PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

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Phil. Trans. R. Soc. Lond. B 1979 **288**, 15-24
doi: 10.1098/rstb.1979.0087

Phil. Trans. R. Soc. Lond. B **288**, 15–24 (1979) [15]
Printed in Great Britain

Trace elements in soils and crops

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To demonstrate the total amounts to be expected in soils, the ranges of contents of some 60 trace elements in ten representative Scottish arable surface soils are compared with ranges in soil-forming rocks and with crustal averages. It is, however, the amounts potentially available to plants rather than the total contents that are biologically significant. In temperate climates, trace element mobilization is greatest when weathering takes place under conditions of impeded pedological drainage, leading to the formation of gleyed soils. Mobilized trace elements occur in arable surface soils largely in adsorbed and chelated forms, which are available to plants to a greater or smaller extent depending on the prevailing soil parameters and on the element in question. Different species take up different amounts of trace elements: the proportions in the various plant parts vary with the element and the stage of growth. Information is required about the mobilization and uptake of many elements about which little is at present known but which may affect the functions of essential elements through inter-element interactions. Systematic soil surveys in which soils are mapped by associations related to parent material, with their series related to genetic soil types, provide a useful countrywide guide to trace element status.

Introduction

The soil is the pre-eminent source of most biologically active trace elements, which reach man through plants and animals. Only grazing and possibly burrowing animals have a significant direct intake of soil, but the availability of its trace constituents in the digestive tract is problematical. Fish and other marine organisms are probably the only foods not dependent on soil that provide trace elements to man.

Knowledge of the distribution of trace elements in the rocks that form soil parent materials stems primarily from the work of V. M. Goldschmidt. A comprehensive summary of the mean contents of almost all major and trace constituents in different rock types has been provided by Turekian & Wedepohl (1961), while Mason (1966) cited their crustal means. Under conditions of temperate weathering, the total contents in soil parent materials can be related directly to those in their parent rocks. Where the parent material is a glacial till it may consist, as often happens in Scotland, of a mixture of more than one rock type. Over restricted areas, levels in soil parent materials can be modified by the presence of local mineral deposits or industrial processes, but such occurrences must be considered in an *ad hoc* manner. The relation of the levels of some trace elements in soils to the different rock types from which their parent materials were derived has been discussed by numerous workers, for instance Mitchell (1964) and Pédro & Delmas (1970). The overall ranges within which some 60 trace elements are likely to occur are indicated, and the principal factors controlling their mobilization during soil development and their uptake by plants, illustrated by Scottish findings, are demonstrated.

The total content of trace elements in soils

For plant growth and animal health a requirement for fewer than 20 trace elements has been claimed, but in appropriate circumstances any element can be deleterious in excess, so it is relevant to look at the total amounts of as many elements as possible. Spark-source mass spectrometry at the Macaulay Institute can now provide information on some 60 trace elements in soils, and A. M. Ure and his colleagues have made available results for ten representative Scottish arable surface soils selected some 25 years ago (Mitchell 1964) to cover the extreme types of boulder clay parent material, derived largely from the serpentine, olivine gabbro, andesite, trachyte, granite, granitic gneiss, quartz mica schist, slate, sandstone or quartzite rocks that are typical of the very complex geology of Scotland.

