

**trace elements  
in soils and agriculture**

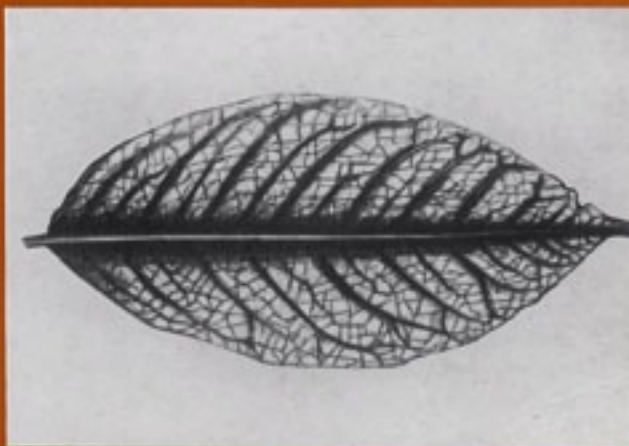


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## I. INTRODUCTION

To meet the demand of the rapidly increasing population of the world, more and more food and fibre must be produced from each hectare of the world's arable land. Modern cultivation methods, improved varieties, better control of plant diseases, pests and weeds and increasing use of mineral fertilizers, increase in irrigated area, etc. are all factors responsible for the general increase in crop yields in recent decades and years (Table 1).

Table 1. Development of world average yields of nine commonly grown crops and consumption of three main fertilizer nutrients (120).

Periods	1948-52	1952-56	1963-67
<u>Crop</u>	Kilograms per hectare		
Wheat	990	1 080	1 280
Rice	1 630	1 820	2 070
Maize	1 590	1 700	2 280
Millet & Sorghum	510	560	740
Barley	1 130	1 250	1 560
Oats	1 140	1 190	1 530
Soybeans	1 000	980	1 180
Cottonseed	440	500	630
Potatoes	10 900	11 100	12 600
<u>Nutrient</u>	Kilograms per arable hectare		
N	3	4	12
P <sub>2</sub> O <sub>5</sub>	4	5	10
K <sub>2</sub> O	3	4	8

In spite of the favourable development in fertilizer use, two to six times more of the main nutrients are still removed annually from the soil than are applied to it as mineral fertilizers. Some of the removed nutrients are replaced by those in straw, farmyard manure, etc. but on average the nutrient balance is likely to remain negative.

Trace elements are not regularly applied to soil by the use of the common fertilizers. Their removal from the soil has been going on for centuries without any systematic replacement. Trace element deficiency cases were first reported at the end of 19th century and today it is known that extensive areas of our soils are incapable of supplying plants with sufficient amounts of micronutrients. The one-sided development in the fertilizing of soils with only main nutrients stimulating increased yields, the loss of trace elements through weathering and leaching, the decreasing proportion of farmyard manure and other natural fertilizer materials used in comparison with chemical fertilizers, the increasing purity of chemical fertilizer materials and several other factors is contributing toward accelerated exhaustion of the available supply of trace elements in soils.

Around nine tenths of a fresh plant consists of water, and about 95 percent of the remaining dry matter of most plants is composed of four elements: carbon, hydrogen, oxygen and nitrogen. Potassium, phosphorus, calcium, magnesium, silicon, aluminium, sulphur, chlorine and sodium compose about four percent of the dry weight and the remaining one percent or less is accounted for by another dozen or more elements including all the essential micronutrients.

On the basis of the amounts in which they are required by plants and of their functions these elements are classified into different categories. Some authors, especially during recent years, have distinguished only two groups, i.e. macronutrients (N, P, K, Mg, Ca, S) and micronutrients (other nutrients), while most research workers have been using the following division into three categories:-

Primary or major nutrients, nitrogen, phosphorus and potassium, which are required in relatively large amounts (often expressed in percent of dry matter basis) and are regularly applied to the soil in mineral fertilizers.

Secondary elements or nutrients is the description given to silicon, calcium, magnesium and sulphur because of their relatively abundant existence in both soils and plants. They are frequently present as accessory elements in fertilizer materials or are applied to soils separately in soil amendments such as liming materials and gypsum. It is not certain that silicon is essential to all plants.

Trace elements (minor elements, microelements or micronutrients) which exist only in small amounts in ordinary soils and plants. Their proportions are usually given in parts per million (p.p.m.). Sometimes the name "nutrient" is used only for those elements which have been proved to be essential for plant growth or for the nutrition of animals to distinguish them from other, non-essential elements. This classification is not always practical, because some elements which are essential for plants are not required by animals and vice-versa and because, from time to time, further elements have been proved to be essential. Further, not all plant species require all the elements now listed as essential.

