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Soil as the Source of Trace Elements [and Discussion]

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Soil as the source of trace elements

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The nature of the parent rock determines the trace element content of soils. Ultrabasic and basic rocks, which solidified first from the molten magma, incorporated bioessential trace elements such as Co, Ni, Zn and Cr by isomorphous replacement of Fe and Mg in ferromagnesian minerals, while acidic rocks, the last to solidify, tended to be richer in other elements such as Ba and Pb. Cu, Mn and, to a lesser extent, B, Mo and Se are more evenly distributed. The weathering of rocks by pedological and biological processes such as glacial and hydrodynamic comminution, secretion of acids and liganding species by microbes and plants leads to the formation of sands, silts and clays, and finally the incorporation of organic matter causes humification and the formation of soils as we know them. Part of the soil's store of bioessential elements is held in forms that are available to plants. Availability is controlled by the forms of occurrence and the nature of binding of the trace elements in the soil, which in turn is affected by soil acidity, redox balance (drainage) and organic matter content. These and other factors are discussed along with measures for alleviation of deficiency problems. Future progress in this area will depend to a large extent on interdisciplinary research by biologists, chemists, physicists and statisticians.

Introduction

This paper is concerned with the role of soils in relation to trace element deficiency problems in animals and man. It therefore deals only with those trace elements that are known at present to be biosignificant, and with their supply to plants and herbage at the soil–root interface. The role of trace elements within plants is discussed in the paper by Tinker (this symposium). The ability of soils to supply trace elements varies enormously according to their geological origin and subsequent history, and in this respect it should be noted that most of the following discussion relates to the relatively young soils that have weathered under temperate conditions in the United Kingdom. It should also be observed at the outset *vis-à-vis* any conclusions that may be drawn, that modern man living in an industrial society derives his food from such a wide soil-base that it is doubtful if any valid relation can be traced between soil-supply and human deficiency problems except in some primitive or other atypical situations. The picture is also obscured in respect of animal trace element intake and output to the soil by the practice of intensive animal husbandry.

Lastly, by way of introduction, it should be appreciated that grazing animals such as sheep may ingest 3–5% of their dry matter intake as raw soil under temperate conditions and as much as 50% under arid conditions. Little information has been recorded on the availability to animals of trace elements from ingested soil, but it is interesting to note that it has been observed (Suttle *et al.* 1975) that soil ingestion can induce copper deficiency.

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ROCK SOURCES OF TRACE ELEMENTS

Of the Earth's rocks, 95% are igneous and 5% sedimentary. Of the latter, 80% are shales, 15% sandstones and 5% calcareous. However, sedimentary rocks are rather more important agriculturally than these proportions suggest, since they tend to be concentrated at the Earth's surface. Metamorphic rocks are classed with igneous rocks for the purpose of the present discussion.

Igneous rocks

The first rocks to solidify from the molten silicate magma were the magnesium aluminosilicate-rich ultrabasic and basic rocks, e.g. gabbro, high in minerals such as olivine. These were followed by intermediate rocks, e.g. andesite, and finally acidic rocks, e.g. granites rich in silica. According to Goldschmidt (1954), the first ferromagnesian minerals to crystallize in the ultrabasic and basic rocks incorporated or occluded in their lattices trace metals from the magma such as Co, Cr, Ni and Zn whose ionic radii were close to those of Mg and Fe (*ca.* 0.08 nm). In a similar manner, minerals in the intermediate rocks tended to occlude Cu, Mn and V with smaller amounts of Co and Ni and with the Co/Ni ratio increasing from less than 1 in the ultrabasic to more than 1 in the intermediate rocks. The acidic rocks crystallized their minerals from a magma depleted of most of the bioessential trace elements, and incorporated trace elements by replacement of potassium in potassium-rich minerals, i.e. elements of ionic radii ≈ 0.13 nm, namely Pb^{2+}, Ba^{2+}, Rb^{+}, etc. Thus, soils derived by simple weathering from basic rocks tend to contain a sufficiency of bioessential trace elements such as Mn, Fe, Ni, Co and Zn, and sometimes too much of the more toxic of them, e.g. Ni, while soils similarly derived from granitic rocks tend to be low in bioessential elements. Cu and Mn are fairly uniformly distributed, while Zn varies from about 200 μg/g in ultrabasic to less than 50 μg/g in acidic rocks. The corresponding figures for some other bioessential trace elements are: B, 30–10; Mo, 3–0.1; Se, 0.5–0.1 μg/g. There are, of course, factors other than ionic radii to be taken into consideration, e.g. ionic potential and coordination geometry, but these cannot be discussed here. It may be concluded, however, that soils directly derived from igneous rocks should have fairly well defined total contents of trace elements.

Sedimentary rocks

The position is more complicated for sedimentary rocks (Goldschmidt 1945). These are formed chiefly by hydrological and glacial weathering of igneous rocks and should contain the same mineral constituents, but the ferromagnesian minerals such as olivine, hornblende and biotite are more easily weathered than apatite, garnet and muscovite, while others such as ilmenite, magnetite, tourmaline, quartz and zircon are most resistant. Thus, the first-formed sedimentary rocks would tend to be rich in bioessential elements and secondary minerals from basic and ultrabasic rocks. In the process of weathering, much of the original mineral lattice is broken down and those elements of ionic potential less than 2, e.g. alkaline earths and alkali metals, tend to remain in solution, while most of the bioessential elements will be deposited in hydrolysate matrices of elements of high ionic potential, e.g. Si, Al and P. The more readily weathered rocks thus pass their constituents into the layered clay mineral-rich argillaceous rocks (e.g. shales), which are the predominant (*ca.* 80%) sedimentary rocks on the Earth's surface. There the secondary (clay) minerals such as montmorillonite, illite and kaolinite incorporate bioessential elements such as Fe, Mg, Zn, Cr and Mn by replacement of Al within their layer lattices, but they also have large specific surfaces with high cation exchange capacities so that they adsorb considerable amounts of Cu, Co, Mn, Ni and Zn, which, though strongly held, are much more readily available than the corresponding lattice-held ions, which can only be released slowly or by further weathering. Some typical total contents of argillaceous rocks are (in micrograms per gram): Cu, 20–200; Co, 10–50; Mn, 500–5000; Zn, 20–200; B, 20–200; Mo and Se, 0.1–5. These values are not greatly different from those of igneous rocks, but the relatively large amounts of Mo and Se are significant. The bituminous shales of biological origin tend to have higher contents of elements that show a strong affinity for sulphur, e.g. Se, U and Mo. The presence of these large concentrations of otherwise bioessential elements such as Mo and Se in bituminous shales should be noted in relation to potential toxicity.

Arenaceous rocks (sandstones), which constitute *ca.* 15% of the sedimentary rocks, form from the more resistant igneous rocks and minerals and, as expected, commonly have lower contents of bioessential elements. Limestones and dolomites (5% of sedimentaries) also tend to have low bioessential trace element contents.

Metamorphic rocks, classified here as igneous, are produced by the effects of extreme pressure and temperature. In altered argillaceous rocks the recrystallization of clay minerals may cause partial reversion to primary minerals and hence decrease the availability of trace elements. Slates, schists and gneiss have elemental contents similar to their parent sedimentary rocks, but some volatile elements, e.g. B, Sn, Zn and Pb, may partly have been distilled off into adjacent strata.