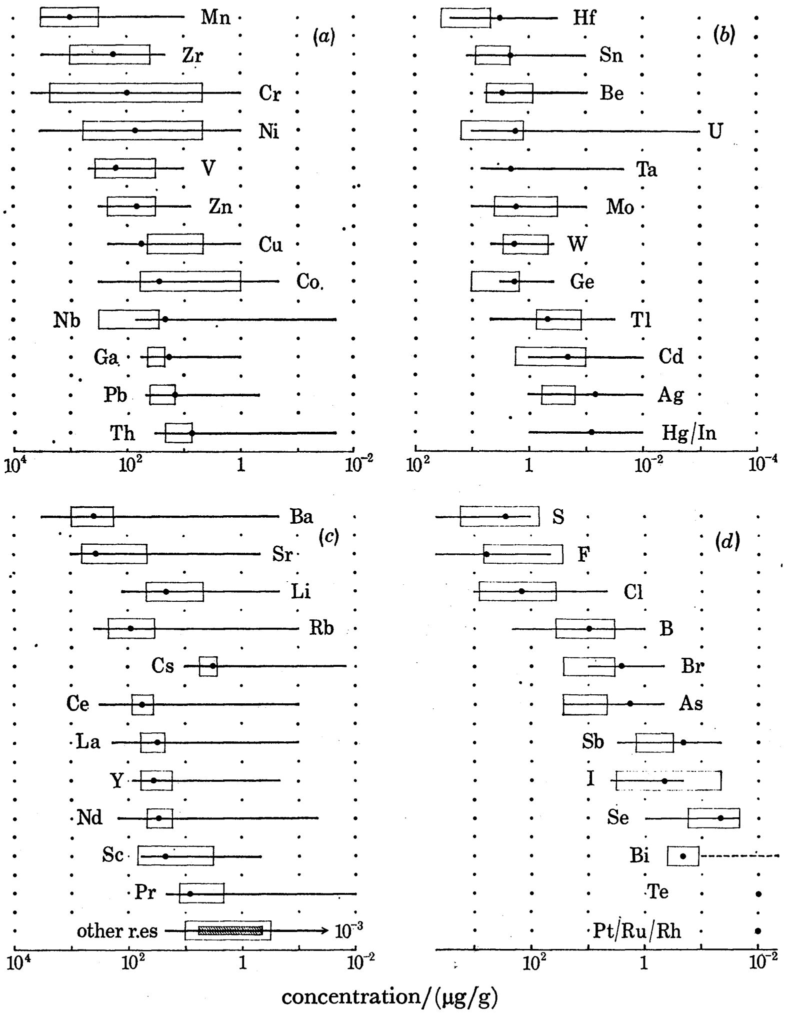

Figure 1. Trace elements in rocks and Scottish soils. Open block: range in ten representative Scottish surface soils; line: range in soil-forming rocks (based on Turekian & Wedepohl 1961); solid dot: mean content in crustal rocks (Mason 1966).

The ranges found in these soils are reported (open blocks) in figure 1, in which they are compared with the crustal means (solid dots) quoted by Mason (1966) and the ranges for soil-forming rocks (heavy lines) based largely on those of Turekian & Wedepohl (1961). The nine most abundant constituents of the crustal rocks (O, Si, Al, Fe, Ca, Na, K, Mg and Ti) and four major constituents of biological materials (H, P, C and N) are outside the scope of this paper. Because of contamination and analytical problems, results are not available for Ta, Hg and In in these soils, while the sensitivity of the method is not adequate for the eight platinum metals (mostly less than 10^{-2} μg/g in the crust). No attempt has been made to assess the remaining nine radioactive elements (less than 10^{-10} μg/g) nor the five inert gases (10^{-5} to 10^{-9} μg/g). The results quoted by Turekian & Wedepohl for rocks are mean values and the ranges used in figure 1 have been taken as twice the highest mean to half the lowest mean: some less common rocks may occasionally have contents falling outside this range. Figure 1*a* and *b* cover most of the heavy metals, figure 1*c* deals with the alkalis, alkaline earths, rare earths and some related metals, while figure 1*d* includes the metalloids and non-metals.

For the six most abundant metals in figure 1*a* the soil range falls in its expected position relative to the crustal mean and rock range, but it is below the crustal mean for Cu and is higher than might be expected for Nb, Ga, Pb and Th and for Hf, Sn, U, Ge and Ag in figure 1*b*. The low Cu and, to some degree, Co levels can probably be explained by removal from surface soils by leaching or crop uptake. Atmospheric deposition possibly contributes, at least in part, to the high Pb level, but biological concentration may well be the explanation for the other elements. In Scottish soils similar to those considered here, Swaine & Mitchell (1960) report low total (but not extractable) Cu and Co and high Pb levels in surface soils compared with deeper horizons in the same profiles. To clarify this, information on plant uptake is required for the last four elements in figure 1*a* and all but Mo in figure 1*b*. The similarity in content of Mo, W and U, which are all, like Cr, group VI B elements giving hexavalent compounds, would appear to justify the further consideration of the biological importance of the last two.

