1. Trace elements in rocks and minerals

Normal soils inherit their trace elements primarily from the rocks through geochemical and pedochemical weathering processes to which the soil forming materials have been subjected. The products of decay of plants and animals, as well as natural waters, materials from the atmosphere, fertilizers, insecticides and fungicides are secondary sources.

Almost 99 percent of the crust of the Earth is comprised of oxygen (46.6%), silicon (27.7%), aluminium (8.1%), iron (5.0%), calcium (3.6%) sodium (2.8%), potassium (2.6%) and magnesium (2.1%). Some of the less common constituents are given in Table 2.

Table 2. Average content of twenty trace elements (ppm) in the Earth's crust (137)

Mn	1 000	Cr	200	Cu	70	As	5
P	800	Sr	150	Sn	40	Cs	3.2
S	520	v	150	Co	40	Mo	2.3
C1	480	Ni	100	Pb	16	I	0.3
Ba	430	Zn	80	в	10	Se	0.09

Igneous and metamorphic rocks comprise the great majority of the Earth's outer crust. About 80 percent of the remaining sedimentary rocks are shales, 15 percent sandstones and 5 percent limestones. The distribution of trace elements varies greatly with the rocks and minerals, as shown in Tables 3 and 4.

Table 3. Major and trace constituents of sedimentary rocks (258).

Main rock types		
Sandstones	Si	Zr, Ti, Sn, Rare earths, Th, Au, Pt, etc.
Shales and bituminous shales	Al, Si, K	V, U, As, Sb, Mo, Cu, Ni, Co, Cd, Ag, Au, Pt, B, Se
Iron ores	Fe	V, P, As, Sb, Se
Manganese ores	Mn	Li, K, Ba, B, Ti, W, Co, Ni, Cu, Zn, Pb
Limestones and dolomites	Ca, Mg, Fe	Ba, Sr, Pb, Mn
Salt deposits	K, Na, Ca, Mg	B, I

Table 4.	Major and trace constituents	of	common i	minerals	of	igneous	rocks	and	their
	relative stability (258)								

Stability	Mineral	Major constituents	Trace constituents
Easily veathered	Olivine Hornblende Augite Biotite Apatite Anorthite	Mg, Pe, Si Mg, Fe, Ca, Al, Si Ca, Mg, Al, Si K, Mn, Fe, Al, Si Ca, P, F Ca, Al, Si	Ni, Co, Mn, Li, Zn, Cu, Mo Ni, Co, Mn, Sc, Li, V, Zn, Cu, Ga Ni, Co, Mn, Sc, Li, V, Zn, Pb, Cu, Ga Rb, Ba, Ni, Co, Sc, Li, Mn, V, Zn, Cu,Ga Rare earths, Pb, Sr Sr, Cu, Ga, Mn
	Andesine Oligoclase	Ca, Na, Al, Si Na, Ca, Al, Si	Sr, Cu, Ga, Mn Cu, Ga
Moderately stable	Albite Garnet Orthoclase Muscovite Titanite Ilmenite Magnetite Tourmaline Zircon	Ha, Al, Si Ca, Mg, Fe, Al, Si K, Al, Si K, Al, Si Ca, Ti, Si Fe, Ti Fe Ca, Mg, Fe, B, Al, Si Zr, Si	Cu, Ga Mn, Cr, Ga Rb, Ba, Sr, Cu, Ga F, Rb, Ea, Sr, Ga, V Rare earths, V, Sn Co, Ni, Cr, V Zn, Co, Ni, Cr, V Li, F, Ga Hf
Very stable	Quartz	Si	

Trace elements in soils

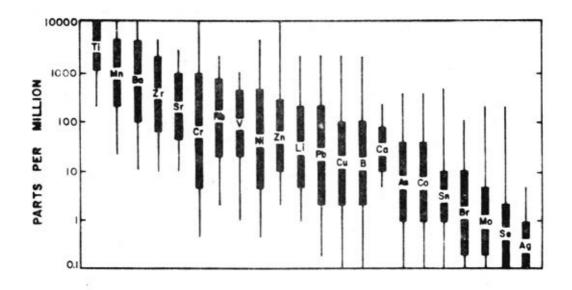
(a) Total contents

In spite of changes in the trace element composition of rocks and minerals during weathering and soil formation processes, the total trace element content of soils usually reflects quite clearly the composition of the materials from which they have been derived, as has been shown by several authors (140, 260, 353, 399). The relationship between the concentrations of a trace element in a soil and in its parent material, however, is not always close enough for satisfactory quantitative estimation of the former from the latter (109, 276). Especially in areas of glacial translocations and mixing of heterogeneous parent materials, such a direct comparison is difficult (327a).

