Plants and the Chemical Elements

Biochemistry, Uptake, Tolerance and Toxicity

Edited by Margaret E. Farago

Weinheim · New York · Basel · Cambridge · Tokyo

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Preface

Twenty years ago in his preface to his book on plant mineral nutrition E. J. Hewitt wrote: *"The study of plant mineral nutrition is a vast and complex subject . . ."*, and over those twenty years the whole subject has become considerably more complex and of ever widening scope as the boundaries of the subject have been pushed back to encompass many multidisciplinary areas. The subject was rooted in the agricultural aspects of the effects of mineral nutrients, the effects of their deficiencies and excesses, largely in the production of food. More recently, the wider environmental aspects of plants in relation to chemical elements have, in addition, come to the fore. This area includes the study of toxicity and tolerance in particular where anthropogenic inputs have resulted in high concentrations of toxic elements, the use of plants as biomonitors of contamination. In order to arrive at some understanding of the mechanisms and processes involved in some 92 elements and their compounds moving from a number of differing soil types, under different environmental conditions, and their fate in various plant species, taking into account the dynamic aspects including plant responses to environmental change, then workers in a number of disciplines must attack this mammoth task. These will include: soil scientists, plant physiologists, microbiologists, geneticists, chemists, analytical chemists, environmental scientists, statisticians and modellers, and probably many more.

This book summarises many of the important aspects of this very large topic. In Chapter 1, Brian Davies sets the scene with a review of soil chemistry and in particular bioavailability of trace elements to plants, and discusses how we assess this. In the second Chapter Aradhana Mehra and Margaret Farago give a general account of the role of some elements in plant life. In Chapter 3 Mark Macnair and Alan Baker discuss the rapid evolution of adaptation to high concentrations of potentially toxic elements to give metal tolerant plants. This is followed by a review of plants that hyperaccumulate metals by Robert Brooks (Chapter 4), and it is suggested that these plants represent the ultimate in plant tolerance to extremely hostile edaphic environments. Robert Hay discusses the plant enzymes that require enzymes for activity in Chapter 5, and in particular concentrates on their chemistry and structure. In Chapter 6, J. Vangronsveld and H. Clijsters examine some aspects of the toxic effects of metals on plants, in particular those which occur at the cellular level. The pathways and mechanisms involved in the incorporation of man-made nuclides into plants are examined by G. Shaw and J. N. B. Bell in Chapter 7. The use of plants to indicate and biomonitor both natural mineralisation and anthropogenic pollution is discussed in Chapter 8 (Margaret Farago). Finally, the experimental techniques used in the study of elements in plants are discussed; methods of multielement analysis for the determination of concentrations in plant tissues (Chapter 9, Margaret Farago and Aradhana Mehra) and phytochemical methods where the role of the element within the plant is deduced (Chapter 10, Margaret Farago).

I am most grateful to the authors for their hard work and time, and in particular to my co-author Dr. Aradhana Mehra, for producing work at short notice when some chapters originally agreed were not able to be produced. Thanks are also due to Dr. Don Emerson and Mrs. Christa Schultz of VCH and Mrs. Judith Johnson for the copy editing.

London, April 1994 *Margaret E. Farago*

Contents

1 Soil Chemistry and Bioavailability with Special Reference to Trace Elements ... 1
Brian E. Davies

2 Metal Ions and Plant Nutrition ... 31
Aradhana Mehra and *Margaret E. Farago*

3 Metal-Tolerant Plants: An Evolutionary Perspective ... 67
Mark R. Macnair and *Alan J. M. Baker*

4 Plants that Hyperaccumulate Heavy Metals ... 87
Robert R. Brooks

5 Plant Metalloenzymes ... 107
Robert W. Hay

6 Toxic Effects of Metals ... 149
Jaco Vangronsveld and *Herman Clijsters*

7 Plants and Radionuclides ... 179
G. Shaw and *J. N. B. Bell*

8 Plants as Indicators of Mineralisation and Pollution ... 221
Margaret E. Farago

9 Analytical Techniques for Plant Analysis ... 241
Margaret E. Farago and *Aradhana Mehra*

10 Phytochemistry: Methods for the Study of Inorganic Species in Plant Tissues .. 265
Margaret E. Farago

Index ... 285

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1 Soil Chemistry and Bioavailability with Special Reference to Trace Elements

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Contents

Introduction 2

Rock Geochemistry 2

- The Elements and their Abundances 2
- The Essential Elements 4
- Igneous Rocks 6
- Sedimentary and Metamorphic Rocks 7
- Ore and Sulphide Minerals 9

Soil Geochemistry 11

- The Nature of Soils 11
- Influence of the Parent Material 12
- Profile Development: Influence of Pedogenesis 14
- Natural or Baseline Contents and Pollution 17
- Chemical Forms and Fractions 18

Bioavailability 21

- General 21
- The Soil Solution 21
- Equilibria in the Soil Solution 22
- Plant Roots and the Rhizosphere 25
- Measurement of the Bioavailable Fraction 26

Introduction

Soils are a negligibly thin veneer at the interface between the lithosphere and the atmosphere. Productive agricultural soils are only about 0.001 km in depth yet below these soils lie 10–70 km of crustal rocks which, in turn, overlie 2900 km of mantle rocks: the equatorial radius of the planet is 6378 km. Human nutrition depends on this thin surface since, while acknowledging the important contribution of fish to human diets, most of our food comes from the land. Sadly, soil is dirt and dirt is despised, but if we do not unterstand the dirt beneath our feet we will not know how to keep this planet healthy for our survival and that of all its other inhabitants. This chapter presents an overview of the composition of soils and its relation to plant nutrition.

Most soils contain approximately 95% of their dry mass as mineral material and 5% as organic material. This chapter is largely concerned with the mineral material, and organic matter is discussed only so far as it influences the fate of the inorganic elements. The mineral material is derived from the break down of rocks. Embryonic soils are little more than a few millimetres of rock debris colonised by lichens while at the other extreme, in the tropics, tens of metres of weathered material may overlie unaltered rock. In all cases, however, the chemical nature of the soil will be influenced by the geochemical nature of the parent rock. In turn, plant contents tend to reflect soil contents, albeit indirectly.