In figure 1*c*, the crustal mean lies within the soil range for all the elements, including the ten less abundant individual rare earths which are shown in a single diagram. The very narrow soil ranges of Cs and most of the rare earths, compared with their rock ranges, are difficult to explain.

Among the non-metals and metalloids (figure 1*d*) most soil ranges again fall around the crustal means, with only F lower and Br, As and Sb higher than expected. Only S, F and I of all the elements studied show soil ranges extending below their rock ranges, as a result of low contents in the granitic soil. The Bi rock range (dashed) derived from Turekian & Wedepohl's data is, as they suspected, dubious; other sources suggest values more in line with the crustal mean and soil range. Only crustal means are available for Te and the platinum metals.

Apart from I, Se and Te, the platinum metals, the radioactive elements and the inert gases, the trace elements all occur in these soils within a 30000-fold range from 0.1 μg/g upwards, with only Cr of the individual elements having a spread approaching 1000-fold. The wide range (2000–10000-fold) of some individual elements, namely Cr, Ni, Nb, U, Ba, Sr, Rb, Ce, Pr and Nd, in rocks can be attributed to geochemical effects producing very high or very low levels in a particular rock type. Such wide ranges are not observed in these Scottish soils, presumably either because the parent materials were not derived from equally extreme rock types or because glaciation of country with complex geology seldom gives tills derived entirely from one rock type. There is no relation between the total content at which a trace element occurs in soil and its essentiality for plants or animals, but there is as yet no suggestion that any element normally present in soil at concentration below 0.01 μg/g is essential.

THE MOBILIZATION OF TRACE ELEMENTS IN SOILS

It is accepted that the total content of a major plant nutrient in a soil is not a reliable indication of its capacity to supply that element to a plant, but attempts are nevertheless often made to correlate total trace element contents of soils or underlying rocks with plant, animal or even human disorders that arise over quite extensive areas, irrespective of local variations in geological or pedological factors. The wider range of occurrence of most trace elements (10–1000-fold) in different soil parent materials, compared with such major nutrients as K, Ca, Mg or P (seldom above fivefold) makes the total content of a trace element somewhat more significant, but because much of this is generally bound up in the lattice of rock-forming minerals, the processes that bring about mineral weathering are of great importance. Abnormal total contents may give a clue to toxicities or deficiencies, but these more often arise because of pedological factors.

In the surface horizon of arable soils, unavailable trace elements can be present not only in soil minerals but also in the organic residues from crop plants, soil flora and fauna or micro-organisms and in soil additives such as fertilizers or sewage sludges. In naturally freely drained soils, pedological processes are most active at the surface, trace elements being mobilized to a greater or smaller degree as the minerals weather or the other materials decompose, at a rate depending on the nature of the materials present, on the processes that are operative and on such soil variables as pH. The factors involved have been summarized by Mitchell (1964).

After mobilization, only a very small proportion of most trace elements remains in the soil solution in ionic, chelated or colloidal form (Hodgson *et al.* 1965). These forms are potentially highly available to the plant and can be assessed by water extraction or solution displacement. Considerably more, particularly of trace elements that occur in cationic form, will be adsorbed more or less firmly on the exchange-active surface of clay minerals, mineral–organic complexes or organic material. Such electrovalent or covalent bonding provides a pool of trace elements that are potentially highly available, and, depending on the firmness of binding, can be assessed by extraction with ammonium acetate or dilute acetic acid. Elements held in this form in mineral soils include the alkali and alkaline earth metals and such heavy metals as Co, Ni and Mn. Some complex anions, notably those of B and Mo, are probably also held in this form. Other mobilized trace elements in surface soils, for instance Cu, occur largely in chelated form in organic combination and can be extracted by a strong complexing agent such as EDTA, which can also remove adsorbed ions. The potential availability of such chelated trace elements may be high.

Some biologically important trace elements can be removed from the available state by co-precipitation in oxides or hydroxides of Fe, Al or Mn. For Co this effect appears to be most likely to occur in soils on Mn-rich parent materials derived from sedimentary rocks that have undergone extensive geological weathering (McKenzie 1975): it is not observed on the young relatively unweathered soils in Scotland. Trace elements may also be immobilized by incorporation into secondary soil minerals, which, being near the end of the weathering chain, are very stable and the plant availability of their trace element constituents is very low.