The relative variations of the total content of trace elements in different soils are much wider than those of major nutrient elements. Mitchell (258) has presented in graphical form the ranges of content of a number of trace elements found in mineral soils (Fig 1).

Besides the mineralogical composition of the parent material, the total amounts of trace elements present in soils depend on the type and intensity of weathering and on climatic and other factors predominating during the process of soil formation.

The relative resistance to weathering of various rocks and minerals apparently has great influence on both the texture and on the trace element content of soils. Fine textured soils and the finer fractions in other soils are likely to have been derived from the more easily weathered minerals, which are also the main source of trace elements. Coarse soils and coarse fractions are derived from minerals, such as quartz, which are resistant to weathering and have low contents of the micronutrients (see Table 4). The lower trace element contents of coarse rather than fine textured soils has been reported by several authors (59, 135, 145, 148, 186, 266, 300, 331, 385 etc.). This kind of relationship



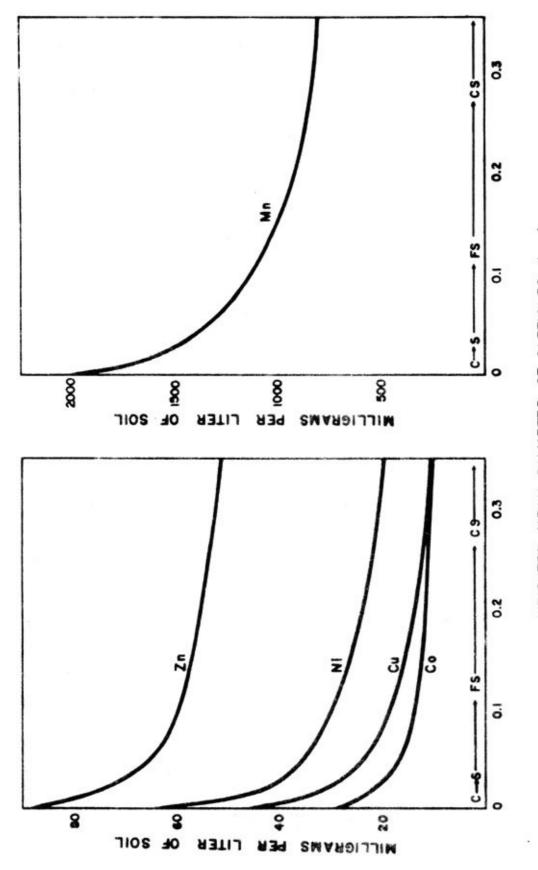
<u>Fig. 1</u>. Total contents of trace elements commonly found in mineral soils. Thin lines indicate more unusual values but extremes have been excluded.

between five elements in material of 160 samples of Finnish mineral soils is shown in Fig.2 (327). The correlations for the given regressions were highly significant while that for the sixth trace element analyzed, lead, was obscured - perhaps owing to its more irregular existence in easily weathered minerals.

Another soil factor often found to be closely related to the total content of soil trace elements is the organic matter of soils. Several authors have reported increasing amounts of trace elements with increasing organic matter in soils, but occasionally opposite results have been obtained. On the other hand, organic soils are among those most often found to be deficient in one or several trace elements on cropping. In some cases analyses show a high content (ppm) of trace elements in peat soils but when the plants grown on peat are also analyzed, the content may be lower than in other soils. The reason for this has been explained, maybe too often, as low availability or high fixation of trace elements in organic soils whereas the actual reason may lie in the low total content. To understand these contradictory results it must be realized that the dimension or unit in which the trace element content is given is of essential importance and should not be overlooked when interpreting the results, For example, if two soils, a mineral soil with a bulk density (or volume weight) of 1.5 and a peat soil with an extremely low bulk density of 0.1, are inalyzed and both show an equal content of 100 ppm of a certain trace element when expressed in the usual way on weight basis, the result is completely different if expressed on volume basis, as shown below:

Soil	Bulk	Trace element on weight basis	content as expressed on volume	
	density	ррм	mg/litre of soil	Kg/ha*
Mineral soil	1.5	100	150	300
Peat soil	0.1	100	10	20

* ha-plough layer, 20 cm in depth = 2 mill. litres

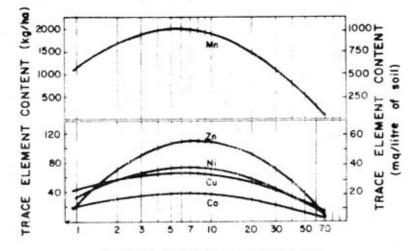




Relation between the total contents of five trace elements and soil texture expressed as weighted mean diameter of particles. Symbols: C = clay soils; S = silt soils; FS = fine sand soils and CS = coarse sand soils. $(1 \text{ m}_{\text{E}}/1 \text{ = } 1 \text{ ppm } \text{if the volume weight} \text{ of soil is } 1.0$). Fig. 2.

Thus, in this extreme example, the 100 ppm in the peat soil actually corresponds to only one fifteenth of that of the mineral soil. Naturally, in areas where peat soils do not exist and the variation in the bulk density of soils is small, the difference between the methods of expressing the results is of less importance.

The relation between the soil organic matter and total content of five trace elements in a material of 2 637 samples with a large variation in organic matter content (from almost plain mineral soils to peats containing very little mineral matter) is given in Fig. 3.



ORGANIC MATTER CONTENT (%)

Fig. 3. Relations between the total content of five trace elements and organic matter content of Finnish soils. For all regressions the correlations were highly significant (327).

The micronutrient content in mineral soils seems to become greater with increasing organic matter, the maximum probably being found in soils containing 5 - 15 percent organic matter. Further increases in organic matter tend to decrease the trace element content until in pure peats they are at a minimum. Although the general trend of the relationship is very similar for all five elements, the basic reason for this does not seem to lie in the similarity of their chemical behaviour, but is presumably pedological in nature: all these trace elements have originated from the mineral matter of soils. Plants growing and decaying on a mineral soil derive trace elements from further below and accumulate them on the surface layer in addition to what was already present in the mineral soil. This causes the trace elements to increase proportionately to the organic matter content of mineral soil. With further increases in the organic matter content, the proportion of the total trace elements made up by the elements in the mineral matter itself begins to decrease because of the simultaneous decrease in the bulk density of the soil. Eventually, the contact between the peat layer on the top and mineral soil below becomes less and less close until finally in the top layer of a deep peat soil the only trace elements present are those gradually transported from the mineral subsoil by plants; the extreme cases of this development are the "raised swamps" of Sphagnum peat which are known to be very low in all nutrients. This general trend may be more apparent in the northern peats where, owing to climatic conditions, the decomposition of plant residues is slow, causing the fast accumulation of peat. Naturally, numerous local factors such as type of mineral subsoil, drainage waters from surrounding areas, and leaching and fluctuations of the water table cause wide variations in this general tendency. (327). It should also be pointed out that if the relationships given in Fig. 3 were expressed on weight basis (i.e. in ppm), the regression lines would be near linearity (Mn and Zn) or even bending upwards (Ni, Cu, and Co) thus giving the impression of increasing trace element content with increasing organic matter throughout the whole range of variation in organic matter.

(b) Soluble contents and availability

The amounts of trace elements removed yearly with normal crop yields (Mn 500, Zn 250, Cu 50, Mo 10 and Co 1 grams/ha)* represent only a very small proportion, generally less than one percent of the total amounts of the various trace elements present in soils. Thus, it is obvious that the total amounts, even in the most serious deficiency cases, far exceed the requirements of crops, and the availability of trace elements is primarily dependent on their solubility as determined by various soil factors. Even the amounts of trace elements soluble in the usual extraction solutions generally exceed the amounts required by plants by a considerable margin, which consideration should be taken into account when interpreting the results of chemical extractions.