Rock Geochemistry

The Elements and their Abundances

The chemical elements are often listed as the familiar periodic table which can be seen in any standard chemistry text book and will show 92 naturally occurring elements. A useful source of factual data about the elements has been provided by Emsley (1989). However, we are not concerned with all the 92 elements. Five of the 'inert gases' of Group 0 (He, Ne, Ar, Kr and Xe) need no further consideration because they are inert and therefore form no natural compounds. Radon, although it is also a Group 0 element, is of environmental interest because it is a radioactive gas and concentrations can rise to unacceptable levels in closed environments above certain rocks, especially granites (Hewitt and Kelly, 1990). However, this is a specialised topic and not one within the scope of this chapter. Promethium may occur as traces in uranium ores but its longest persisting isotope is ^{145}Pm which has a half life of only 17.7 years so that, effectively, it exists only as an artifact. Astatine also has a short half life (^{210}At = 8.3 h) and it too can be omitted. Geochemists and soil chemists therefore have some 84 naturally occurring elements as their subject matter.

Beyond element 92 (U) lie the transuranic elements of the actinide series. These are all artificial but $^{239}_{94}Pu$ is of interest because it is produced in nuclear reactors from $^{238}_{92}U$ and may be released to the environment from accidents or weapons testing. It has a very long half life (2.4×10^4 years) and is a very dangerous alpha emitter, but, like radon, its geochemistry is too specialised to be included in this chapter. Choppin and Stout (1991) have written an overview of the general chemistry of Pu, to mark the 50th anniversary of its original isolation, and Rai *et al.* (1980) have discussed its soil chemistry.

The naturally occurring elements do not occur everywhere in equal amounts or abundances. Assuming the universe did indeed begin at a finite instant of time (the 'big bang' theory) then in less than four minutes it consisted entirely of light, neutrons, subatomic particles and hydrogen and helium. It took another 700000 years for the universe to be cool enough for the hydrogen to accrete into stars and only after these had formed, evolved and finally exploded did the heavier elements, which are synthesised in the stars, join the two light gases. The consequence is that hydrogen is still the most common element in the universe.

Table 1-1 (from Emsley, 1989) lists those elements with crustal concentrations >0.1% (10000 mg kg^{-1}). The table shows that only 8 elements account for over 99% of the mass of crustal rock and 12 account for 99.9% of crustal rocks. These are the *major elements* and the remaining elements are conveniently referred to as the *trace elements.* On earth, hydrogen and helium are rare because they are too volatile to be retained by terrestrial gravity and when released to the atmosphere they eventually diffuse back to space.

Oxygen is not easily determined directly in rocks or soils and therefore the major elements are usually reported as their oxides and as *percentages.* Trace elements are

Table 1-1. Elements with a crustal abundance >0.1% (data from Emsley, 1989).

Element	Content (mg kg^{-1})
O	455000
Si	272000
Al	83000
Fe	62000
Ca	46600
Mg	27640
Na	22700
K	18400
Ti	6320
H	1520
P	1120
Mn	1060

reported as, loosely, parts per million (ppm) or per thousand million, ie, billion (ppb) but more accurately in units such as mg kg^{-1}. For geochemists the trace elements are often little more than interesting impurities in natural minerals. For biologists, however, the trace elements include essential elements, without which the organism must die or grow deformed, and highly toxic elements.

The Essential Elements

As rocks are transformed to soil so a proportion of each element is usually converted to a form which plant roots can absorb. Consequently, most of the elements in the Periodic Table would probably be detected in any plant sample if sufficiently sensitive analytical methods were used. Uptake of an element is no evidence that it plays any role in the development of the plant since a root has no power to reject any soluble element entirely. One must therefore differentiate between those elements which are needed, the essential nutrients, and the rest. The conventional criteria by which the presence of an element is regarded as essential rather than adventitious are these: the plant cannot complete its life cycle in the absence of the element; the action of the element must be specific in that no other element can wholly substitute for it nor is the element simply involved in beneficially altering the plants root environment; the element must be shown to be a constituent of an essential metabolite, or required for the proper functioning of an essential enzyme system or be uniquely involved in maintaining the overall ionic composition of tissue. Table 1-2 lists the elements which are generally accepted as being essential for plants. Major or macronutrients are separated from micronutrients, the latter being present in tissue concentration $<0.1\%$.

Table 1-2. The essential plant nutrients. The major or macronutrients are divided into (a) the major structural elements and (b) the other macronutrients.

Macronutrients
(a) Carbon, hydrogen, oxygen, nitrogen
(b) Phosphorus, potassium, sulphur, calcium, magnesium
Micronutrients
Boron, chlorine, cobalt, copper, iron, manganese, molybdenum, nickel, silicon, sodium, zinc

There is no reason to suppose that all the essential micronutrients have been identified and careful experimentation will undoubtedly prove the essentiality of other elements in due course. The agricultural significance of the most recently discovered plant micronutrients, sodium and nickel, is uncertain. There is no evidence to suggest that they limit crop production anywhere since they are required in such tiny amounts that most soils can probably satisfy a plant's normal requirements.

Both the micronutrients and most of the non-essential trace elements are known to have undesirable effects on plant and animal growth if present in excess concentration in their tissues. Plants commonly have their growth affected by excess manganese and aluminium in acid soils, and by nickel, cobalt and chromium on acid soils derived from ultramafic igneous rocks. In addition there is growing concern that several toxic elements are accumulating in some soils as a consequence of man's industrial or urban activities which lead to soil pollution or because of the use of metal-contaminated sewage sludge as a substitute for farm yard manures. Whenever an element or its compounds are heated, dissolved or pulverised it becomes environmentally labile and may escape from the working environment and ultimately accumulate in soils or sediments. Much research has been carried out on the 'heavy' metals, especially cadmium, copper, lead, mercury and zinc. The qualifier 'heavy' is not rigorously defined but most authors use it to describe metallic elements having a density greater than 6000 km m^{-3}. The more important heavy metals are listed in Table 1-3 together with

Table 1-3. Some heavy metals with their densities, average crustal rock contents and whether they are essential (E) for life processes and whether they are a known environmental pollutant (P). From Davies (1980).

Element	Density ($\times 10^3$) ($kg\ m^{-3}$)	Mean content crustal rocks ($mg\ kg^{-1}$)	Essential or pollutant
Ag	10.5	0.07	P
Au	19.3	0.05	–
Bi	9.8	0.17	P
Cd	8.7	0.2	P
Cr	7.2	100	EP
Co	8.9	25	EP
Cu	8.9	55	EP
Fe	7.9	60000	EP
Hg	13.6	0.08	P
La	6.2	25	–
Mn	7.4	950	E
Pb	11.3	13	P
Mo	10.2	1.5	EP
Ni	8.9	75	EP
Pt	21.5	0,05	–
Tl	11.9	0.45	P
Th	11.5	9.6	P
Sn	7.3	2	EP
U	19.1	2.7	P
V	6.1	135	E
W	19.3	1.5	EP
Zn	7.1	70	EP
Zr	6.5	165	–

an indication of whether they are also essential and whether they have been identified as important pollutants. Contamination of land and crops by arsenic and fluorine can also present problems locally.