It is the type of parent rock that dictates the trace element content of soils derived from it, and the subsequent history of weathering and soil management practices dictate the availability to plants of the store of trace elements contained in the soil. At best the total trace element content of a soil can only serve as a rough guide to its potential ability, or inability, to supply bioessential trace elements. Very few soils are 'deficient' in the absolute sense that they do not contain sufficient total amounts of trace elements, but some cannot provide an immediate sufficiency for plant growth. Some soils provide an over-generous supply of 'available' trace elements and consequently cause toxic effects, but this aspect will not be considered further in the context of this Discussion Meeting.

Pedological and biological weathering

Action of ice

In the present-day temperate regions of the world, many of the soils have been derived by glacial comminution of the parent rocks to produce boulder clay or glacial till. Glaciated landscapes are easily recognized from their topography. In the process, soils thus formed may have been transported long distances from their parent rocks to overlie totally different base rocks completely unrelated to them. While this factor makes it difficult to relate soil properties to local geology, it does not affect the trace element status of the soil. However, other aspects of glaciation do have such an effect, chiefly the mixing up of soils formed from many different rocks, resulting, for example, in the northern part of the U.K. having many totally different soils with widely varying trace element characteristics within small areas. The soil map of the Soil Survey for Scotland (Glentworth & Muir 1963) shows 40 different soils in the 400 square miles around the village of Inverurie. These soils are derived from parent materials varying from ultrabasic to acid igneous rocks and from sandstones to slates and argillaceous schists.

Thus typically in Scotland there may be several widely differing soils within the boundaries of a single field. Another aspect of glaciation of soils that deserves mention is the existence of indurated layers within the soil. These heavily cemented layers, which probably arise from compaction at the permafrost layer and the packing of pores by silt and clay, restrict the downward movement of water as well as the access of roots to subsoil. As will be seen later, restricted drainage is one of the major factors that modifies the ability of soils to supply trace elements.

Action of water and wind

Hydrodynamic weathering, i.e. the action of flowing water, is another major weathering process, and plays a large part in the formation of sands, gravels and silts, causing in the process a considerable amount of size sorting of different soil fractions. These two main physical weathering processes will lead generally to the formation of sediments and should be linked to similar wind erosion processes, which lead to the formation of aeolian clays (loess) in the plains of central Europe, Asia, etc.

The primary physical weathering of rocks by wind, water, ice and solar radiation, produces the inorganic or mineral skeleton of the soils, which, under normal circumstances in most localities, will be modified by the incorporation of organic matter from plants, animals and microbiota to become the exceedingly heterogeneous and complex mixtures normally thought of as soils.

Chemical action

Soils themselves develop progressively under further physical weathering and additionally from chemical and biological forces. These would best be reviewed by consideration of the multilayered cross section – usually known as the soil profile – that may be exposed vertically in the solum. The context of this paper and the time available does not, however, permit a discussion of the development of horizons within soil profiles, but it may be observed that the upper ones are, not unexpectedly, richer in organic matter than the lower ones and frequently more acidic. Two features common to many soils of the temperate and semi-arctic zones, in addition to the indurated layers already mentioned, are the development of white or light-coloured bands at varying depths below the surface horizons and of thin sharply defined brown/black metallic-like layers. The former are due to podzolization (Russian: white ash), a process whereby a combination of circumstances results in acidic surface conditions with the percolation of water, rich in organic acids from vegetation, depleting the upper soil of iron, aluminium and other major mineral elements to leave in extreme cases an infertile silica-rich white band. The red–brown/black layers are known as iron or manganese pans and are quite frequently found below the podzolized horizons where leached iron or manganese is deposited in the regions of higher pH as sharply defined oxide layers or pans. Not unexpectedly, iron pans often occur on top of indurated layers where, if extensive, they can completely inhibit drainage and give reducing conditions, which can greatly increase the availability of trace elements to plants. Various other oxide–sesquioxide bands in intermediate illuvial horizons also affect the availability of trace elements by adsorption–occlusion processes. The distribution of trace elements as a function of depth in the profile will be discussed subsequently. Apart from their effects on the availability of trace elements, it should be noted that indurated layers and iron pans prevent root penetration and thus have quite drastic effects on plant growth.

Action of plants

If crops or forage are harvested or grazed and not returned to the soil as waste products, depletion of trace elements, such as Co and Cu which are translocated extensively to the above ground parts of the plant, particularly the inflorescence, may occur. On the other hand, the accumulation of trace elements in roots and litter may tend to promote biological accumulation of other elements, e.g. Pb and Sn, which are not translocated above ground extensively. It is probable that some plants release non-essential or potentially toxic elements by leaf or root detachment, thus increasing their concentrations at the surface. Wherever plant residues accumulate or grazing animals return ingested trace elements to the soil, biological accumulation of many elements, including Co, Ni, Cu, Mo and Mn, may be seen. Table 1, based on Mitchell (1963), shows the amounts of some trace elements removed from the soil by an average crop during the course of a growing season and compares these with the total amounts of the same elements in the top *ca.* 20 cm of the soil. The figures for a major nutrient, K, are included for comparison. It is clear that there is an adequate total of most trace elements, i.e. enough to last for several hundreds or thousands of years even under a static system and equally that if the trace elements were not held chiefly in forms unavailable to plants within a growing season, severe toxicity might occur due to oversupply; additionally, loss from the soil would occur by leaching. Generally, in most soils where modern intensive cropping and removal has not been practised for a long time the effect of organic accumulations in the surface horizons has been to concentrate and retain trace elements in plant-available forms.

TABLE 1. AMOUNTS OF TRACE ELEMENTS REMOVED FROM AN ARABLE SOIL BY AN AVERAGE CROP YIELDING 5 t ha^{-1} COMPARED WITH THE ESTIMATED TOTAL CONTENT IN THE TOP 20 cm OF THE SAME SOIL

	removed in crop	total content in 20 cm
	kg ha^{-1}	kg ha^{-1}
Se	0.00002	0.1–2
Co	0.001	2–100
Cu	0.1	2–200
Zn	0.2	20–500
Mn	0.5	100–10000
K	100	5000–50000

Action of man

Man himself, in his working of the soil, has had one of the most profound effects on its fertility and trace element availability. His conventional ploughing techniques stir up the surface horizons and tend to distribute the trace elements more uniformly in the plough horizon in arable soils, and traditionally he has enriched the organic matter content of the soil, thus enhancing both the trace element status and retention of the surface soils. It is significant that, quite commonly, land-use capability maps (Ragg & Duncan 1973) show the most fertile soils to occur around cities of long standing. Modern intensive arable farming with repeated high cropping densities, involving much higher removal rates of organic matter and the increasing withdrawal of grazing animals into indoor intensive units, are likely to modify the situation. The practice of minimum cultivation techniques is another new factor that remains to be assessed in relation to trace element supply and demand. Figure 1 (Mitchell & Burridge 1979;

Ure *et al.* 1979) shows the total trace element content range of the surface horizons of ten representative Scottish soils in relation to the total content range and the mean content of the Earth's crustal rocks. It is interesting to note evidence of the depletion of Cu, and to a lesser extent Co, and the considerable enrichment and, coincidentally, narrow range of Nb, Ga, Pb and Th.

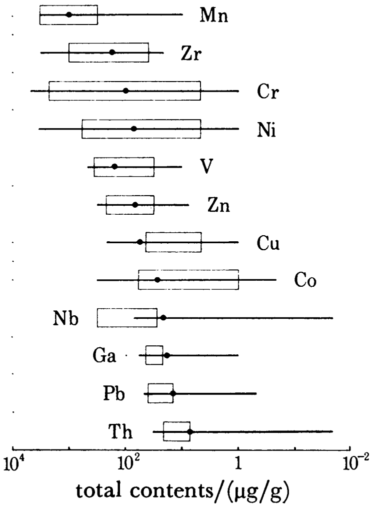

Figure 1. Range of 12 trace elements in 10 representative Scottish soils (rectangles) compared with the range (bars) and means (dots) in the Earth's crustal rocks.