The total amounts of trace elements in soil naturally have an essential influence on the soluble or plant-available amounts. However, owing to several factors such as pH, texture, organic matter, clay minerals, moisture content, redox potential and interrelations of trace elements etc. that influence the solubility and availability to plants, the total content is seldom a reliable index of the available trace element status of the soil. In spite of which, total contents are still widely used in estimating the trace element status of soils, the main reasons for which are apparently the difficulties in determination of soluble or available forms.

Trace elements are bound in different ways in soils and the demarcation between different forms is diffuse. Trace elements in soils may exist in the following forms, as summarized by Lakanen (212): (1) Trace elements in the soil solution. (2) Exchangeable ions bound by the electric charges of soil particles. These ions form a plant-available fraction of trace elements, similar to that of exchangeable potassium, calcium and magnesium. The trace elements are, however, more firmly bound and less available. (3) Trace elements complexed with organic material. Most trace elements are typical heavy metals, which are able to form complexes with ligands derived from soil organic material or from biological residues in the soil. The plant-availability varies. (4) Precipitated trace elements. The concentrations of Fe and Mn are high enough to allow precipitation. This fraction is to some extent plant-available. (5) Trace elements occluded during development of new solid phases in which they are not principal constituents. This is a long-term equilibrium reaction about which little is known. (6) Constituents of soil minerals. These trace elements are released during weathering. Ions which have entered the crystal lattice of clay minerals belong to this group. The availability of the last mentioned is strictly limited.

The availability of different trace elements to plants, and the factors affecting it, varies considerably from one trace element and medium to another. Cottenie <u>et al.</u> (92) reported that out of seven elements, the plant uptake of Fe and Cu from trace element fertilized sand cultures varied less than that of the others. B and Mo uptake correlated with their content in the medium, while the uptake of Mn and Zn were more affected by other conditions prevailing. Factors affecting the availability of trace elements and their extractability by diagnostic reagents are excellently reviewed by Hodgson (168) and Mitchell (262).

Some of the soil factors affecting the availability of trace elements have been the subject of numerous studies, and valuable information about them has been presented. One of the factors that has received the most attention is soil pH. Organic matter is considered to have a high sorption capacity, but further investigations are needed to establish its ability to absorb trace elements in unavailable forms. Soil texture has been found to affect the total amounts of many trace elements, but less information about its effect on their solubility is available.

Soil pH can markedly affect the availability and consequently the plant uptake of trace elements. Reducing acidity reduces the solubility and uptake of Al, Co, Cu, Fe, Ni, Sn, Zn, and particularly of Mn and increases that of Mo and S (e.g. 203, 212, 259, 271, 299, 300, 319, 324, 328, 331 etc.). Cases have also been reported in which the ability of

Approximate data collected from various sources.

plants to utilize trace elements decreases with decreasing acidity (increase in pH) to a minimum at pH 5.2-6.5, while utilization at higher pH remained constant or even increased (160, 212, 320, 411). The effect of soil pH on the availability of a number of elements as summarized by Truog (367) is given in Fig. 4 and an example of plant uptake of four trace elements in Table 5.

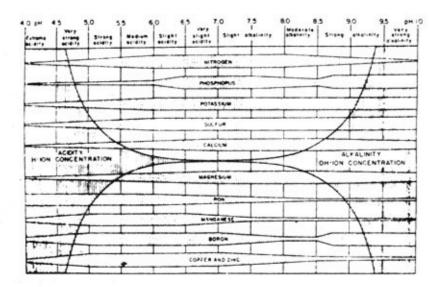


Fig. 4. The availability of plant nutrients in relation to soil pH (367).

Table 5. Effect of liming on soil pH and on trace element content of plants (259).