Igneous Rocks

The crust and the upper part of the earth mantle are solid and comprise rigid, interlocking plates which ride over the partially molten mantle (the *asthenosphere*) in which rising convection currents force the crustal plates to move away from or into and under each other. Where the plates are parting, under the oceans, new rock is formed from the upwelling molten material, called *magma*. The new and spreading sub-oceanic crust is rich in iron and magnesium and is basaltic. The terrestrial crust formed early in the earth's history and is granitic in character. However, the rocks are continually being reworked. In particular, where one plate slides under another the consequent heating causes remelting and plumes of magma force their way back up through the crustal rocks and may emerge at the surface as volcanic ejecta or lava.

Whatever the particular mode of formation of the crustal rocks, all have in common the fact that they have originally resulted from crystallisation processes in a cooling magma. These rocks are therefore called *igneous rocks* and they are made up from intergrown and interlocking minerals (crystals) which formed as the magma cooled. Silicate minerals dominate the igneous rocks and, despite their complexity and variety, they form from a very simple building unit, a silicon-oxygen tetrahedron. Silicon has 4 electrons in its outer (M) shell ($3s^2$, $3p^2$) and loss of these gives the inert gas electron arrangement of the Si^{4+} ion. Oxygen atoms ($2s^2$, $2p^4$ electrons) accept these electrons. According to Degens (1989) there are a few thousand different minerals accessible to visible examination but only about twenty make up most rocks.

Atoms and ions of the different elements have different sizes. The theoretical ion Si^{4+} has a radius of 41 pm and that of O^{2-} is 140 pm. For a crystal to form there must be a *stable geometrical arrangement* which results in a coordination polyhedron of anions surrounding a central cation. The geometry can be predicted by deriving the cation/anion radius quotient, assuming undistorted spheres. For Si/O the radius quotient is 0.293 which corresponds to a tetrahedron. The Si–O building block is therefore a central Si^{4+} surrounded by four O^{2-} each at the apex of a regular tetrahedron. This unit is written in conventional form as $(SiO_4)^{4-}$ and each O^{2-} is half saturated by the electrons donated from the silicon. The remaining negative charges can be satisfied in two ways. Firstly, the tetrahedra can and do polymerise through shared oxygens. For example, the next most complex structure would be a double tetrahedron corresponding to $(Si_2O_7)^{6-}$. Doublets can form rings, single chains, double chains, sheets or three-dimensional frameworks. The other way involves the metals of the group of major elements. The silicate minerals consist of threedimensional arrays of silica tetrahedra held together by metal ions that saturate

the unshared oxygens. The formation of the tetrahedra can be regarded as an ionic process, but the Si–O bonds are not entirely ionic in character. Using the conventional Pauli methodology and assuming that the electronegativity of Si = 1.8 and of O = 3.5 then the Si–O bond has only 51% ionic character. Thus, the silicate minerals are neither purely ionic nor purely covalent in character.

The first minerals to crystallise, at highest temperatures and pressures, are poor in silicon (<50% SiO_2) and are rich in calcium, iron and magnesium and they form minerals, such as olivine and the pyroxenes, which make up the basic or mafic rocks. The acidic or silicic rocks are the last to form, are rich in silicon (>65% SiO_2) and are dominated by quartz, the potash feldspars and muscovite.

The discussion of crystals and ion geometry leads to a question. If the mineral crystals in the igneous rocks can largely be accounted for by Si–O tetrahedra plus the major elements, how do the trace elements occur? The answer lies in the natural impurity of the minerals. As magma cools and the minerals appropriate to a particular fluid composition and temperature–pressure combination form, then other elements in the magma are incorporated into the growing crystals, but this is not a haphazard affair and involves *isomorphous substitution*, ie, substitution by an ion of similar size.

When two ions replace each other in a crystal lattice the differences between their ionic radii must not exceed 15% and their charge differences must not be greater than one. For ions of the same charge the smaller ion tends to be incorporated preferentially and if their radii are the same but their charges differ then the ion with the greater charge is incorporated. The ionic radii of magnesium and iron are 66 pm and 74 pm, respectively and they can be replaced by cobalt (72 pm), trivalent chromium (63 pm), nickel (69 pm), zinc (74 pm) and to some extent by divalent copper (72 pm). Sometimes the ions are so similar that a complete interchange is possible (solid solution). This happens in the olivine family where the two end members are fayalite (Fe_2SiO_4) and forsterite (Mg_2SiO_4) and the relevant ionic radii are Fe^{2+} = 74 pm and Mg^{2+} = 66 pm.

Since the primary minerals are electrically neutral a compensation must occur when differently charged elements replace each other. In plagioclase feldspars Si^{4+} can be replaced by Al^{3+} but, simultaneously Na^+ is replaced by Ca^{2+}. Large, well formed crystals are prized as gems and their colours depend on these ionic substitutions. Corundum (Al_2O_3) is colourless, yet just a few Cr^{3+} ions turn it into a ruby (Burns, 1983). For a fuller discussion of igneous rocks the reader is referred to Dercourt and Paquet (1985).

Sedimentary and Metamorphic Rocks

The minerals which make up the igneous rocks form at temperatures (typically, 200–1200 °C) higher than those found at the surface of the earth (5–25 °C) (again, see Dercourt and Paquet, 1985). Unsurprisingly, they are generally unstable and break

down, albeit slowly, when exposed at the surface, the process called weathering. Two kinds of weathering may be distinguished, chemical and physical.

Physical weathering involves the mechanical disruption of rock fragments to release the individual mineral grains. The two most important processes are ice formation and crystal formation. When water enters pores or cracks in the rock and then freezes its volume expands by 9% and the mineral grains are wedged apart. Similarly, since the same water carries dissolved constituents, should the water evaporate, the residual precipitates will also wedge apart the mineral grains. Mechanical abrasion (in sand storms) or shock, entry of plant roots into cracks and differential expansion and contraction of the mineral grains over heating and cooling cycles will also contribute to physical weathering.