Action of microbes

Lastly, in relation to weathering, attention should be drawn to microbiological processes. The soil itself abounds in microbes, and the surfaces of the soil and of rocks in temperate regions are rich in fungi, algae and lichen associations. Lichens, for example, exude oxalic acid, which attacks and breaks down rock minerals. Such lichens, e.g. *Pertusaria corallina*, are able to survive even on ultrabasic rocks such as basalt, rich in heavy metals, by isomorphic incorporation of large concentrations of metals that would be toxic to them in solution culture, within the lattices of crystals of calcium oxalate stored in their thallus (Jones *et al.* 1980, 1981). These elements are passed to the soil in due course by the lichen.

Some acidic secretions of a few common soil fungi in solution culture are shown in table 2 (Henderson & Duff 1963). The attack of *Aspergillus niger* M on the clay, silt and sand fractions of granitic topsoils and subsoils via the liberation of soluble silica upon incubation is shown in table 3, and on iron and manganese hard pans via the liberation of Fe and Mn in table 4. While these last experiments were done on aqueous suspensions in a laboratory, they are indicative of microbial weathering of soil under field conditions.

At this point it is relevant to indicate that microbial activity beneath the surface of the soil is most intense in the rhizosphere of growing plants, where the exudation of organic species, including carbohydrates, amino acids, organic acids and chelating species, by the root provides foodstuffs for microbial growth. A metabolic product of bacterial colonies under these conditions has been identified as 2-oxogluconic acid (Duff & Webley 1959; Duff *et al.* 1963), which is a powerful calcium chelant capable of attacking and solubilizing many calcium-based minerals, e.g. apatite, and in the process releasing plant nutrients such as phosphate and trace elements.

It is therefore apparent that the weathering of soils by microbes and other life forms such as plants, animals and man must be considered alongside the elemental forces of sunshine, wind, water and ice.

TABLE 2. RELATIVE PERCENTAGE COMPOSITIONS OF ACID SECRETIONS PRODUCED BY FUNGI IN 4% GLUCOSE CULTURE MEDIUM

A. niger M	citric, 6.3; fumaric, 7.8; oxalic, 85.9
Spicaria sp.	acetic, 36; formic, 15.5; oxalic, 48.5
Penicillium	citric, 100

TABLE 3. RELEASE OF SOLUBLE SILICA (MILLIGRAMS PER 10 cm^3 CULTURE SOLUTION) FROM GRANITIC SOIL FRACTIONS UPON INCUBATION WITH *A. NIGER* M

	SiO_2 released	
fraction	top soil	till
clay	0.8	4.1
silt	2.3	3.6
sand	1.8	1.2

TABLE 4. RELEASE OF IRON AND MANGANESE (MILLIGRAMS PER 10 cm^3 CULTURE SOLUTION) FROM HARD PANS UPON INCUBATION WITH *A. NIGER* M†

pan	Fe released	Mn released
iron	6	0.6
iron–manganese	3	0.9
manganese	3	4.3

† The blank values for the control flasks have been subtracted. In the iron analyses the maximum for the control was *ca.* 0.8% of the total; for manganese the figure was 13%.

BIOSIGNIFICANT TRACE ELEMENTS

Since this paper is concerned with the supply of trace elements from soils, it is necessary only to list these here, since their functions in biological systems are discussed in other papers at this symposium. B, Co, Cu, Fe, Mn, Mo and Zn have been shown to have specific functions in plants, and Cr, Ni, Se, Si and V to have beneficial effects on plant growth at low concentrations, though their absolute essentiality remains to be demonstrated at the present time (West 1979). Of these, only B, which is essential to plants, e.g. in relation to the translocation of sugars (Gauch & Dugger 1954) and, *inter alia*, as a cell wall structural agent, seems to play no currently known role in animals. The others are essential to animals, as is iodine, which seems to play no known essential role in terrestrial plants. Plants also take up many other trace elements that are not known to be essential, e.g. Ag, Cd, Ga, Ge, Pb and Sn. The reasons for this are obscure, but it is probable that they enter the root passively on the transpiration stream. In some cases they may be absorbed because they resemble essential ions which are, not infrequently, taken up actively. There appears to be a tendency for many non-essential elements, particularly heavy metals, to accumulate in roots, thus resulting in some enrichment of surface horizons, as mentioned previously. Some plants accumulate much higher concentrations of trace elements in their tissues than exist in the surrounding soil. For example, *Astragalus bisulcatus* may commonly have 1.5 mg Se/g in its tissues, and exceptionally 15 mg/g on seleniferous soils (Trelease 1945). Lastly, it is appropriate to indicate that a greater than normal availability of most bioessential trace elements can be quite toxic to plants, that levels of, for example, Co and Cu that are quite adequate for plants may be insufficient for grazing animals and equally that levels of some elements that are not injurious to plants may be toxic to animals, e.g. Cu, Mo and Se.

FORMS OF OCCURRENCE OF TRACE ELEMENTS IN SOILS

Very little of the total trace element content of the soil exists in free ionic or chelated forms in true or colloidal solution. Typical values for such free solution levels are: Co and Cu, 10^{-7} to 10^{-8} M; Zn, 10^{-6} to 10^{-4} M; Mn, 10^{-4} to 10^{-6} M (West 1979). If the levels were higher, there would be very serious leaching losses from the soil. Considerable amounts are adsorbed on the negatively charged surface of clay minerals and soil organic matter where they can be removed by processes of ion-exchange with hydrogen and other cationic species. This labile or exchangeable fraction of the total trace element content is largely available to plants during the growing season. Trace elements occluded in precipitated oxides of, for example, Al, Fe, Mn or carbonates, or bound within insoluble organic species or the lattices of secondary minerals, are largely unavailable to plants during a growing season, but can replenish the soil solution or exchangeable pool within a reasonably short time. Trace elements locked within primary minerals and many secondary minerals can only be utilized on a very long-term basis. The situation is summarized in figure 2 (West 1979).

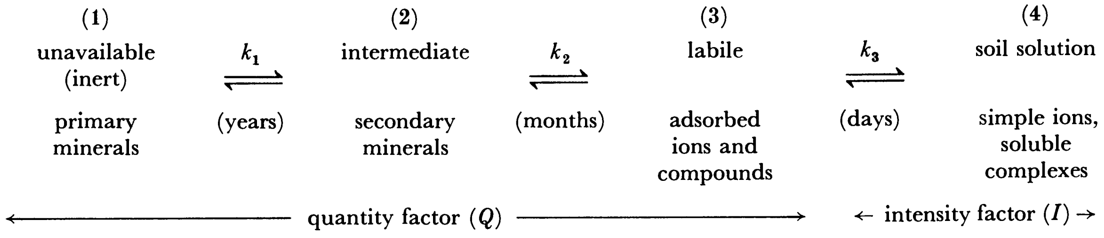

FIGURE 2

The first three categories constitute the soils' 'bank' or potential to supply trace elements. They represent the trace element 'quantity factor'. Typically the equilibria between forms (1) and (2) occur over a period of years, between (2) and (3) over a period of months, and between (3) and (4) over a period of days. Form 4 therefore represents the soils' trace-element 'intensity factor'. The amount that can become available to plants during a growing season is therefore largely restricted to that which can be transported from the labile compartment to the soil solution.