Soil additives may adventitiously include readily soluble trace elements in sufficient quantity to be deleterious to plant growth, for instance Ni, Zn or B in sewage sludges (Berrow & Webber 1972; Purves 1977). Fortunately their availability may be reduced by the above-mentioned processes. For instance, Pb in the amounts reaching the soil by atmospheric deposition, although sufficient to affect materially the level in or on vegetation, particularly senescent tissue (Mitchell & Reith 1966), does not appear to influence plant uptake through the root.

Comprehensive information on mobilization in soils and uptake by plants is available only for some 20 of the 61 trace elements considered in figure 1. For the biologically essential trace elements an appreciable amount – sometimes as much as a 1 µg/g of soil – is retained in normal soil in potentially available form. Any assessment of the trace element status of a particular element in a soil must take this, as well as the total content, into account.

The magnitude of some of the factors involved in mobilization and uptake can be illustrated by reference to Co (Mitchell 1972*a*). A somewhat leached surface soil derived from serpentine contained 40 µg/g total, 4.2 µg/g acetic acid soluble and 0.43 µg/g ammonium acetate extractable Co, while in an equally freely drained soil on granitic gneiss till the corresponding values were 10, 0.34 and 0.02 µg/g, respectively. The soil of ultrabasic origin not only contains more Co but this is present in more readily mobilized form, as 1% of the total is ammonium acetate extractable, compared with only one-fifth of this in the soil from granitic gneiss.

Mobilization depends not only on the nature of the parent material but also on the operative soil processes. The effect of impeded pedological drainage is illustrated in figure 2 by some findings provided by M. L. Berrow (see Mitchell 1972*b*) which show the levels of extractable Co in adjoining soil profiles, one freely drained and one very poorly drained, on a parent material derived largely from olivine gabbro and containing around 25 µg Co/g in all horizons. In the lower gleyed horizons of the poorly drained soil there is much more extractable Co, almost one-third of the total cobalt being extractable by acetic acid or EDTA. In the soil surface, which is rich in organic matter, there is an appreciable amount of Co extractable only by EDTA, presumably chelated and present as a result of biological accumulation. In the freely drained profile the highest level of extractable Co is, as expected, in the surface horizon. The amounts of extractable Co are much less than in the poorly drained soil and there is no evidence of chelated Co at the surface nor of mobilization in the lower horizons.

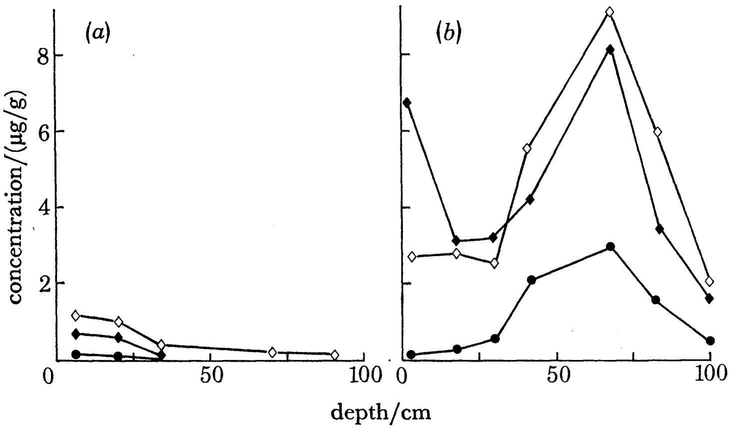

FIGURE 2. Extractable Co in freely and very poorly drained soils. Contents of Co extractable by neutral normal ammonium acetate (●), 2.5% acetic acid (◇) and 0.05 M EDTA (◆) in adjoining (*a*) freely and (*b*) very poorly drained profiles on olivine gabbro parent material.

The effect of impeded drainage on mobilization is by far the most obvious effect that has been observed in Scottish soils, but other soil-forming processes, such as those producing brown forest soils or podzols, can affect the trace element status by, for instance, leaching from the surface horizons and accumulation in lower horizons in the course of podzolization. In arid conditions some trace elements (e.g. B, Se) may occur in water-soluble surface salt deposits.