As physical weathering continues, the relative surface area of the rock fragments increases and the rock is increasingly subject to chemical attack through interaction with water and its dissolved constituents. This is chemical weathering. Minerals which form at the highest temperatures decompose most readily and, since these tend to contain the greatest variety and contents of essential trace elements soils which form on basic rocks are generally well endowed with micronutrients and crop deficiencies are rare. Indeed, toxicities may occur where soils form in ultrabasic rocks such as serpentine since they contain high concentrations of chromium and nickel. In contrast, acid igneous rocks are generally poor in some of the micronutrients but are enriched in lithium, tin or tungsten. For example, cobalt deficiencies in stock are common where soils are formed from granite or rhyolite.

Without water chemical weathering cannot take place. Desert soils are thin and barely distinguishable from the underlying rock or sediment whereas soils of the humid tropics may be tens of metres thick. Higher temperatures as well as the ubiquity of water account for deep weathering in the tropics and a familiar rule of thumb is that a change of 10 °C in mean temperatures corresponds to a doubling, or halving, in weathering rates. The polar nature of the water molecule makes it effective in dissolving ionic compounds and therefore all silicates are to some extent, at least, water soluble. However, the major weathering process is hydrolysis where hydrogen and hydroxyl ions react with silicate lattices leading both to breakdown products and to a synthesis of new, secondary minerals. Hydrolysis also involves the dissolved constituents in water such as carbon dioxide or organic acids released from lichens (the first colonisers of rock surfaces) or higher plant roots. The decomposition of forsterite (olivine) exemplifies a simple case of hydrolysis:

$$Mg_2SiO_4 + 4H_2O = 2Mg^{2+} + 4OH^- + H_4SiO_4$$

During the process of weathering, new kinds of minerals, the secondary minerals, are synthesised. As well as precipitates (hydroxides, oxides, sulphates, carbonates and phosphates) there are the clay minerals. For example, potassium feldspar can hydrolyse and lead to the formation of kaolinite:

$$2KAlSi_3O_8 + 9H_2O + 2H^+ = Al_2Si_2O_5(OH)_4 + 2K^+ + 4H_4SiO_4$$

The general structure of clay minerals involves the silicon–oxygen tetrahedra, as described above, and aluminium at the centre of an octahedral arrangement of hydroxyl ions. The octahedral and tetrahedral units link through shared oxygens and the minerals are formed as sheet structures of polymerised tetrahedral units bonded to sheet of polymerised octahedral units. The two broad classes of clay minerals are the 1:1 minerals (chiefly kaolinite) comprising one tetrahedral and one octahedral sheet and the 2:1 minerals (illite, momtmorillonite) where the octahedral sheet is sandwiched between two tetrahedral sheets. Isomorphous replacement of Si and Al occurs, typically, Si is substituted by aluminium or Al by Mg or Fe(II). In each case the consequence is the development of a negative charge on the surface of the mineral which is neutralised by the adsorption of cations from the weathering or soil solution. These cations are held only by electrostatic forces and therefore readily exchange with other cations. The cation exchange process is of great importance in the chemistry of soils and the reader is referred to Sposito (1989) or Talibudeen (1981) for a detailed account.

Erosion processes ultimately redistribute the weathering products and new sediments are formed. When buried they undergo diagenesis to form the sedimentary rocks. Ultimately, these sedimentary rocks will be exposed and will themselves undergo weathering and form the parent materials of new soils.

More extreme subterranean processes (especially heat) cause substantial changes in the sediments and lead to the formation of metamorphic rock. Thus, marble is heat metamorphosed limestone and slate is pressure metamorphosed shale.

From an agricultural viewpoint the sedimentary rocks are far more important than the igneous rocks since, although they represent only 15% of the crustal volume they occur spread over the igneous basement and amount to approximately 75% of the earth's surface. The most common sedimentary rocks are shales and mudstones (80%); sandstones, conglomerates and limestones account for the remaining 20%.

Generally for sedimentary rocks substitution in silicate lattices of primary minerals is of lesser importance. As the primary minerals decompose during weathering the alkaline earths and alkali metals tend to remain in solution and some of the metallic micronutrients pass into the lattices of the secondary or clay minerals. Others become adsorbed onto clay sized particles, are incorporated into humified organic matter by complexation or separate as precipitates following changes in redox potential.

Ore and Sulphide Minerals

Ores are metalliferous minerals which can be extracted from their host rocks to yield their metals economically, ie, the costs of mining and extraction must be compared with the revenue from selling the ore concentrates. Ores are therefore localised concentration of metal compounds. These minerals are not usually the parent materials for

soils but they are of importance because mining, ore processing and smelting and the later use of metal compounds can cause soil contamination as metals are lost to the environment during processing. It is helpful to know a little about certain ore minerals in order to understand better the chemistry of contaminated soils.

The greatest interest centres on sulphide ore minerals. Metals react as electron-pair acceptors with electron-pair donors and both donors and acceptors may be classified as hard or soft (Pearson, 1967). Soft donors preferentially bind to soft acceptors such as SH^-, S^-. Thus, zinc or lead, being soft acceptors, bind to sulphide and geochemists classify them as chalcophilic metals. They occur as localised concentrations within the host rock from which they are liberated during mining. Some rock formations may contain sulphide minerals in too low a content to make economic extraction feasible but their presence will modify the total content of metals in the rock. When ore minerals form contemporaneously with the host rock they are called syngenetic. Often hot seawater or groundwater will react with igneous rocks and the elements dissolved from the primary silicates may then be reprecipitated in faults in the overlying sedimentary rocks. These are the epigenetic minerals.

Isomorphous substitution can occur both for the metal ion in the mineral or for the sulphide. The minor elemental constituents of the ore minerals may have considerable economic importance. For example, galena (PbS) can contain several percent Ag, and Cd is a prominent 'guest' in sphalerite (ZnS).

Alterations to the bulk rock content arising from the presence of dispersed sulphide phases are not confined to igneous rocks. The black shales are intermediary between shales and organic deposits (coal, lignite). They are deposited in still, marine basins and incorporate organic matter under reducing conditions. Pyrite (FeS_2) forms and they are enriched in the chalcophilic metals. Altschuler *et al.* (1983) have studied sulphur diagenesis in peat of the Florida (USA) Everglades. They concluded that pyrite forms directly from the reduction of organic oxysulphur compounds which generate HS^- or organic sulphides which react with ferrous iron in degrading tissues. These mechanisms can probably be applied to the formation of coals and organic sediments.

Thomson *et al.* (1973) have reported that clinical copper deficiency in farm animals is associated with black shales in England as a consequence of them, and their superjacent soils, being enriched in molybdenum. The resulting excess molybdenum in the diet of the grazing animals reduces the utilisation of dietary copper.