PLANT AVAILABILITY OF TRACE ELEMENTS

Analysis of plants

It would appear to be logical to analyse plants for their trace element content as a measure of the ability of the soils on which they grow to supply sufficient trace elements for grazing stock. However, the distribution of bioessential elements in plants is very much a function of the part of the plant sampled and the time of sampling. This is illustrated for the distribution of copper in *Avena sativa* (figure 3) grown on a granitic soil of the Countesswells Association (J. C. Burridge, unpublished). It will be seen that the total copper content of the plant decreases progressively during the growing season except for a slight flush as senescence sets in. Generally, the copper is mobilized progressively into the seed grain although the concentration within the grain is diluted by the storage there of organic matter. Similar patterns can be established for other trace elements, e.g. Zn and Mn, and in other cereals.

			[Cu]/(μg/g)			
whole	6.39	2.98	1.53	1.31	1.46	
inflorescence			2.00	1.61	1.70	☒
stem			1.08	1.00	1.08	▥
sheath		2.04	1.14	1.05	1.25	▧
blade	6.39	3.97	2.54	1.40	1.68	▨

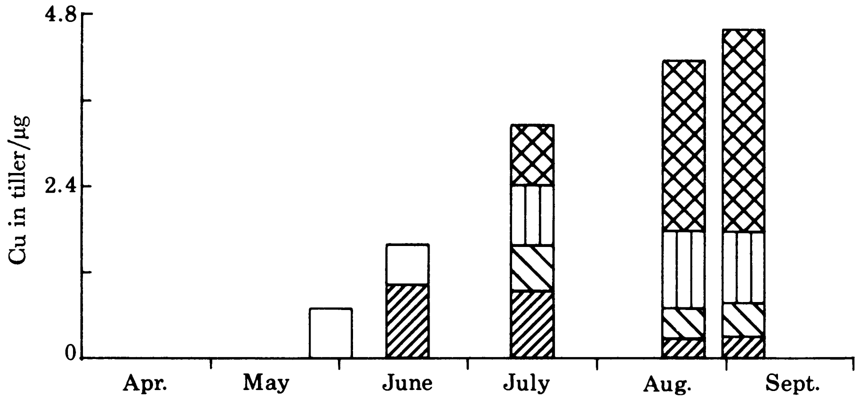

FIGURE 3. Seasonal variations in the distribution of copper in the different parts of the cultivated oat, *Avena sativa*, grown on a soil derived from granite.

Another surprising feature is that the copper content of the grain of oats or barley grown on copper-deficient soil scarcely differs from that of the same cultivar grown on copper-sufficient soil or on the same soil suitably amended with copper sulphate. Yet, as will be seen later, the yield of oats or barley grown on a copper-deficient soil can be virtually doubled by suitable amendment of the soil with a copper salt. It is usually found in grazing swards that the copper content of grasses scarcely varies with the copper status of the soil and that the copper is fairly evenly distributed through the plant. In contrast to copper, zinc (Davey & Mitchell 1968) tends to be concentrated markedly in the young leaves of grasses such as cocksfoot and in meristematic plant tissues. Clover shows a marked ability to concentrate copper from marginal or sufficient soils but serves as a good indicator plant in conditions of deficiency, where many grasses show higher uptake rates than clover. While figure 3 illustrates variation of copper contents in different parts of the oat plant and at different stages in the season, it is also important to stress that the speciation of the bioessential elements in the plant may be equally critical. Thus it is well known that molybdenum in green forage is much more readily available to animals than an equal amount in dried forage. It is also uncertain that the trace element availability of different parts of the plant is the same for animals.

It would clearly be a mistake to fence off part of a grazing stock field for sampling since the animal may graze selectively and, furthermore, cropping alters the plants' ability to take up trace elements from the soil. In addition, clovers, which concentrate trace elements, may predominate at mid-season, and grasses, which do not do so to the same extent, at the beginning and end.

Contamination of plants by soil

All of this casts doubt on the validity of sampling and measuring the trace element content of grazing sward as a measure of the trace element status of a soil for grazing livestock. Another inherent problem in sampling is the contamination of herbage by soil. For elements such as Cu and Mo, where the plant contains about as much as the soil, slight contamination may not be a problem, but for elements that are more abundant in the soil the problem can be serious. For example, mixed pasture species usually contains less than 150 μg Fe/g; more commonly 50–80 μg/g. Contamination of the herbage sample by soil to the extent of only 0.05% may raise the apparent plant content by 100 μg/g. For elements such as Co and Ni, where the soil may contain typically *ca.* 100 times as much as the plant, contamination by soil will again constitute a serious problem. Mitchell (1951) advocated the use of Ti analysis of plant matter as a marker for soil contamination. Soils usually contain *ca.* 1% Ti and most plant species 1 μg/g.

Analysis of soils

For these reasons it is generally considered best to measure the trace element availability status of soils directly on soil samples by use of chemical extracting agents that correlate well with the observed behaviour of plants grown on the same or similar soils, and it is at this point that mention should be made of the value of the work of the soil surveyor. Basically the surveyor classifies soils into associations, based on the nature of the soil's parent rocks, i.e. its mineral composition, and series, based on the weathering history, which, as remarked previously, dictates much of the trace element availability status of soils. Thus extracting agents established for a given association and series can be used to assess other related associations and series.

Choice of soil extractant

Referring back to the discussion of forms of occurrence of trace elements in soils, it will be seen that one of the common factors of the surface horizons is their relatively high organic matter content and their binding of bioessential elements such as copper and zinc. Table 5 shows the conditional stability constants of an important (fulvate) chelating fraction of the soil organic matter with some bioessential elements (Schnitzer & Hansen 1970) and relates them to the corresponding thermodynamic stability constants for the powerful chelant EDTA (ethylenediamine tetraacetic acid). It will be seen that while the fulvate chelates are quite stable and follow the well known Irving & Williams (1948) order of stability constants, they will easily break down upon equilibration with EDTA to give some measure of the organically available trace elements listed in table 5. Space does not permit a more extended discussion of the means of choosing soil extractants, but it may be remarked in summary that for the acidic (usually podzolized) type of soil common in the northern part of the British Isles, water may be used for trace elements existing ionically in the soil solution, e.g. B; ammonium acetate (1.0 M) additionally for readily exchangeable ions, e.g. Mn and Mo; acetic acid (0.5 M) for firmly bound exchangeable species, e.g. Co, Ni and Zn, and EDTA (5×10^{-2} M) for chelated species, e.g. Cu and Zn. Oxalic acid may be used for trace elements incorporated in sesquioxides, etc., and sulphuric acid – sometimes hydrofluoric acid – for assessing the content of secondary minerals.

These and other extractants, set up empirically over a number of years by various workers, show good correlation with plant uptake and are used routinely (Scott *et al.* 1971) in many places. Figure 4 shows the correlation for Co uptake by various pasture species and extraction with 0.5 M acetic acid (Mitchell *et al.* 1957).

