagging hopper is being continuously filled and emptied, there is little chance of segregation. Segregation can still occur in bags, but it is not likely to be serious unless there is extreme disparity in particle size. Segregation can also occur in the field by the action of some types of mechanical spreaders, but this is not likely to be a problem in developing countries.

Another problem with blends is the sparse distribution of micronutrient carriers. For example, only one granule in thirty may be a micronutrient carrier. The larger the granules the less likely that any one plant will have a micronutrient granule within reach of its root system. Also, the higher the concentration of micronutrient material, the fewer the granules required to

provide a given application rate. This problem is not unique to bulk blends but would also be encountered in direct application of granular micronutrient materials. One method for coping with the problem is intentional dilution of the micronutrient with either an inert material or a primary nutrient material. For example, micronutrient chelates are granulated with clay or vermiculite to produce granules containing 1%–5% of a micronutrient element or similar percentages of two or more micronutrients. Several products are available that contain 1%–10% of one or more micronutrients granulated with one or more primary nutrients. These products may be used in blends.

Incorporation of micronutrients in granular fertilizers In most cases incorportation of micronutrients in granular fertilizers containing one or more primary elements is not technically difficult. However, it is often uneconomical to produce small lots of special grades in large granulation plants, so the practice is economical only when there is a substantial demand for micronutrient-enriched fertilizers. In several countries in Europe, there is a need for boron for root crops such as sugar beets and fodder turnips. Because these crops are important ones, there is sufficient demand to justify an economical scale of operation. The boron often is incorporated in a superphosphate-based PK mixture in amounts to supply 0.2%–0.5% B. One company in Germany produces a granular 0-15-25 grade containing 2.5% borax (about 0.3% B) in which the phosphorus is supplied by Rhenania phosphate. Production of ground and granulated phosphate rock containing added "trace elements" has been reported in France. Copper deficiencies often are encountered in Denmark, and NPK fertilizers containing copper are marketed there. One German company has produced an NPK fertilizer in which scrap metal filings or turnings are incorporated (copper, zinc, or brass). One company in Ireland produces a fertilizer based on superphosphate and ammonium sulfate containing boron added as colemanite.

Several companies in the United States market "premium" fertilizers containing small percentages of two, three, or more micronutrients. For example, mixtures containing manganese, iron, and zinc are intended for soybeans. One company markets premium fertilizer containing polyphosphates with zinc and iron incorporated in the polyphosphate. Boron is recommended for cotton in portions of Alabama, Geogia, and Mississippi, and mixed, granular fertilizers are marketed containing 0.2% or 0.3% B. In general no important technical problem would be expected in incorporating the small amounts of micronutrients that are commonly used. When larger percentages of micronutrients are incorporated, some problems may occur. TVA has made a series of tests aimed at producing materials with relatively large percentages of micronutrients for use in bulk blending. Concentrated superphosphate was granulated with steam in a conventional drum granulator with addition of anyhydrous sodium tetraborate ($Na_2B_4O_7$); a small amount of ammonia was added to decrease the free acid content of the superphosphate.

The scale of the operation was 10 tph. The product after drying contained 47% available P_2O_5 and 3.4% B [26]. No unusual problems were encountered when using the anhydrous borate. When the pentahydrate was used, however, large balls formed in the dryer, and the granules were soft and weak. This condition was attributed to release of water of hydration in the dryer. It was concluded that the anhydrous sodium tetraborate should be used for production of this product.

In pilot-plants tests ammonium nitrate was granulated with zinc oxide, borax, or both to produce granules containing 2.3% Zn and 0.5% B, or 1.9% Zn and 0.7% B [15]. The micronutrient materials were added to hot concentrated ammonium nitrate solution (95% NH_4NO_3), and the mixture was granulated in a pan granulator. The granules were dried and screened, and the fines and crushed oversize were recycled to the granulator. The boron content of the products was fully water soluble, and the zinc content was 30%–40% water soluble. The compound $3Zn(OH)_2 \cdot NH_4NO_3$ was identified in the water-insoluble portion of the zinc-containing products. The water-soluble zinc may have been zinc amine nitrate. Tests showed that the physical properties of the products were as good as straight ammonium nitrate and that the sensitivity of ammonium nitrate to detonation was not increased by borax or zinc oxide. In subsequent work, granular ammonium nitrate containing up to 8% Zn was produced by addition of zinc oxide. One company now markets a product containing 30% N and 10% Zn.