Ore metals and their crystal 'guests' may accumulate in soils and then move up the food chain. In organisms they will bind to the SH-groups of proteins (including enzymes) and thereby denature them. Thus they are toxic to organisms, and metals like Cd are well known for their pronounced toxicity. The trace constituents of the sulphide ore minerals are therefore of more than geochemical interest.

Table 1-4 provides some data selected from El Shazly *et al.* (1956) for epigenetic sphalerite. The high concentrations of Cd should be noted. During smelting the ZnS is reduced to Zn metal and the Cd is then an impurity in the ingot metal. Subsequent

Table 1-4. Concentrations ($\mu g\ g^{-1}$) of 'guest' trace elements in selected samples of epigenetic sphalerite. Data from El Shazly *et al.* (1956).

Location	Ga	Ge	Sb	Cd
Wales	20	100	200	1%
	30	200	100	1%
	200	200	100	2000
	200	250	100	1000
Salop	200	100	–	5000
Devon	100	10	–	3000

refining may isolate the Cd as a valuable coproduct or it may be passed on to the Zn compounds used in industry. Thus, environmental contamination by Zn often implies simultaneous contamination by Cd. Galena can contain appreciable amounts of Ag. El Shazly *et al.* (1956) reported as much as 5000 μg Ag g^{-1} in samples of epigenetic galena from Wales and the West of England. Jones *et al.* (1986) reported that while uncontaminated soils in West Wales contained <0.1 μg Ag g^{-1} those affected by past lead mining could contain as much as 9 μg Ag^{-1}.

Soil Geochemistry

The Nature of Soils

Soil formation is more than a simple chemical and physical attack on rocks since it also involves the participation of living organisms, such as plants or microbes, in the weathering process. Biological and non-biological weathering are not always distinguishable but it is the biological factor which differentiates soil from any other loose surface material which is referred to as regolith. It should be noted that this restrictive understanding of the word soil is not that of the engineer for whom soil includes regolith.

Soil must not be thought of as simply a residual layer which supplies nutrients for plant, and hence animal, growth. Soils are dynamic bodies in the landscape which change and evolve as environmental conditions change. Soils are the consequence of the interaction of climate and organisms on their parent material over time and modified by local topography. Human influences can be considered as a particularly intensive subset of the general effects of organisms.

The characteristic feature of soils and the way in which they are classified and recognised is the presence of distinct layers or horizons formed by pedogenesis. The smallest volume of soil which can be recognised as having all the distinctive features of that particular soil is called a pedon and a profile is the vertical section through

the pedon to reveal the arrangement of horizons. A pedon is not as distinctive as, say, a plant species. It is more like the unit cell of a mineral crystal. The soil landscape can be visualised as a mosaic of pedons. For practical mapping and classificatory purposes the *soil series* is used as the fundamental soil unit. Soils are grouped together within a series on the basis of similar assemblages of horizons, a common parent material and formation under similar environmental conditions.

Influence of the Parent Material

The soil inherits from the parent material a stock of trace elements which, in turn, is controlled by the geochemical nature of the parent material (West, 1981). In global terms this relationship can be illustrated by comparing the commonly accepted mean contents of soil elemental constituents with crustal rock abundances. Reasonably reliable data are available for 67 elements.

Figure 1-1 illustrates the relationship between soil and rock composition and is based on soil data derived from Ure and Berrow (1982) and rock data from Emsley

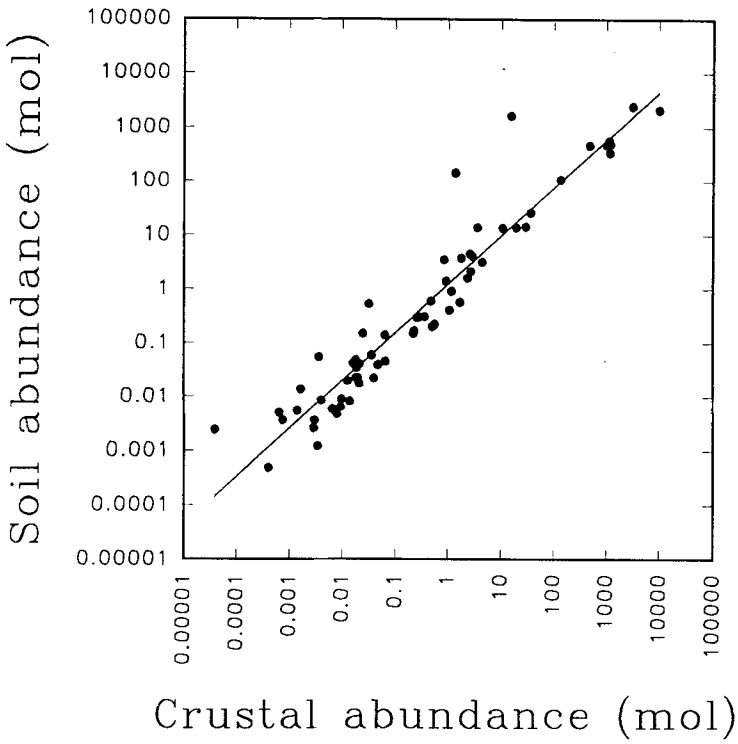

Fig. 1-1. A log–log plot of elemental abundances in soil and rock to demonstrate the close relationship of the former on the latter (data from Emsley, 1989 and Ure and Berrow, 1982).

Table 1-5. Chromium and nickel contents ($\mu g\ g^{-1}$) of soil in relation to parent material. Data taken from Berrow and Reaves (1986).

Rock type	Cr	Ni
Granitic	49	16
Intermediate igneous	100	42
Basic and ultrabasic	280	89
Metamorphic	54	26
Sands, gravels	30	16
Shales	190	53

(1989). For most elements there is a close relationship between rock and soil. The graph indicates an overall enrichment in soil compared with rock and this can be explained by a tendency to lose Si (silicic acid) to the drainage water during weathering. Among the elements showing a strong enrichment in soils (mol ratio > 1.5) are carbon and nitrogen which is accounted for by the accumulation of humus in surface horizons.