In the Soil Survey of Scotland, soils are mapped by soil association, for which the important criterion is the nature of the parent material (Glentworth & Muir 1963). An association is subdivided into a number of series representing the genetic soil groups, which frequently form a hydrological sequence related to topography. Thus it is possible from a 1:63360 or 1:50000 Systematic Soil Survey Map, together with knowledge of the trace elements in different rock types, to get a reasonable impression of the probable levels of different elements and of their degree of mobilization. As a mapped series may occupy an area as small as 10 ha, there would appear to be no equally feasible means of providing a countrywide guide to trace element distribution, as it would be quite impracticable to carry out sufficient analyses to produce adequate individual maps for all important trace elements. The method depends on the ability of trained soil surveyors to define precisely the parent material of any association. It is most likely to break down when a constituent rock, particularly a sedimentary rock, varies greatly in its content of a specific element as a result for instance of local mineralization. A system of soil survey that does not correlate series with soil parent material, or association, cannot equally effectively assess trace element status.

Trace element mobilization and plant uptake

The effect of impeded drainage on mobilization is not confined to soils derived from basic igneous parent materials. In table 1, from Mitchell (1972*b*), which deals with adjoining freely and poorly drained areas of a soil derived from slate, the increased extractability of Co, Ni, Mo and Cu in the latter is very obvious, as is its effect on the uptake of these elements by red clover, and, except for Cu, by rye-grass. Mitchell *et al.* (1957*a*) studied 12 elements in three species over a 2 year period at this location, finding increased extractability also for Fe, V, Cr and Ti, but without similar increases in uptake into the above-ground parts of the plants.

Table 1. Effect of soil drainage conditions on uptake

(Contents, in micrograms per gram, of 2.5% acetic-acid-soluble Co and Ni and of 0.05 M EDTA-extractable Mo and Cu in adjoining freely drained and very poorly drained soils on slate till and the dry matter contents of red clover and rye-grass grown thereon.)

element ...	cobalt		nickel		molybdenum		copper	
drainage	free	poor	free	poor	free	poor	free	poor
soil extract	1.3	2.9	1.3	3.4	0.06	0.19	2.6	6.6
red clover	0.16	1.4	2.0	5.9	1.0	3.1	7.9	10.3
rye-grass	0.18	1.5	1.0	3.4	0.7	1.2	4.0	3.4

These results imply that mobilization alone is not the sole criterion of plant availability, as uptake varies from element to element and from species to species. The form in which a mobilized element is held varies in its significance for different elements, different extraction techniques being required for the assessment of their availability. The amounts removed from soil by crops and further aspects of plant uptake are discussed elsewhere (Mitchell 1964). A few of the factors that control the transfer of a trace element from the soil to the plant, and so to the animal, can be illustrated briefly.

Table 2. Effect of chelation on gallium uptake

(Content of Ga in micrograms per gram dry matter of mustard grown in culture solution containing $Ga(NO_3)_3$ or EDTA-chelated Ga equivalent to 2 mg Ga/l.)

	root	stem	leaf	plant height cm	appearance
Ga^{3+}	2000	0.9	0.5	11	very chlorotic
Ga-EDTA	100	34	67	23	dark green

Table 2 shows the effect of chelation on the uptake of Ga from culture solution by mustard (DeKock & Mitchell 1957). For Ga and such other trivalent elements as Cr, Al and In, the unchelated ion is not transferred to the above-ground portion of the plant, being concentrated in or at the root, with deleterious effects on growth. The EDTA-chelated form is, on the other hand, taken up into the plant without affecting growth. In contrast, EDTA-chelated Co, Ni, Zn and Cu are taken up into the green parts of mustard less freely than the ionic or tridentate chelated forms, and it appears from experiments with other chelates that the valency of the cation and the dentation of the complexing agent are both important. Although in soils it is difficult to identify the nature of the chelates involved, this effect may well operate, and, in appropriate circumstances, lead to much higher or lower uptake of a trace element than expected: some poorly drained soils, relatively rich in organic matter, on a mixed acid and basic igneous parent material, for instance, have been found to carry vegetation with much higher Ti contents than normal.