Such extraction techniques also supply interesting data on trace element availability at various depths in the soil, the forms of occurrence of the plant-available trace element, and the significance of this for plants of varying root patterns, effects of deep ploughing, etc. Figure 5 (Berrow & Mitchell 1980) shows the distribution of Co in two soils under conditions of free drainage (f.d.) and poor drainage (p.d.). The most significant feature is that Co is less available in all forms from the freely drained soils and that impeded drainage leading to reduced gleyed horizons greatly increases plant availability at all depths shown. In the freely drained soil there is little difference between the behaviour of the extractants, but Co availability is higher in the surface horizon and, with acetic acid being most effective, it may be deduced that a considerable fraction of the Co is associated with secondary minerals, sesquioxides, etc., i.e. in forms not so accessible to EDTA. In the organic matter-rich surface of the gleyed horizons, cobalt is much more freely available and, as the EDTA curve indicates, exists to a much greater extent as chelated or complexed species, but there is also considerably more acetic acid extractable (inorganically bound) Co. All three extractants show greater mobilization in the lower horizons of the gleyed soils. Similar availability patterns are revealed for other bioessential elements such as Cu, Fe, Mn, Ni and Zn, i.e. greatest availability in the surface horizon of the freely drained

TABLE 5. CONDITIONAL STABILITY CONSTANTS OF SOME FULVIC ACID COMPLEXES COMPARED WITH THERMODYNAMIC CONSTANTS FOR EDTA

	$-\lg K$		
ion	pH 3.0	pH 5.0	EDTA
Cu^{2+}	3.3	4.0	18.8
Ni^{2+}	3.1	4.2	18.6
Co^{2+}	2.9	4.2	16.3
Pb^{2+}	2.6	4.1	18.0
Zn^{2+}	2.4	3.7	16.3
Mn^{2+}	2.1	3.7	14.0

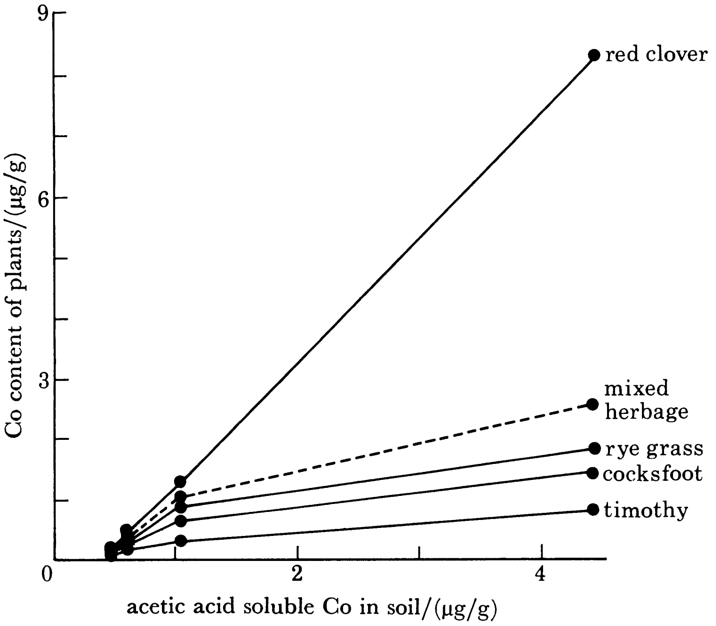

FIGURE 4. Relation between acetic-acid-extractable cobalt and the contents of herbage species grown on a soil derived from granite and subjected to incremental additions of $CoSO_4$.

soils, but considerably more from poorly drained soils with additional peak zones at various depths in the soil profile.

The present situation is that soil extractants are available that closely simulate the ability of plants to absorb bioessential elements from various soils and that these provide a generally satisfactory guide for situations of sufficiency or deficiency in the trace element status of the soil for plant growth and animal nutrition. However, the situation is empirical and its value to practical farming depends at least as greatly on the interpretative skill and experience of the agricultural adviser as it does on the analyst who produces the data.

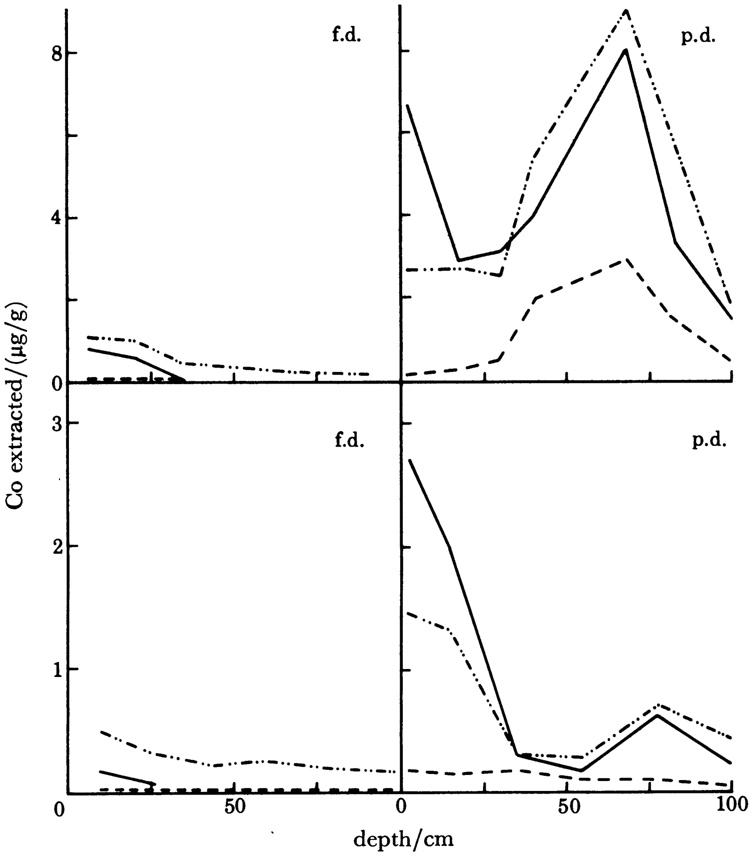

Figure 5. Amount of cobalt extracted by ammonium acetate (– – –), acetic acid (– · · –) and EDTA (—) as a function of depth in the profile for freely drained (f.d.) and poorly drained (p.d.) soils. The soil in the upper half is from the Insch Association (basic rock): that in the lower half is from the Countesswells Association (acid rock).

It is not within the province of this paper to discuss the reasons for increased trace element availability from gleyed soil horizons, but it should be noted that increased availability by gleying does not signify increased leaching of these elements from the soil and that gleyed soils that have been drained continue to show higher availability.

EFFECTS OF SOIL MANAGEMENT ON TRACE ELEMENT SUPPLY

The soil management factors that chiefly influence the supply of trace elements to plants and animals are those affecting drainage, acidity, organic matter content and, to a lesser extent, the application of chemical fertilizers. Modern practices, such as repeated intensive cropping, minimum cultivation techniques and the application of fungicides, animal slurries and sewage sludges, are other factors that require consideration because of their possible long-term effects.

Drainage

There is little doubt that under temperate conditions such as those that prevail in the U.K. the pedological drainage status of the soil is the most significant factor in relation to trace element supply from a particular type of soil. However, it is not practical, for reasons that scarcely need be mentioned, to try and use impeded drainage to remedy a situation of trace element deficiency.