Zinc oxide was incorporated in ammonium polyphosphate (15-60-0) during granulation without difficulty at levels of 1%–3% Zn; 80%–100% of the zinc was water soluble [15]. Although the zinc oxide did not react with ammonium polyphosphate in absence of water, when the granules were placed in the soil the ammonium polyphosphate and 80% of the zinc dissolved and diffused in the soil. In similar tests with diammonium phosphate-zinc oxide granules, most of the diammonium phosphate dissolved and diffused into the soil while the zinc remained at the granule site as $ZnNH_4PO_4$.

Substantial percentages of iron, manganese, and copper were soluble when appropriate compounds of these elements were incorporated in granular ammonium polyphosphate.

Coating of micronutrients on granular fertilizers When small percentages of micronutrient materials are to be added to granular fertilizers, they may be added as a coating on the surface of the granules. This method has several advantages. The coating may be added to homogeneous granular compound fertilizers, to bulk blends, or to straight (single nutrient) fertilizers. The coating may be added just before shipment, thereby avoiding storage of additional grades. Each granule is coated with a micronutrient as opposed to bulk blends containing granular micronutrient materials in which only one granule in thirty may be a micronutrient carrier. The operation is simple,

and the equipment is inexpensive. Conceivably the coating could be done at the village level or by individual farmers.

One drawback of the coating method is that the addition of a micronutrient material (whether coated or not) lowers the primary nutrient grade. This is a problem in countries where only prescribed, registered grades can be marketed. Bulk blenders, however, can easily deal with this problem. In areas where they are required to make only registered, whole-numbered grades, the grade is often adjusted by adding a filler such as crushed, screened limestone; thus, dilution by a micronutrient can be compensated for by adding less filler. Another method for grade adjustment is to use two materials of different concentration, such as ammonium sulfate and urea, in varying proportions. Finally, the problem can be solved by legislation or regulation if the appropriate officials recognize the problem.

In some states of the United States, bulk blenders are not required to produce guaranteed grades; the farmer is invoiced for the separate materials, and the merchant is responsible only for the analysis of the materials used in the blend. He will then mix the materials as a service to the farmer. This system has the advantage that prescription mixing is easy. Disadvantages are that infractions such as adulteration or errors in proportions are difficult to detect and the merchant has no incentive to produce uniform mixtures. In addition, bulk blending by local retailers has some disadvantages in developing countries; bulk materials cannot be transported within the country without loss or deterioration of quality. The alternative - to transport materials in bags to a local mixer who will make various mixtures and bag them - is obviously expensive.

Some micronutrient materials will adhere to some granular fertilizers without a binder. One example is a finely powdered zinc oxide (80% Zn) which was applied as a coating to granular ammonium nitrate in a rotary drum such as is commonly used for coating fertilizers with clay or other conditioning agents. Up to 8% Zn was applied as a zinc oxide coating with up to 93% adherence in industrial-scale equipment [26]. However, adherence decreased to 47% after 6 months' bagged storage. The addition of steam in the coating drum increased adherence after 6 months' storage to 72%. More complete adherence was obtained in pilot-plant tests with lower percentages of zinc oxide or by using a small amount of 70% ammonium nitrate solution as a binder. Achorn and Balay [2] have described plant practices for adding micronutrients to bulk blends.

Most micronutrients require a binder for good adherence on the surface of granular fertilizers. The binder may be oil, wax, water, or fertilizer solution. TVA has developed and studied procedures for coating. A batch method was selected because most bulk blenders in the United States use a batch mixer. The batch method consisted of the following steps [35]:

1. Charge the mixer with the granular fertilizer to be blended and the powdered micronutrient.

2. Blend dry for 1 minute by rotating the drum mixer.
3. Add the liquid binder through a spray nozzle while continuing rotation of the mixer (1 minute).
4. Continue mixing for 1 minute.
5. Discharge the coated material.