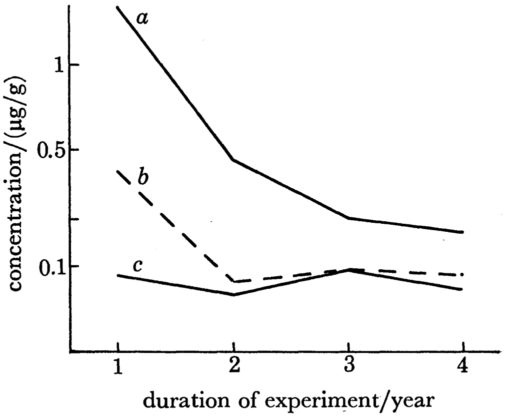

Figure 3. Effect of Co application to soil on crop content: (*a*) Co added as crystalline cobalt sulphate at 4.4 kg/ha; (*b*) equivalent amount as Co–EDTA; (*c*) untreated soil.

Another aspect of this effect may be observed when a trace element is added to a deficient soil to increase plant growth or plant uptake. This is illustrated in figure 3, which shows, on a freely drained mineral soil on a granitic gneiss parent material, the effect of Co added as cobalt sulphate at a rate of 4.4 kg/ha and of Co added as Co–EDTA at an equivalent rate. Co added as sulphate increases the rye-grass content for at least 4 years, while the chelated Co is scarcely effective in the second year. Results for other rates of application and for different pasture herbage plants (Reith & Mitchell 1964; Mitchell, 1972*a*) confirm the persistence of the increase in uptake in the fourth year, particularly for clover in slightly acid conditions. Reith (1976) has reported that the effects of $CuSO_4$ added at around 20 kg/ha to light sandy soils can be observed in cereal yields for some 20 years.

The application of a deficient trace element to the soil to improve plant growth does not necessarily produce an increase in the content of that element in the plant at maturity, and its trace element status is not necessarily reflected by its content at this stage. This is particularly true for Cu in cereals. While in the initial stages of growth a deficiency is obvious from the whole-plant content, later it is the grain yield rather than the content that is affected (Mitchell *et al.* 1957*b*; Reith & Mitchell 1964). Soil treatment to increase plant content of, for instance, Co or Cu for animal consumption is generally less successful with grasses or cereals than with clovers or other plants that show 'luxury' uptake beyond plant requirement.

TABLE 3. EFFECT OF LIMING ON UPTAKE BY RED CLOVER

(Contents in micrograms per gram dry matter of red clover grown in unlimed and limed plots of a soil derived from granitic gneiss.)

(soil) pH	Co	Ni	Mn	Zn	Cu	Mo
5.4	0.26	2.02	56	61	12.5	0.31
6.1	0.20	1.40	42	44	14.0	1.60
6.4	0.16	1.04	25	51	13.0	1.78

In acid soils, the soil parameter most readily modified by agricultural operations is the pH. The addition of a few tonnes of $CaCO_3$ per hectare can reduce the soil acidity by 1 pH unit, a change that has a very marked effect on the uptake of certain trace elements by crops. In table 3, from Mitchell (1972*b*), the uptake of six trace elements by red clover from a freely drained granitic gneiss soil at pH levels of 5.4, 6.1 and 6.4 is illustrated. The plant contents of Co, Ni and Mn have been reduced to around one-half, those of Cu and Zn are scarcely affected, while that of Mo has been increased sixfold. These differences can be related to the forms in which the available trace elements occur, Co, Ni and Mn being in the main strongly adsorbed in cationic form, Cu and Zn appreciably complexed and Mo absorbed in anionic form.

THE TRACE ELEMENT CONTENT OF PLANTS

The plant content depends in the last resort not only on soil factors, but also on the stage of growth and the plant part analysed. A practical effect on the Co content of a pasture herbage is shown in table 4 from Mitchell (1972*a*) in which, on freely and poorly drained soils of the same association, the effects of previous regular cutting every 3 weeks or of growing uncut to the hay stage are reported. Little difference is observed between the clover contents, but the grasses in the hay stage sample are much lower in Co. The mixed herbage values may also reflect changes in the sward composition as a result of cutting. These findings demonstrate the danger of using a fenced-off portion of a field as a guide to the intake of grazing stock.