Detailed, localised studies have broadly confirmed the close relationship between rock and soil elemental contents. Table 1-5 illustrates the relationship between soil contents and rock type for chromium and nickel in Scottish soil (Berrow and Reaves, 1986). The two elements are more abundant in basic than in granitic rocks and the data confirm the control of parent material. There have been few multi-element studies of different soil series. Pierce *et al.* (1982) analysed soil samples for Cd, Cr, Cu, Ni, Pb and Zn from two dominant soil series from each of six parent materials and four series from a seventh parent material in Minnesota (USA). Differences were attributed to their differing parent materials and they concluded that the soil series is a basic sampling unit for assessing the metal content of soils. In contrast, Khan and Nortcliff (1982) working in England evaluted the micronutrient variability of a single soil series, the Sonning series, which has developed in terrace sands and gravels in the Thames valley. They concluded that relatively homogeneous units delineated by soil surveyors were not homogeneous for micronutrients when a considerably finer subdivision was needed. More studies are needed to settle the question whether the soil series is useful in classifying trace element data.

The weathering pathways of trace elements are complex and diagenesis causes further changes in the composition of sediments so that only general guidance is possible concerning the composition of sedimentary rocks. Trace element concentrations in sandstones are generally low since these rocks are frequently dominated by quartz particles, although the matrix may be formed from other resistant minerals, and it is the matrix cement which carries the micronutrients which eventually become available to plants. Consequently, micronutrient deficiencies in plants or animals are often more frequent in areas where soils have developed in arenaceous sediments. Purves and Ragg (1962) found that the distribution of 'wither tip', the classical symptom of cop-

per deficiency in cereals, and low soil copper contents were directly related to the presence of one soil series, the Eckford series developed in fluvioglacial sands. Similar problems are encountered on other light textured parent materials such as aeolian sands, fluvioglacial sands, cover sands and coarse glacial outwash deposits. Carbonate sediments may also present micronutrient fertility problems. Where the sediments are very pure the only significant source of trace elements in the soil may be from extraneous materials. In southern England copper deficiencies occur in cereals growing in shallow rendzinas except where the soil is influenced by Pleistocene loess or other incorporations of non-carbonate materials. Isomorphous substitution for calcium is possible by barium, strontium and lead and limestones are often solid solutions of calcium and magnesium carbonates. However many carbonate rocks are impure and their trace element contents may be boosted by iron/manganese oxides and clays. In between the two extremes of sandstone and limestone are the shales which generally have a satisfactory trace element composition but they are so variable in composition that broad guidelines may be of little help. Special mention must be made of the black shales which are enriched in sulphide minerals and organic matter and grade into bituminous shales and coals. They tend to contain very high concentrations of chalcophilic micronutrients and in England and Wales they have been associated with molybdenum induced hypocuprosis in sheep and cattle. Tinker (1986) has written a general overview of trace element problems in arable agriculture in Britain.

These geochemical generalisations are useful when considering young soils where soil composition is broadly similar to that of the parent material, but little general guidance is available for old, deeply weathered soils rich in iron, manganese and aluminium oxides and the published literature tends of be contradictory. In Ghana, a survey of 19 profiles representing most of the major soils of the forest zone led to the conclusion that total trace element content was related to the underlying geological formations (Burridge and Ahn, 1965). On the other hand, Oertel (1961) concluded from studies of Australian soils that the soil/rock relationship is often not close enough for the satisfactory prediction of soil contents from parent material values because of the influence of pedogenetic factors.

Profile Development: Influence of Pedogenesis

Nearly all the changes which occur during pedogenesis require liquid water: in dry or frozen soils the rate of weathering or pedogenesis is negligible. In general, water moves vertically up or down in a soil carrying with it (leaching) the soluble or colloidal products of weathering. Some lateral movement does occur but the overall trend of movements is downwards. The matrix constituents of soils are not all equally soluble, quartz can be regarded as essentially insoluble.

The profile development process is therefore marked by differential movement of constituents: some, such as salts of potassium or sodium may be leached completely

from the soil into the drainage water, others will accumulate relatively because they are left behind while others will accumulate in subsoil horizons because of changes in the chemical conditions within the soil. Figure 1-2 illustrates this for Cu, Ni and Cr in a podsol and in a brown earth using data from Finch *et al.* (1964) and Swaine and Mitchell (1960). Bache (1983) has described how the composition of surface waters reflects that of the soil through which water has passed but when the residence time in soil is low then surface waters more nearly resemble local precipitation in composition.

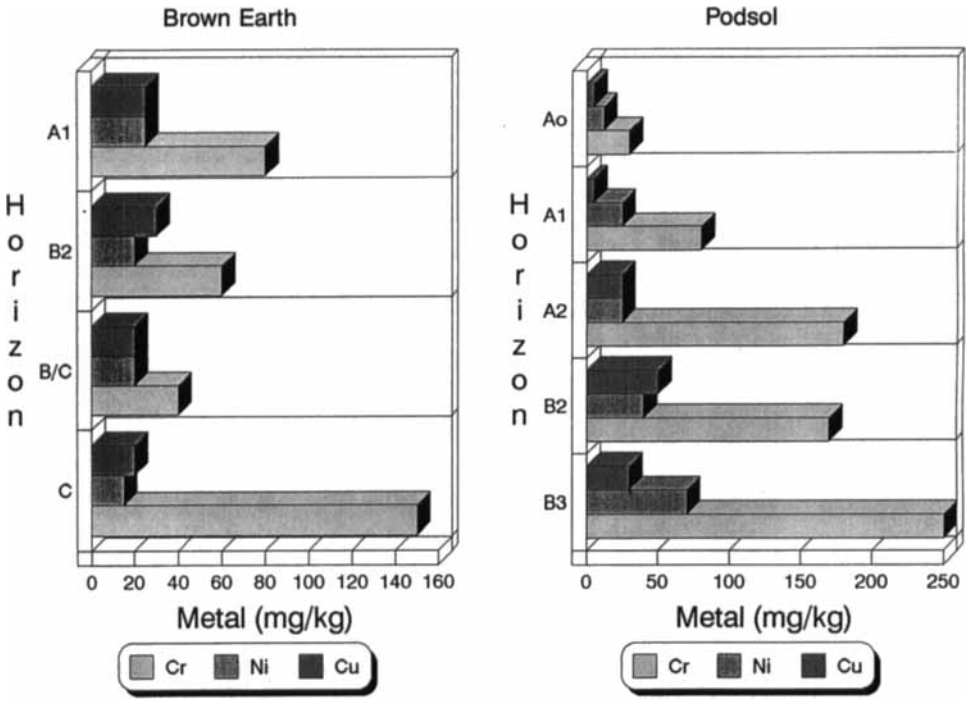

Fig. 1-2. Chromium, copper and nickel contents of genetic soil horizons of a brown earth and a podsol. In the podsol there is a marked depletion of metals in A horizons compared with B horizons whereas differences are less pronounced in brown earths (data from Finch *et al.*, 1964 and Swaine and Mitchell, 1960).