This procedure gave a more uniform coating than did the addition of the binder before mixing. Silverberg et al. [32] have reported the results of tests with this procedure in some detail. In general the best results were obtained when the micronutrient material was finely ground (minus 100-mesh or finer). Oils ranging from No. 2 fuel oil to used motor oil gave good results, but the less viscous oils were absorbed into the more porous granular fertilizer causing some loss of adherence with time. A 1:2 mixture of Nos. 2 and 6 fuel oil and a 1:2 mixture of microcrystalline wax and No. 2 fuel oil gave the best long-term adherence. The amounts of binder ranged rom 0.5% to 5.0% of the mixture. In some cases, the addition of 2% clay improved adherence when water was used as a binder. Ammonium polyphosphate solution (11-37-0) was an excellent binder for zinc, manganese, and iron oxides. The oxides reacted with the solution to give a hard, smooth coating. As much as 13% of a mixture of these oxides was coated on granular TSP using 3% of the APP solution as a binder. Adherence was 100% even after 2 weeks' storage. Achorn and Balay [2] have described some U.S. plant practices for coating micronutrients on blends.

Use of a 64% solution of ammonium nitrate as a binder for coating micronutrients on bulk blends has been described [12]. Over 97% adherence was obtained. The use of liquid fertilizers as a binder was patented [27], and the process trade named "Micro-Charger" may still be in commercial use.

Coating with oil and clay is a common practice in European plants for both bulk blends and chemically granulated mixtures. The usual proportions are about 0.5% oil and 1.0% clay. The coating usually is done in a continuous drum mixer. The oil is specially formulated for the purpose. One company in the United States produces specially formulated oils for dust control on granular fertilizer [11]. At least one bulk blender coats micronutrients on blends using clay and water or oil as a binder [29].

In some developing countries an oil coating is objectionable to the farmer because it soils the fertilizer bags which he wishes to reuse for grain storage. A possible solution to this problem is to use a waxy material that is a solid at atmospheric temperatures. For example, adherence of 5% of a powdered micronutrient frit was satisfactory in laboratory tests with 1% of either petrolatum or a petrolatum-rosin-paraffin wax mixture as a binder [16]. The granules were preheated to 49°C, the molten wax mixture was poured over them in a rotating mixer, and then the frit was added. Possibly further study is needed to identify acceptable, low-coat binders. Also most Asian farmers use urea, and methods for coating mictronutrients on urea seem to have received little attention. Some micronutrient materials (e.g., zinc sulfate)

form adducts with urea, which might be advantageous in coating or incorporation.

Fluid fertilizers Fluid fertilizers are used in substantial amounts in only a few developing countries. Two types of fluid fertilizers are recognized:

1. Clear liquids are fluids in which all or nearly all of the ingredients are in aqueous solution.
2. Suspensions are fluids that contain solid particles.

The solids may be soluble salts suspended in their saturated solution, they may be insoluble materials, or both types of solids may be present.

Fluid fertilizers may be used for foliar application or for application to the soil. Micronutrient sprays are often used for correcting deficiencies particularly for tree crops. A soluble salt or chelate of the micronutrient material may be dissolved in water to form a solution of suitable concentration. Finely powdered insoluble materials also may be used for foliar application. Because some metal salts form acidic solutions, the slightly soluble basic salts may be preferable for foliar application [28]. An example is $CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$, a basic copper sulfate.

It is common practice to combine foliar application of micronutrients with pesticide sprays or with foliar application of primary nutrients. When two or more materials are combined for foliar application, care must be taken to ensure that the materials are compatible. Many pesticides are incompatible with solutions of micronutrients. Incompatibility means that some chemical or physical change takes place that renders the mixture unusable or harmful. In general, micronutrient solutions should be applied separately unless compatibility is shown.

Liquid fertilizers containing micronutrients and one or more of the primary nutrients are suitable for application to the soil or for foliar application when diluted sufficiently to avoid leaf burn. Such liquid fertilizers may be produced merely by dissolving fertilizer salts in water. Dry mixtures of water-soluble fertilizer salts are available that may be marketed as such and dissolved in water prior to use. However, for large-scale use it is more common for the manufacturer to prepare the liquid mixed fertilizer at his plant for shipment to the farmer.

In formulating liquid mixed fertilizers, it is not sufficient to know that all ingredients are water soluble. Many reactions may occur that result in formation of water-insoluble compounds of micronutrients.

In general, most micronutrients are soluble in aqua ammonia or in solutions containing ammonium nitrate and urea provided that proper choice is made of the micronutrient compounds and that free ammonia is present or added to keep the solution pH above 7. Hester [14] describes the formulation and preparation of a solution based on aqua ammonia containing all micronutrients except iron. The solution contained 17.5% N as ammonia and ammonium sulfate, 0.29% Mo, 1.1% Cu, 2.0% Mn, 1.9% Zn, 0.9% B, and

0.12% Co. The metallic elements were added as sulfates, but they were present in the solution as complex metal amine sulfates. Boron and molybdenum were added as boric acid and molybdic acid.