1		Element content (ppm in Oven Dry materials)							
Soil treatment	Soil pH	Mixed pasture Red clover							
		Co	Ni	Mo	Mn	Co	Ni	Mo	Mn
Unlimed	5.4	0.28	1.83	0.42	125	0.22	1.98	0.28	58
14.4 tons caCo3/ha	6.1	0.19				0.18		1.48	41
27.1 tons CaCo3/ha	6.4	0.15	1.08	2.14	72	0.12	1.10	1.53	40

The effect of pH on the solubility and plant-availability of different trace elements is often more varied than might be supposed from Fig. 4. In general the availability of Mn is more dependent on pH than is the case for other trace elements. For example, a reduction of exchangeable Mn content down to 1/50 - 1/20 due to liming has been reported (90), while in some cases the uptake of Cu was only slightly or not at all affected by pH (129, 233). It is also often found that pH has a greater influence on the extraction of many trace elements with chemical solvents than on their uptake from the soil by plants. This is presumably due to an increased efficiency in the process of plant uptake at higher pH values, but opposite results have also been presented (77, 78, 168). Apparently, there are also differences in the influence of pH on the uptake of native and applied trace elements, the latter being usually more affected (34, 226, 397). Among the actual trace elements Mo is the only one whose availability increases with increasing soil pH.

The relationship between the availability of individual trace elements and soil pH is discussed in more detail in Chapter III.

Soil texture is one of the factors related to the available contents of trace elements in mineral soils. Although there is little information about texture as a factor affecting availability, several analytical results show decreasing amounts of total trace elements with increases in the coarser fractions (see Chapter II.2, a) and many deficiency cases have been reported from sandy soils. For example, in the PAO report "Trace element problems in relation to soil units in Europe" (315) where soils apparently deficient in B, Mn, Co, Cu, Mo, I, Fe and Zn in 16 countries were listed, a great majority of the cases of mineral soils (where texture is clearly mentioned) were sandy or coarse textured.

<u>Table 6</u>. Average total and acid ammonium acetate (pH 4.65) soluble contents of six trace elements (mg/litre of soil) in two texturally different soil groups (328)

Trace group element	Fine mine	ral soils	Coarse mineral soils				
No. of samples WEDP* (nm)	o	60 .017	0	49 .223			
	Total	Soluble	Total	Soluble			
Cobalt (mg/1)	32	0.17	13	0.08			
Copper "	33	0.61	16	0.29			
Manganese"	1 489	31.7	709	8.0			
Nickel "	50	0.73	24	0.20			
Lead "	22	0.32	24	0.25			
Zinc "	69	0.31	48	0.41			

* WMDP - Weighed mean diameter of particles

In Table 6 the contents of six trace elements in two texturally different groups of Finnish soils are given. Statistical analysis of the data showed no clear difference in the relative solubility (percentage soluble/total) of these elements betweer the two soil groups. However, regressions showing decreasing soluble contents with increasingly coarse textured soils were highly significant for four elements (Co, Cu, Mn and Ni) but insignificant for Pb and Zn. It was concluded that among the reasons for the tendency of soluble contents to decrease with coarsening texture is the similar relation between the total contents and texture (See Fig. 2), which can also be seen from Table 6. Similar results have been reported later from larger soil materials (329).

The influence of <u>soil organic matter</u> on the availability of trace elements has been widely studied and contradictory results have been presented. Especially in the earlier literature the view was adopted that the absorbtion of trace elements by organic matter may be great enough to cause deficiency in some cases. The results of several more recent studies, however, do not support this line of thought and the influence of organic compounds on inorganic soil constituents is not clearly defined. As discussed above the effect of decreasing bulk density of soil with increasing organic matter has not always been fully appreciated so that confusion often arises with regard to the role of organic matter with the interpretation of analytical results. Further, there are great differences between the reactions of various trace elements with different organic compounds. Humus holds di- and tri-valent metallic cations more firmly than the alkali metal cations. It has been known for a long time that Cu forms rather strong complexes with organic compounds and is more likely than Mn to be fixed in humus (72, 94, 103, 159, 219). Svanbert <u>et al.</u> (350), however, state that plants obviously have the power to take up Cu from organic compounds while additions of organic matter to mineral soils have been found to increase the exchangeable Mn which is known to be available to plants (90, 116, 316). Opposite results concerning both Mn and other trace elements have also been presented (19, 195, 254, 255, 256, 365). The stability constants of normal chelates of the divalent metals given by Irving and Williams (177) increase in order Ca, Mn, Co, Ni and Cu, with Zn usually being a little weaker than Cu. This is in agreement with the results given in Fig. 5, which show the relations between the relative solubility (percentage of soluble amount of total amount) of six trace elements as a function of the organic matter content of soils.