TABLE 6. UPTAKE (MICROGRAMS PER GRAM IN DRY MATTER) OF SOME TRACE ELEMENTS BY PASTURE SPECIES FROM A SOIL DERIVED FROM ARGILLACEOUS SCHIST UNDER CONDITIONS OF FREE (f.d.) AND POOR (p.d.) DRAINAGE

	Co		Cu		Mn		Mo		Ni		Zn	
	f.d.	p.d.	f.d.	p.d.	f.d.	p.d.	f.d.	p.d.	f.d.	p.d.	f.d.	p.d.
mixed herbage	0.12	0.86	3.6	4.1	47	134	1.5	1.7	0.9	2.3	24	26
rye grass	0.11	0.64	3.2	2.6	62	92	1.3	1.0	0.9	2.1	25	21
cocksfoot	0.13	0.73	4.3	4.8	70	182	1.2	1.4	0.9	2.4	22	18
red clover	0.17	1.2	8.9	10.2	33	46	2.0	2.4	1.0	3.0	35	37

In the context of this meeting, drainage status may be most important from the viewpoint of the trace element nutrition of grazing animals on marginal land, since other considerations will dictate drainage practices for arable land. Table 6 illustrates the effects of free and impeded drainage on the trace element content of various pasture species grown on a soil derived from an argillaceous schist, where it was possible to find adjacent areas of the two conditions on otherwise apparently identical soils (Mitchell *et al.* 1957). It will be seen that while there are individual variations, the uptake of Co, Ni and Mn is higher in the poorly drained (gleyed) soil, whereas that of Cu, Zn and Mo is much less affected. This may be due in part at least to the greater tendency for the latter group of elements to be held by organic matter in the soil.

Acidity

Next to drainage, the acidity of the soil is the most important management factor in relation to the supply of trace elements. The input of organic matter and the leaching of calcium tend to increase the acidity of soils and to make them less suitable for the production of many arable crops. It has long been recognized that several beneficial effects on plant growth accrue from lowering the acidity of the soil by addition of lime. This has quite contrasting effects on the plant availability of bioessential and other trace elements. Generally an increase in pH of 1 in the region of 5–6 will halve the availability of most cationic trace elements with the exception of Cu, which is scarcely affected, but it will considerably increase the availability of Mo and Se, both of which are taken up as anionic species. Thus (Mitchell & Burridge 1979) the Co content of red clover grown on a soil derived from granitic gneiss decreased from 0.26 to 0.16 μg/g from pH 5.4 to 6.4, while the corresponding changes for Mn were 56 to 25 μg/g; Ni 2.02 to 1.04 μg/g; Zn 61 to 51 μg/g. Cu remained almost constant, from 12.5 to 13.0 μg/g, and Mo increased *ca.* sixfold, from 0.31 to 1.78 μg/g. A similar pattern had earlier been observed by Reith (1970) in clovers and ryegrass over a wider pH range. Such changes in pH can be brought about typically by addition of a few tonnes of $CaCO_3$ per hectare and the effects will tend to be maintained to a decreasing extent for at least 4 years. It will be seen that these elements, e.g. Co, Mn and Ni, which are absorbed by plants and bound in inorganic cationic forms by the soil, are more affected than those bound by soil organic matter or taken up as anionic species. The insusceptibility of Cu uptake to such changes in pH is fortunate in view of the pH-enhanced uptake of Mo, which can induce copper deficiency in ruminants. Amendment of the soil by copper application adequate to correct deficiencies for cereals can only marginally raise the copper content of herbage.

Soil organic matter

The maintenance of a good organic matter content of the soil has, as for other aspects of plant growth, a generally beneficial effect on the supply of trace elements, retaining them in the surface horizons, controlling the release of many bioessential trace elements and simultaneously immobilizing some toxic elements, e.g. Pb (Reaves & Berrow 1979), which might otherwise compete with the bioessentials for uptake at root-absorption sites. In this connection, recent work by Cheshire *et al.* (1977) on the electron paramagnetic resonance spectra of bioessential transition trace elements such as Cu, Fe and Mn has revealed some of the forms of speciation of these elements in soils and the changes that occur during absorption through the root and passage to the above-ground parts of the plant (Goodman & Linehan 1979). Mössbauer spectroscopy is particularly useful in studying the speciation of Fe in soils and plants (Goodman 1978, and unpublished).

Application of fertilizers

The addition of relatively large amounts of major plant nutrients (N, P, K) is perhaps the most familiar soil management practice of modern arable agriculture and the mutual inter-element effects are now fairly well recognized, e.g. high levels of K or NH_4^+ may induce Mg deficiency in pasture and sometimes lead to hypomagnesaemia in lactating cattle. Much less is known about the effects of major element fertilization on trace element availability, but the reports that are available indicate only a minor influence within the normal range of fertilization. The effects produced may be associated with decreased or increased availability in the soil, or increased or decreased assimilation by the plant. For example, heavy dressings of nitrogen can reduce the Co content of mixed sward from 0.136 to 0.08 μg/g, thus bringing the Co content of the herbage from adequate to marginally deficient for grazing ruminants (Stewart 1965). In this case the effect was induced by N suppression of the clover content of the sward. There is, however, a small reduction in the cobalt content of most herbage species (Reith & Mitchell 1964). Reports of the effects of N fertilization on Cu uptake are sometimes conflicting. Stewart & Holmes (1953), using high rates of N application, observed an induced increase in the copper content of herbage from 6–10 μg/g to 9–16 μg/g, but Reith & Mitchell (1964) observed erratic effects and induced deficiency in cereals (Mitchell 1972) with regular additions of N, probably owing to the dilution effect of increased growth outstripping the Cu supply. N tends to increase the Mo content of clover and to depress that of grasses. The Mn content of grasses is also depressed by N, but there is little effect on Zn. Phosphorus fertilizer appears to cause a very slight increase in the Mn and Mo content of some herbage, but the effect is irregular. Generally, however, the effect of phosphate is to reduce the Cu, Zn and Fe contents of herbage very slightly. The addition of nitrogen reduces the increased Mn content of herbage obtained with phosphate in the absence of added nitrogen. Potassium fertilizer has been reported to decrease the Mo content of herbage from 2 to 1 μg/g and sulphur fertilizer to decrease the uptake of both Mo and Se. It should be stressed, however, that most of these effects are small and may vary according to the soil status of the added nutrient or uptake element, pH, changing composition of the sward caused by alterations in the plant species and, of course, the stage of observation during the growing season.

Other management practices relevant to the supply of trace elements are the enrichment of surface horizons in species such as Cu due to the use of fungicides and of a wide range of essential and toxic elements by the application of urban sewage sludges as fertilizers to arable soils and grassland. Pig slurries tend to have abnormally high concentrations of copper. There will probably also be effects concomitant with the introduction of minimal cultivation techniques, which will, for example, tend to increase organic matter content by reducing the aeration that normally occurs during ploughing and, at the same time, to alter the drainage characteristics of the soil.

Trace element interactions

Plant and soil

There are very few known trace element interactions for plants under normal soil growth conditions, although features such as induced iron deficiency (chlorosis) produced by excessive liming (pH) or abnormally high concentrations of Mn, Zn, Cu and Mo have been reported from time to time. The interaction of micronutrients has, however, been reviewed fairly recently by Olsen (1972).