Silverberg et al. [32] have discussed the solubility of micronutrients in nitrogen solutions and in various NP and NPK liquid fertilizers. In general only boron (borax) and molybdenum (sodium molybdate) were appreciably soluble in nearly neutral ammonium orthophosphate solutions. Copper, iron, and zinc, however, were soluble in ammonium polyphosphate solutions to the extent of 1%–3%, and manganese was soluble to the extent of 0.2%. The production of liquid fertilizers including ammonium polyphosphate solution has been discussed by Hignett [17] and in a group of 12 papers in "Products and Techniques for Plant Nutrient Efficiency" [4]. Several of these papers discuss the potential advantage of liquid fertilizers in tropical countries and the incorporation of micronutrients in liquids.

When micronutrients are incorporated in suspension fertilizers, solubility is not a technical problem although it may be an agronomic problem. Soluble or insoluble compounds of micronutrient elements are added to suspension fertilizers using materials of small enough particle size that they are easily suspended and will not slog spray nozzles. Production of suspension fertilizers containing micronutrients has been described by Silverberg et al. [32].

Research and development needs

Many developing countries have mineral deposits of micronutrient ores, and the ores are often mined and concentrated in these developing countries; however, relatively few countries produce refined products. The ore concentrates often are shipped to developed countries for further processing. Although there is a trend toward more processing in developing countries, the demand for micronutrient elements in agriculture is often insufficient to justify an economical scale of processing and the demand for industrial products of these elements is also small. Moreover, the processing plants are capital intensive.

There is a need for identification of domestic ores or minerals containing micronutrients that can be applied without chemical processing or with low-cost, simple processing. For this purpose micronutrient sources need not be pure or highly concentrated. The amounts used are so small that even low-grade sources may be economical for local use. For example, a common recommendation for boron on cotton is 0.5 kg of B/ha, and Bautista et al. [3] found that 1.0 kg of Zn/ha on rice was sufficient in most but not all of the locations in the Philippines. Thus materials containing 1%–5% B or Zn would require application rates of 10–100 kg/ha which would not be unreasonably labor intensive and could be economical for low-cost indigenous materials. Use of indigenous minerals or ores with or without concentration should be considered. Many of the micronutrient minerals have not been

tested, particularly under tropical conditions. It seems likely that insoluble minerals would dissolve more rapidly at high soil temperatures, particularly in moist acid soils. In fact some insoluble minerals might be more effective than soluble salts in areas where leaching or runoff is a problem.

More research is needed to determine the effectiveness of the many minerals that contain micronutrient elements. Some sulfide minerals, for example, are known to oxidize rapidly in warm, moist soils. Iron sulfide (pyrite), for example, has been found to be an effective source of iron in some locations and copper sulfide has given good results as a source of copper. Zinc sulfide has given poor results in short-term tests in temperate climates, but no information was found on its use in tropical soils or for longer times. In selection of micronutrient-containing minerals some thought should be given to impurities that might be harmful. Some sulfide ores may contain lead, arsenic, or cadmium, for example, in potentially harmful concentrations.

Many insoluble minerals such as oxides, silicates, and carbonates of metallic micronutrient elements have not been adequately tested under tropical conditions. The same is true of insoluble borates.

Waste products or byproducts containing micronutrients are available in many countries. For example, automobile tires contain a high percentage of zinc oxide. If discarded tires are burned, the ash must contain higher percentages. Sewage sludge contains appreciable amounts of micronutrients [8] as well as primary nutrients. Fly ash from combustion of coal contains various amounts of micronutrients, depending on the coal composition, and represents a disposal problem. Scrap metals and slags also are potential sources.

There is a need to study the technology of producing micronutrient materials from their ores with a view to identifying simple processes with low capital requirements. Many processes that have been used in the past are now regarded as obsolete because they are labor intensive or poorly adapted to large-scale use or because the products are too impure for industrial use. These considerations would not necessarily apply to production of materials for use in agriculture in developing countries.

Finally, more work is needed to identify methods for incorporating micronutrients in the most popular primary nutrient fertilizers in the developing countries. This is especially true of areas where deficiencies of one or more of the micronutrients are common. Urea is the most popular fertilizer in many developing countries, so research on using it as a carrier for micronutrients seems appropriate.

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