The final figure demonstrates the changes in Cu content and in Cu uptake into the above-ground portion of barley or cabbage as the plants develop. In figure 4*a*, for barley, the total uptake per tiller is only 0.8 μg in late May but has risen to around 6 μg at harvest in early September, more than 4 μg being in the seed head. The Cu content of the whole plant has

Table 4. Effect of cutting on cobalt in pasture herbage

(Co contents, micrograms per gram, of dry matter samples taken in July from pasture herbage cut every 3 weeks or grown to the hay stage on freely drained and poorly drained mixed till.)

	freely drained		poorly drained	
	regularly cut	uncut	regularly cut	uncut
clover spp.	0.19	0.19	0.34	0.39
rye-grass	0.18	0.06	0.27	0.12
cocksfoot	0.12	0.07	0.21	0.12
timothy	—	—	0.09	0.09
buttercup	—	—	0.51	0.36
mixed herbage	0.18	0.07	0.31	0.15

meanwhile fallen from 8.1 to 3.5 µg/g, the amounts of Cu in and the Cu contents of the individual parts apart from the seed head having fallen steadily over the period of growth.

The Cu levels (figure 4*b*) in cabbage, which is harvested before seed production, again show a large gain in uptake per plant (from 1.2 to 280 µg) and a fall in whole plant content from 4.8 to

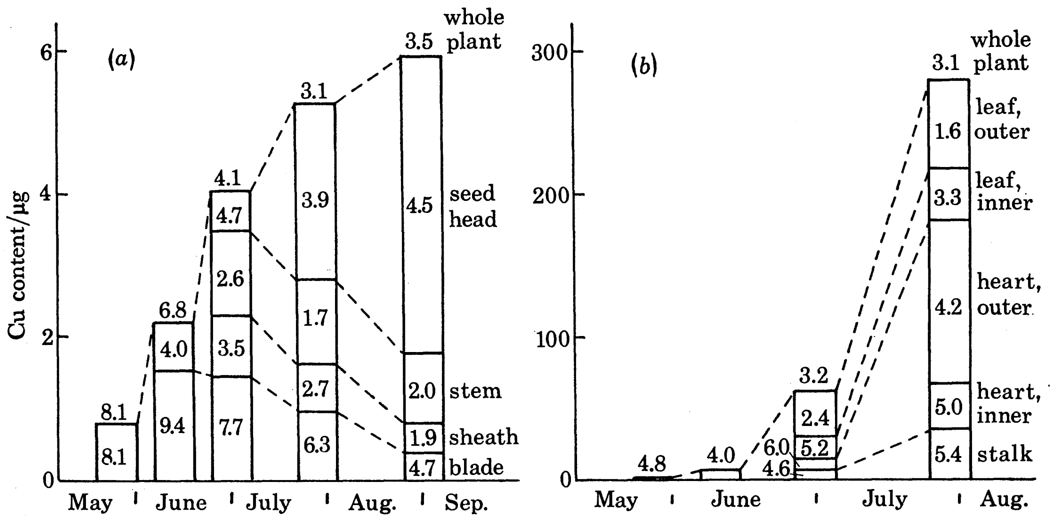

Figure 4. Uptake of copper by barley and cabbage. Block diagrams showing the progressive uptake of Cu by (*a*) barley (expressed per tiller) and (*b*) cabbage (expressed per plant) from a freely drained olivine gabbro soil. The figures associated with blocks show the Cu contents of the plant parts in microgram per gram dry matter at each stage of growth.

3.1 µg/g. At harvest, there is a much greater Cu content in the immature inner heart leaves (5.0 µg/g) than in the outermost green leaves (1.6 µg/g) that are usually discarded before cooking.

The variations in plant composition, resulting from soil factors, from species effects, from stage of growth and from plant-part differences, make it quite impracticable to produce individual trace element ranges for plant content similar to those given for total trace element content of soils, even if the analytical facilities could provide information for all the elements in question. There is an undoubted requirement for information about soil availability and plant uptake of such as yet unstudied trace elements as Nb, Th, Hf, Ta, U, W, Ge or Sb, in view of the possibility of interelement interactions like that involving Cu, Mo and S, although the elements themselves may not be essential to plants or animals. Only when such information is available and when it is known to what extent soil factors can influence the forms in which trace elements occur in plants will it be possible to assess fully the relation between soil and health.

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