Animals

It is well known that copper deficiency may be induced in ruminants by higher than normal Mo contents of herbage even where the copper status is itself sufficient for normal nutrition and that, additionally, sulphur is a partner in the interaction. Thus a knowledge of the relative proportion of these elements in a soil gives a useful measure of the likelihood of animal welfare problems on soils. This is the best known example of interelement effects in animal nutrition, but there are many others and the advent of new simultaneous multi-element analytical techniques combined with sophisticated data processing systems and increasing sensitivity of determination now presents a very versatile tool for the study of known interelement effects and, equally important, the discovery of others. For example, figure 6 shows the total amounts of various major and trace elements in two soils relative to their mean concentrations in ten representative Scottish soils, as determined by spark source mass spectrometry (Ure *et al.* 1979). It will be seen that in the soil derived from trachyte (figure 6*a*) the proportions of Cu and Mo are such that Mo-induced copper deficiency is likely on such soils, and similarly, general trace element deficiencies may occur on the granitic soil (figure 6*b*). These 'fingerprints' of the relative total trace element contents supply only a guide for the possibility of deficiency, etc., since they do not take availability into account. Potentially, however, they are extremely useful. For example, the similarity in the chemistry of tungsten and molybdenum is such that it would

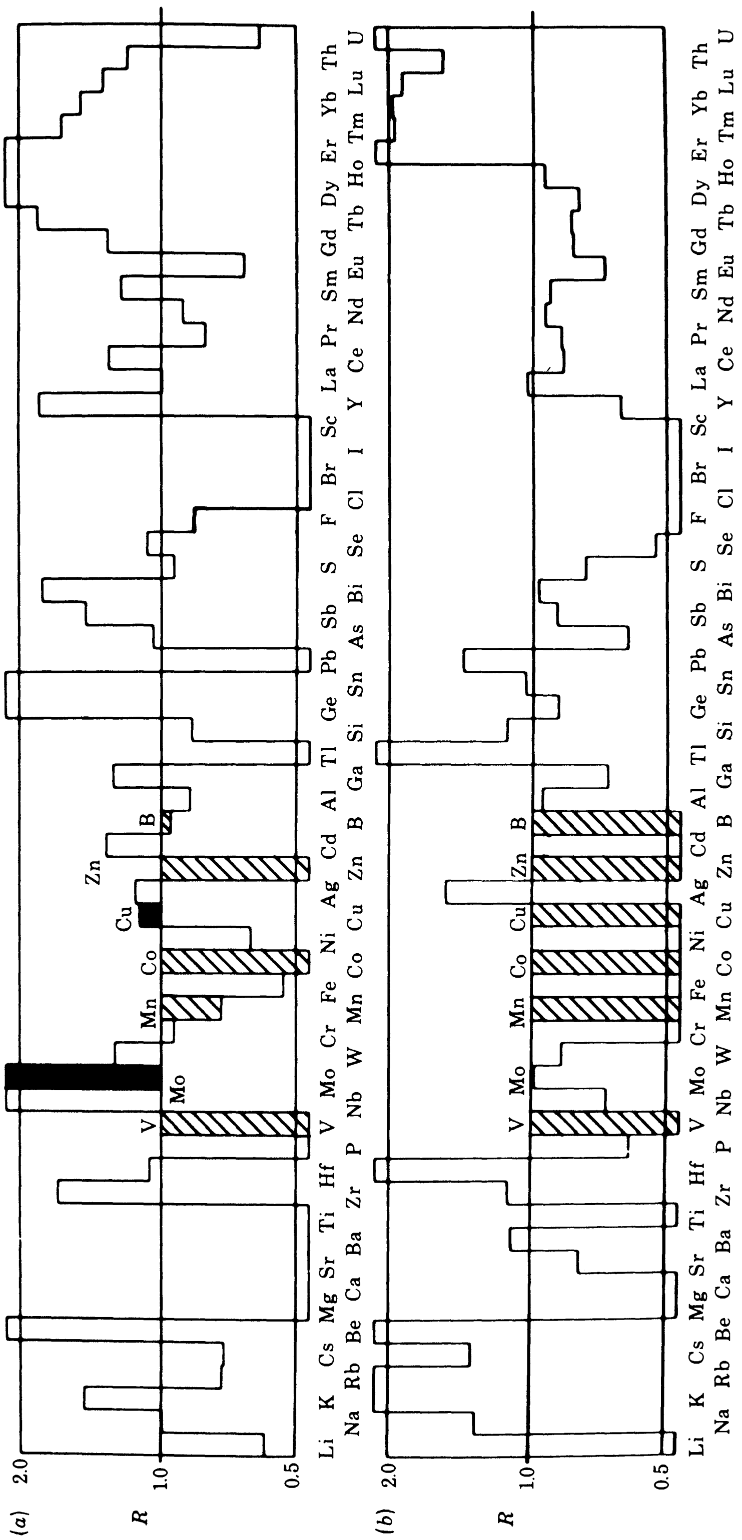

FIGURE 6. Elemental contents of individual soils expressed as a ratio, *R*, of the mean content for each element in ten representative Scottish soils: (*a*) trachyte-derived soil; (*b*) granite-derived soil.

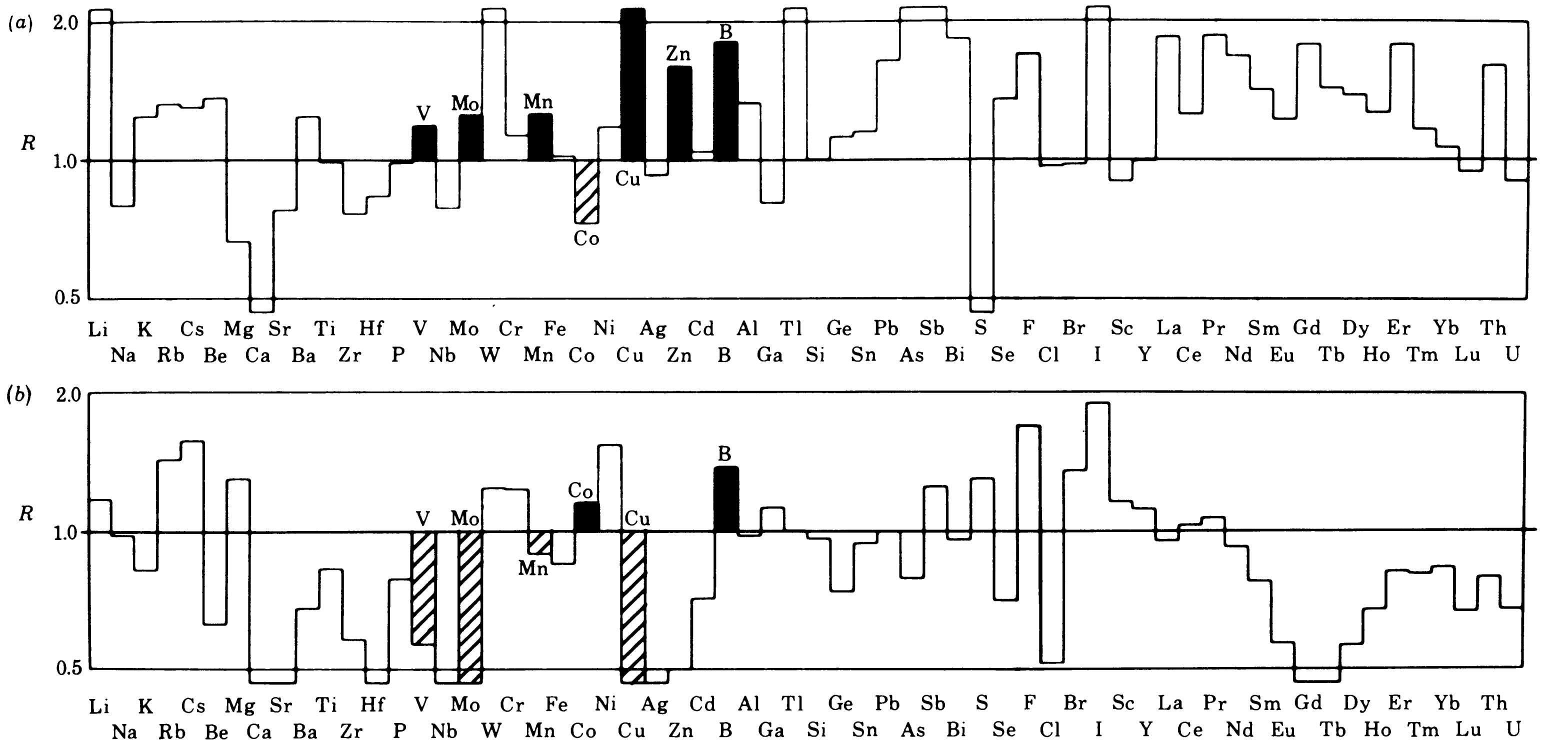

FIGURE 7. Elemental contents of individual soils expressed as a ratio, R, of the mean content for each element in ten representative Scottish soils: (*a*) quartz–mica-schist-derived soil; (*b*) shale-derived soil.