As silicate minerals decompose, trace elements are released and enter the soil solution. Thereafter their fate depends on a number of factors. Immediately, they may precipitate or remain in solution and the likelihood of this happening can be predicted by considering the ion's charge/radius (in nm) ratio, which is often called the *ionic potential* (IP). Values of IP >95 refer to soluble anions of the elements B, Cr(VI), Mo(VI), Si and W. Soluble cations are found in a group where IP <30, namely Cd, Co, Cu, Fe(II), Pb, Mn(II), Hg, Ni, Ag, Sr, Sn and Zn.

Elements may be trapped in those soil fractions formed from compounds of elements where IP ranges from 30 to 95. This is a group of elements which tend to accumulate in weathering residues and includes the elements Cr(III), Fe(III), Mn(III), Mo(IV), V(III) and V(V). Iron and manganese dominate the group and in most soils these elements precipitate as hydrous oxides either in concretionary forms or as coatings on mineral and clay surfaces. They exert a chemical control on the activities of other ions far greater than might be supposed from their concentrations (Jenne, 1968). The hydrous oxides act as sinks for other trace elements through several mechanisms (Hem, 1977; Loganathan *et al.*, 1977; Okazaki *et al.*, 1986). As they form, other trace metals can be occluded in the oxide precipitate and cobalt is notable for its association with manganese oxides. They tend to have high adsorption affinities which increase with pH and the trace cations are readily sorbed onto the oxide surfaces after which they may enter the precipitate through solid state diffusion. Superimposed on these mechanisms is the possibility that the hydrous oxides can dissolve and then precipitate again in response to changes in the soil's redox potential or pH.

Two important chemical parameters control the nature of the leaching regime. The first is acidity, ie, pH. Desert and semidesert soils may have pH values up to about 10 because of the presence of sodium bicarbonate in the soil solution but usually a pH value of about 8.3 represents the upper limit. Soils with pH values in the range 7.0–8.3 are those formed on limestone and the soil solution is dominated by carbonate/bicarbonate. Many metal carbonates have low solubilities and leaching losses are therefore minimal. With increasing acidity leaching losses become more pronounced and at pH = ca. 4.0 the clay minerals start to degrade and aluminium dominates the soil solution. Agricultural soils are usually maintained at pH values above 6 and enhanced solubility of metal ions under the more extreme acid conditions is not important. However, in recent years concern has mounted over the effects of 'acid rain', ie, increased wet and dry deposition of sulphates or nitrates from industrial sources. Berggren *et al.* (1990) have reported that forest soils in southern Scandinavia have become, on average, 0.5–1.0 pH units lower during the course of recent decades. The solubility of Al, major cations, Mn, Cd and Zn has increased and large areas of forest soils now have acidity conditions such that any additional input of strong mineral acids causes a rapid increase in the release rates of these elements.

The second control is the reduction–oxidation potential, *Eh*. In most soils the dissolved oxygen content of the soil solution is high enough to ensure that oxidising conditions prevail. Where water percolates slowly through the profile or where water is stagnant in the soil, reducing conditions are found and the process of *gleisation* occurs. Sulphate reduces to sulphide and most metal sulphides are very insoluble. For agricultural soils marked reductions in soil *Eh* do not occur but the control of redox potential on metal solubility is an important consideration for padi rice and in wetland soils which may be drained and aerated during reclamation. De Laune *et al.* (1981) maintained sediment suspensions at pH values of 5.0, 6.5 and 8.0 and *Eh* values of −200 mV, 0 mV, 250 mV and 500 mV. Iron and Mn concentrations decreased

significantly as pH and *Eh* were raised. Calmano *et al.* (1986) have reported how changes from neutral, reducing environments to moderately acid, oxic environments lead to increased bioavailability of Cd.

Weathering and leaching are not the only processes that cause the development of horizons. Plants draw their moisture and nutrients from a relatively large volume of soil but, assuming they are not harvested, will return their inorganic constituents to the *surface* through leaf fall or generally to the upper layers through root death. The fresh organic material is food for many organisms, which, in turn, live on each other. Thus, organic material changes until the end product, a black or brown organic material with a lignin-like structure, called humus which enriches the surface layers. Humus is a store of trace metals through adsorption, since it carries a negative charge like the clays, or through complexation (chelation). Metals may be released as humus oxidises (mineralises) or by desorption or decomplexation (Shuman, 1988; Livens, 1991).

Natural or Baseline Contents and Pollution

Little has yet been done to put the presentation of soil data on a firm statistical footing and most compilations merely summarise the elemental values recorded in the literature. Such summaries may well be biased by an inherent research interest in unusually high or unusually low concentrations. In recent years there has been a movement towards reporting trace element concentrations in terms of probability ranges for carefully defined parent materials.

There is no simple, unequivocal way of recognising when a soil has been contaminated or polluted by trace elements since all the naturally occurring elements are present in all soils, albeit at very low concentrations. The problem of recognising whether contamination by metals has taken place becomes one of deciding whether the measured concentration of a particular element is within the range of what could occur naturally for that soil or whether the measured concentration is *anomalous*.

It is not clear what is the best model to describe the variability of soil metal concentrations. Ahrens (1954, 1966) has proposed that the distribution of elements in igneous rocks approximates to a log-normal distribution. This model does not necessarily apply to soils but the available evidence suggests it may. Its applicability underlies the interpretation of geochemical data in mineral exploration.

Rose *et al.* (1979) discuss the concept of *threshold*, the upper limit of normal background fluctuations. Values above background are considered anomalous. This approach is directly applicable to contamination studies since a contaminated soil is an anomalous soil. The simplest way of identifying threshold concentrations is by collecting samples from apparently uncontaminated areas (eg, those remote from urban or industrial influences). After analysis the geometric means and deviations are calculated. The threshold is then the value lying two or more standard deviations from

the mean, depending on the probability level required. An anomalous value is one which lies above the threshold. Negative anomalies may also be recognised and are applicable to nutrient deficiency studies.

Very often it is not possible *a priori* to separate contaminated and uncontaminated soils at the time of sampling. The best that can be done in this situation is to assume the data comprise several overlapping log-normal populations. A plot of percent cumulative frequency versus concentration (either arithmetic or log-transformed values) on probability paper produces a straight line for a normal or log-normal population. Overlapping populations plot as intersecting lines. These are called broken line plots and Tennant and White (1959) and Sinclair (1974) have explained how these composite curves may be partitioned so as to separate out the background population and then estimate its mean and standard deviation. Davies (1983) applied the technique to soils in England and Wales and thereby estimated the upper limits for lead content in uncontaminated soils.