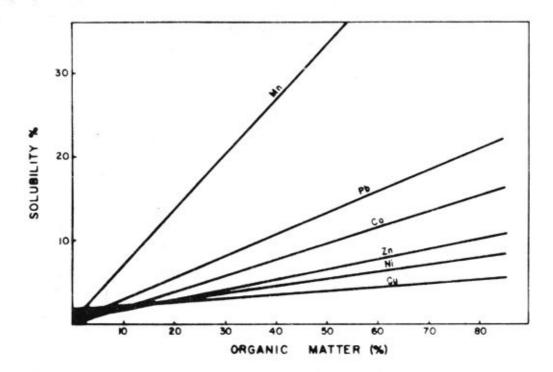


Fig. 5. Relations between the relative solubility (acid ammoh.ium acetate) of six trace elements and organic matter content of soils (328).

The regressions are all highly significant and show considerable differences between the individual elements. The increase in the solubility of Mn with increasing organic matter seems to be exceptionally high, while in the case of Cu both the regression and correlation coefficients are the lowest among the six elements. The chemical behaviour of the trace elements and especially their affinity for chelate formation with humus is likely to explain some of the differences. Chelate-bound Mn, for example, is not likely to play an important role in these soils, particularly not in organic soils where the pH varies from 3.6 to 5.8 (about 1 pH unit lower than in mineral soils), since its affinity for chelate formation in acid conditions is known to be weak. The same applies, even though to a lesser extent, to other elements and decreasing pH with increasing organic matter content is apparently partly responsible for the higher solubility in organic soils.

Plants are able to absorb many forms of organic matter-bound trace elements and it is apparent that many of the trace element deficiency cases found in peat soils are not due to the low degree of availability but to the inadequate total trace element sources in these soils (see p. 8-9). Trace element-organic matter relations have been widely reviewed, e.g. by Wallace (388) and Mortenson (265).

Other factors which may cause considerable differences in the availability of trace elements to plants are microbiological activity in soils, soil drainage and oxidationreduction conditions, weather conditions and seasonal variation. Because of the mutual interactions between these factors, the extent of their single effects is often difficult to define.

Microbiological activity is largely dependent on all the above mentioned factors as well as on the chemical composition of soil, pH, quantity and quality of soil organic matter, etc. There is some evidence that Zn deficiency may sometimes be directly caused by the soil micro-organisms competing with the plants for the small quantities of the available Zn present (86). More indirectly, micro-organisms may affect the availability of trace elements by releasing ions during the decomposition of organic matter, by immobilization of ions through incorporation into microbial tissue, by oxidizing elements to less available forms, by reduction of oxidized forms and by indirect transformations such as changes in pH or oxidation potential (7).

Obviously the availability of Mn and Fe is more affected by oxidation and reduction than that of other trace elements, but reduction caused by high moisture content or flooding can increase the availability of S, Cu, Mo, Ni, Zn, Pb, V and Co (139, 168, 210, 248, 273) in some cases (Mn, Fe, Mo, S) up to toxic levels (185, 379, 412). However, in other conditions opposite results for Co, Mo and Mn have also been obtained (10, 247, 258, 353). The low availability of Mn and Fe in oxidized conditions is usually explained in terms of the lower solubility of the trivalent as compared with the reduced divalent form. However, oxidation-reduction processes are usually accompanied by changes in soil pH, which may complicate the picture, as well as big interactions between Mn and Fe and other elements.

The availability of many trace elements has been found to fluctuate with seasonal variations. It is difficult, however, to point out any general trends in availability due to weather changes because of the complexity of factors simultaneously involved. High soil temperature has often been found to be associated both with high uptake of trace elements and with dry soil conditions, the latter factor being often shown to be responsible for low availability. Also microbiological activity is largely controlled by temperature and may alter the availability according to the state of oxidation-reduction, type of micro-organism, organic matter, etc. Excessive phosphorus fertilization has been found to reduce the availability of Cu and Zn, increase that of Mn, and have variable effects on the uptake of B and Mo (48, 49, 50, 78, 82, 340). Several possible explanations for the P-induced Zn or Cu deficiency have been offered, including the immobilization of the trace element within the plant by abnormal amounts of P being present, precipitation by P within the conducting tissue of the plant shoot, possible P-Zn antagonism within the root and reactions occurring outside the physiologically active roots so reducing the uptake of Cu and Zn.