be interesting to look for the possibility of a tungsten-induced copper deficiency situation. Figure 7*a* shows a mass spectrometry fingerprint for a quartz–mica–schist in which the copper content is high compared with the molybdenum, but the soil additionally contains a relatively high amount of tungsten. Again, the high Ni/Co ratio and relatively low cobalt status suggests that there may be additional problems in this soil. In the shale-derived soil (figure 7*b*) the Ni/Co ratio looks satisfactory but the low copper, low molybdenum and relatively high tungsten contents might provide an even better example to search on such a soil for an effect of tungsten on copper.

REMEDIAL MEASURES FOR TRACE ELEMENT DEFICIENCY

There are five main palliative measures that may be considered to overcome the transmission of trace element deficiencies from the soil through plants to animals: (1) trace element salts may, for example, be incorporated in standard fertilizers in amounts appropriate for given areas; (2) they may alternatively be added directly to the soil, or (3) to the plant by foliar application; (4) the relative proportion of trace element accumulators such as clover in grazing sward may be controlled, or (5) the animal itself may be treated by incorporation of the trace element in its feedstuffs, by injection or by a suitable implant. Before discussing the merits of the various possibilities for soils it is worthwhile to re-examine the rate of removal of trace elements by crops from the soil (table 1). It is obvious that an appreciable fraction of the soil's total content of K is removed each year and that K replenishment is essential on an annual basis. As far as trace elements are concerned, however, it is apparent that even without stirring the soil up or returning some parts of the crop to the soil there is likely to be an ample supply for several hundreds or thousands of years, and even where deficiencies already exist, or may be induced, only small amounts may need to be applied.

Apart from boron, which is readily leached from the soil and which is fairly essential for many root crops and brassicas, there is little to be said for the amendment of NPK fertilizers with trace elements in most parts of the U.K. because soils can vary enormously in trace element availability from one small area to another. Even, and perhaps particularly, with boron one has to be careful because boronated fertilizers, e.g. for turnips, are likely to be toxic to cereals. Where soils are of fairly uniform composition, trace elements may, however, be blended quite satisfactorily into standard fertilizers.

The direct addition of small amounts of trace elements formulated to meet local needs is quite a practical proposition and usually only 1 or 2 kg may be necessary per hectare. Cobalt is, for example, best added as $CoSO_4$ rather than as the EDTA chelate. The action of 2 kg ha^{-1} may persist for up to 4 years typically. Cu added as $CuSO_4$ has been shown to persist in its beneficial action for at least 20 years (Reith 1976), while selenium as selenate scarcely lasts for more than 2 years (these data relate to acidic soils; the situation will differ considerably for calcareous soils, tropical soils, paddy soils, etc.). It is often not appreciated that apart from maintaining the trace element content of seed, grass or vegetable tissue, trace elements can have beneficial effects on crop yields. An example of this is shown in table 7, from which it can be seen that on a marginally Cu-deficient soil the addition of 10 kg $CuSO_4.5H_2O$ ha^{-1} can double the yield of the cultivated oat *Avena sativa* even 8 years after application. The yield of barley and mixed herbage is also increased, though not so dramatically as for oats.

As far as foliar and soil application is concerned, it is generally better and more economic to use inorganic salts than chelates, though there may be exceptions for some trace elements in particular circumstances. Lastly, it is not always practical to grow a trace element accumulator such as clover in grazing sward to remedy an inherent trace element deficiency for grazing livestock. Clover serves well for elements such as Co and Cu on soils that are marginally or only slightly deficient and is better than most grasses, but on really deficient soils grasses show superior uptake. Where low densities of grazing stock are involved it may be more economic to treat the animal than to add the trace element to the soil.

TABLE 7. RESIDUAL EFFECTS OF $CuSO_4.5H_2O$ APPLICATION (10 kg ha^{-1}) ON THE YIELD OF CEREAL CROPS AND A HERBAGE CROP GROWN ON A COPPER-DEFICIENT GRANITIC SOIL

		yield/(t ha^{-1})	
crop	year	control	experiment
oat grain	3	1.3	2.2
	8	1.4	2.9
barley grain	6	3.9	4.1
herbage d.m.	6	6.1	6.8

SOIL RESEARCH IN RELATION TO TRACE ELEMENT DEFICIENCIES IN ANIMALS AND MAN

As indicated at the outset, it is scarcely practicable to relate deficiency problems in human diet directly to soil factors except in primitive communities that derive their food supply from a localized area. However, much can be done in relation to grazing livestock and crops. To this end, chemists in soil research could profitably concentrate on devising ever more sensitive multi-element techniques such as spark source mass spectrometry and atomic emission spectrometry with radio-frequency inductively coupled plasmas for the analysis of soils, soil extracts and plant materials with extensions into biological, i.e. animal, tissues, thus to allow inter-element effects to be elucidated, Much of the present preoccupation with methods based on single-channel techniques such as atomic absorption spectrometry is of more limited value. More work also remains to be done by chemists in relation to trace element speciation in soils and plants by techniques such as electron paramagnetic resonance spectrometry, Mössbauer spectrometry, nuclear magnetic resonance spectrometry, X-ray induced electron microscopy and microprobe analysis. The situation with respect to elemental composition and quantitation is now well advanced, but much of our knowledge of the chemical forms and entities to which the trace elements are bound in plants and soils is indirect and circumstantial. The newer electrochemical techniques must also offer considerable advantages in this work since the movement of nutrient ions in the soil solution and in plant cells is largely controlled by electrochemical principles. Radiochemical and thermochemical techniques will also have a considerable continuing role to play in such investigations. Soil physicists should also make a significant contribution in studying the energetics of trace element uptake and the influence thereon of variations in temperature (foliage, soil surface, rooting zone). They should also be able to contribute considerably to the effects on trace element uptake of rhizosphere texture, compaction of soils by heavy machinery, stoniness, etc. Microbiologists may be more important than most others since trace elements are absorbed by the root from the rhizosphere where microbial activity is maximized both in symbiotic and asymbiotic situations. Lastly, there is little doubt that in all of this statisticians and mathematicians will become increasingly vital in establishing data banks of information on trace elements in soils, plants and animals to allow conclusions to be drawn and predictions to be made.

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Discussion

T. L. Coombs (*N.E.R.C., Institute of Marine Biochemistry, Aberdeen, U.K.*). In the soil profile, are there any areas of anaerobiosis? If so, can Dr West indicate what influence this may have on the availability and translocation of trace elements?

T. S. West. In a normal soil profile the CO_2 content of the soil atmosphere is only slightly higher than that above ground. Flooding and impeded drainage can cause anaerobic (gleyed) horizons. Trace elements are generally more plant-available from such horizons, sometimes toxically so. Greater availability is probably due to partial reduction of Fe and Mn oxides with which the trace elements may be associated, but there are other factors such as the swelling of minerals, e.g. montmorillonite. I am unaware of any changes in trace element translocation within the soil due to anaerobic conditions.