It should not be assumed that anomalous concentrations necessarily indicate contamination. Bolviken and Låg (1977) have described areas in Norway where the absence of vegetation is due to the toxic effects of high concentrations of metals in soils as a result of weathering of sulphide ores close to the surface. This is a natural process having nothing to do with contamination.

Identification of a geochemical anomaly should, in the first instance, be considered as only that, an anomaly. Other evidence must be taken into account to decide whether the anomaly is natural or is a *neoanomaly*, one caused by anthropogenic contamination.

Chemical Forms and Fractions

Soil is a mechanically and chemically complex and heterogeneous material. A casual glance at a spadeful will show that it is composed of particles of very different sizes, some large (gravel, stones, boulders) and other small (sand, silt, clay). Soil scientists classify soil into *texture classes* based on the proportions of different particle diameters. The particles are usually stuck together to give aggregates of different sizes and shapes, collectively described as soil *structure*. Closer examination reveals even greater complexity. A microscopic examination of thin slices of intact soil will reveal its microstructure a characteristic of which is the formation of *cutans*. These are distinct deposits of manganese or iron oxides on surfaces or orientated clay or precipitate fillings of pores and channels. Soils contain humified organic matter. Some soils have visible nodules of iron oxides or calcium carbonate or sulphate. This chemical heterogeneity has led to the concept that bulk soil can be thought to contain different chemical fractions and that trace elements are distributed non-uniformly among these fractions. Various dilute solutions have been used which are believed to dissolve these fractions selectively and thereby yield evidence for the dominant chemical locations of the trace elements.

An early method which passed into general use was that of Bascomb (1968) in relation to iron and organic carbon. His classification of iron compounds is a good example of one based on previous field and laboratory experience. He postulated that inorganic iron compounds could be classified as (1) silicates, (2) well crystallised oxides, (3) amorphous but 'aged' hydrous oxides and (4) amorphous 'gel' hydrous oxides. His fractionation method was based, in part, on an assumption that a potassium pyrophosphate solution (0.1M) at pH 10.0 would extract only category (4) whereas the same reagent at pH 7.0 would also extract category (3). Other reagents were used for the organic fractions and the remaining iron categories.

McLaren and Crawford (1973) studied the fractionation of soil copper and proposed that it could occur in soils in several forms, namely:

(a) in the soil solution as ions or complexes
(b) on normal cation exchange sites
(c) on specific sorption sites, ie, adsorbed copper which cannot be removed by the reagents normally used for determining the exchangeable ions
(d) occluded in soil oxide material
(e) in living organisms or in organic residues
(f) in the lattice structure of soil minerals

This classification of fractions was also based on a generally agreed understanding of the composition of soils derived from many years of field and laboratory experience. The reagents proposed were also a selection of those in common use in soils laboratories. The soil solution and exchangeable copper were extracted by 0.05 M $CaCl_2$; specifically sorbed copper was extracted with 2.5% (v:v) acetic (ethanoic) acid; 1.0 M potassium pyrophosphate extracted organically bound copper; an ammonium oxalate/oxalic acid mixed solution at pH 3.25 extracted copper occluded by free iron oxides while the residual lattice copper was determined using hydrofluoric acid. There are now many schemes in use (eg, Clevenger, 1990) and that of Tessier *et al.* (1979) is often followed or adapted.

Some of the more commonly used reagents are listed in Table 1-6 together with an indication of which chemical fraction they are thought to extract. The order in the table is one of increasing vigour of attack on the soil so that a solution which extracts, say, metals from the humus in soil will also extract from the soil solution and from the exchangeable pool. All are empirical and, while the fractions proposed are based on much research, the fractions as measured are usually operationally defined in the sense that an individual fraction is presumed to attack a certain chemical reservoir. Shuman (1991) should be consulted for a recent critical review of the chemical forms of micronutrients in soils. Fig. 1-3 uses data from Shuman (1985) to illustrate the results from a typical fractionation study.

Table 1-6. Some common diagnostic soil extractants and the chemical forms they are thought to extract.

Soil fraction	Common extractant
Soil solution	H_2O; 0.01M $CaCl_2$
Readily exchangeable	0.5M CH_3COONH_4; 0.2M $MgSO_4$; 0.1M NH_4Cl; 1M NH_4NO_3
Specifically sorbed	0.5M CH_3COOH; 0.1M HCl; 0.1M HNO_3
Organically bound	0.05M EDTA[a]; 0.05M EDDAH[b]; 0.005M DTPA + 0.01M TEA + 0.05M $CaCl_2$[b]
Hydrous oxide bound	1M CH_3COONH_4 + 0.002M $C_6H_5(OH)_2$ 0.2M $(COO)_2(NH_4)_2$ + 0.15M $(COOH)_2$ @pH 3.3
Residual	HF; mixtures of mineral acids, concentrated hot, namely: HNO_3 + $HClO_4$; HNO_3; HNO_3 + HCl; also fusion mixtures

[a] ethylene diamine tetraacetic acid, disodium or diammonium salt
[b] ethylene diamine di-*o*-hydroxyphenyl acetic acid
[c] diethylene triaminepentaacetic acid and triethanolamine with calcium chloride at pH 7.3

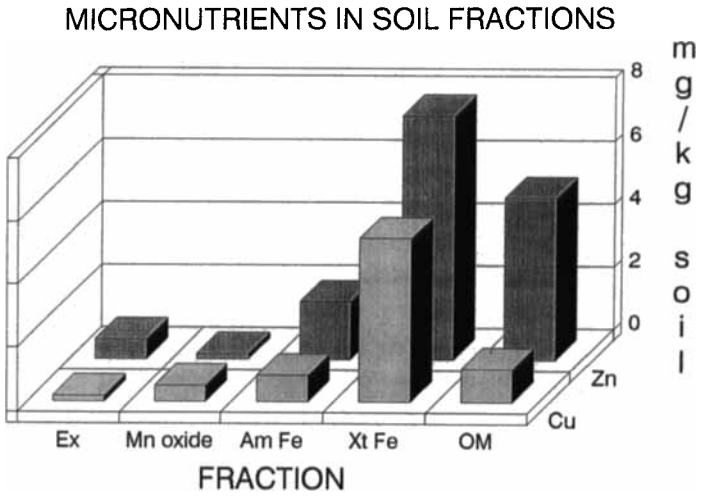

Fig. 1-3. Copper and zinc concentrations in soil chemical fractions (data from Shuman, 1985).