Excellent reviews of the above factors affecting the availability of trace elements have been presented by Alexander (7), Quastel (296), Hodgson (168) and Grable (139) and for individual trace elements these subjects are further discussed in Chapter III.

Plants are the <u>source of trace elements for animals</u>. The ability of a plant to absorb trace elements varies considerably due to the soil resources and factors affecting the availability. Further, considerable differences exist in the nutritional requirements of various plant species as will be discussed in the following chapter under the individual trace elements. The margins between the amounts required for normal growth and those producing symptoms of toxicity vary both with plant species as well as with trace elements concerned. Because of the differences in the trace element requirements and in the trace element tolerance of various plant species it is possible to use certain plants as indicators of deficient and toxic areas. Certain plants have a more marked requirement for a certain trace element than other plants and develop characteristic, easily identifiable symptoms of dericiency when grown on deficient soils. Wallace (389) mentions sugarbeet, mangold, globe beet, apple, sweet cherry and respberry as good indicators of Mn deficiency in soils low in this element. Cauliflower can be used as an indicator for Mo deficiency, orange and apple for Zn deficiency, apple for B deficiency and cauliflower, broccoli, marrow-stem, kale, cabbage, apple, pear, plum and raspberry for Fe deficiency. On the other hand, plants which are exceptionally tolerant to high soil concentrations of certain elements have been used as indicators of ore (Cu, Fe, Zn, Mn, Pb, etc.) deposits in biogeochemical prospecting.

Contrary to earlier views, it seems that heavy metal tolerance is usually not due to a mechanism of differential ion uptake. There is now considerable evidence based on analyses of many metals in several plants grown in different parts of the world on toxic soils, that tolerant species may contain similar quantities of metals without the signs of toxicity shown by other less tolerant species (73, 111, 117, 142, 274, 304). In some experiments the uptake of Zn and Cu was the same for both tolerant and non-tolerant populations of <u>Agrostis tenuis</u> (65, 369). Therefore, when reviewing the heavy metal tolerance in plants, Turner (368) concluded that it seems to be a general rule that plants do not exclude poisonous compounds, in other words there is true tolerance.

An interesting aspect concerning the direct use of soil trace element resources by grazing animals has recently been presented by Healy and his co-workers (156). It was pointed out that over a year sheep can ingest up to 100 lb (45 kg) of soil and dairy cows ten times as much. However, soil type, stocking rate, management, seasonal variations and individual animal differences influence the amount of soil taken in and even high soil intakes amount to probably less than 2 percent of the fresh herbage intakes and less than 10 percent of D.M. intakes. Most elements are present at greater concentrations in soil than are found in pasture plants and so ingested soil is a possible direct source of elements to grazing animals as it passes through the alimentary tract. When the ability of rumen and duodenum liquors to extrace elements from soils was studied in vitro, substantial amounts of elements of nutritional interest were shown to be extracted from soil, while, in some cases, element concentrations in solution were reduced after contact with soil. For example, the concentrations of Fe in the rumen liquor were increased up to nine times the baseline Fe level due to contact with soil. The increases for Mn, Se and Zn were up to 100, 10 and 1.65 times respectively. In the duodenum liquor the increases of Se and Zn were similar to those in rumen liquor while Mn increased only slightly and the content of Fe decreased. In general, the increases were greatest where the soil trace element contents were highest; for instance, in Papakauri, Maikiwi and Timaru soils having Se contents of 1.82, 0.75 and 0.44 ppm were associated, respectively, with 10-fold, 4-fold and 2.2-fold increases in Se in ruman liquor. Healy also refers to the unpublished data of McCabe, Wilson and Healy obtained with soil containing radio-isotopes of Co, Mn, Se and Zn in animal trials. They estimated that the amounts absorbed from the soil were 75SE, 34%; ⁶⁵Zn, 14%; ⁶⁰Co, 1%; and ⁵⁴Mn, 0.4%.