Today, more than half a dozen trace elements, including boron, chlorine, copper, iron, manganese, molybdenum, sodium, zinc, and possibly cobalt are known or suspected to be essential for the normal growth of plants. Some of these (chlorine, cobalt, copper, iron, manganese, molybdenum, sodium and zinc) are also essential for animal nutrition. Other trace elements required by animals are chromium, iodine, selenium and perhaps fluorine. Deficiencies of barium and strontium have been found in certain conditions to cause growth or other abnormalities but whether they are essential is still doubtful.

In addition to those mentioned above, there are a number of elements found in most soils and plants, which apparently are not essential for plant or animal nutrition. Some of these, like vanadium, may effect the growth of plants indirectly because of their importance in certain micro-biological functions and others like aluminium play an important chemical role in soils, especially in affecting the availability of phosphorus. The importance of many elements found in soils and plants is based on their harmful effects rather than on their role as growth stimulating factors. In general all trace elements are toxic to plants and animals if present in the soil in concentrations appreciably in excess of the normal or average. In some cases (e.g. boron, copper, fluorine, molybdenum and selenium) their toxic effects appear even with relatively low concentrations. These factors, together with the large number of trace elements and their complicated functions in biological processes, and the difficulties in identifying deficiency or toxicity symptoms, if not severe, make the correction of trace element problems often laborious and time consuming and in cases of toxicity even risky. To ascertain the exact nature of the problem, field experimentation is usually needed. However, in cases of slight deficiencies the only full symptoms may be lower crop yields or low production in animals without any visible external symptoms.

It is apparent that hidden trace element deficiencies are far more widespread than is generally estimated. Trace element problems, which today may be considered only local, in the relatively near future may well become more serious, occurring over extensive new areas and creating widespread and complicated production restrictions, if they are not properly studied and diagnosed in time. Even though much of the nature of trace element functions is known, the application of this knowledge is not easy. To avoid serious mistakes in this application, much research and especially extensive experimentation is still needed.

The purpose of this paper is to give the reader some general information on the importance of the numerous trace elements in agricultural production, their origin, existence and behaviour in different soils, requirements by plants and main biological functions and deficiency corrections. In addition, it is hoped to stimulate agriculturists into a clearer realization of the role of trace elements in agriculture. The bibliography, included, will furnish the reader with more detailed information not offered by this review.

## II. TRACE ELEMENT RESOURCES

### 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
F 800	Sr 150	Sn 40	Cs 3.2
S 520	V 150	Co 40	Mo 2.3
Cl 480	Ni 100	Pb 16	I 0.3
Ba 430	Zn 80	B 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 minerals of igneous rocks and their relative stability (258)

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

## 2. Trace elements in soils

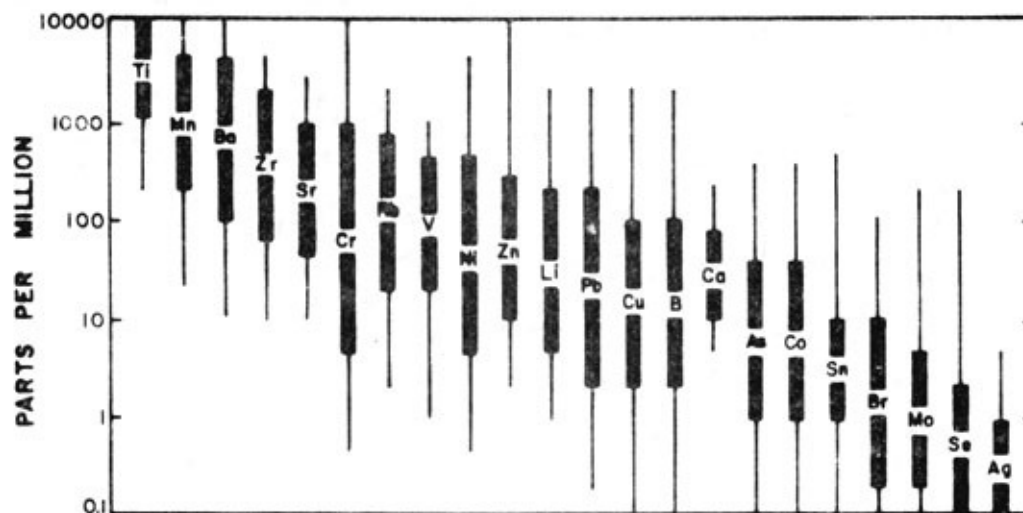
### (a) Total contents

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



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

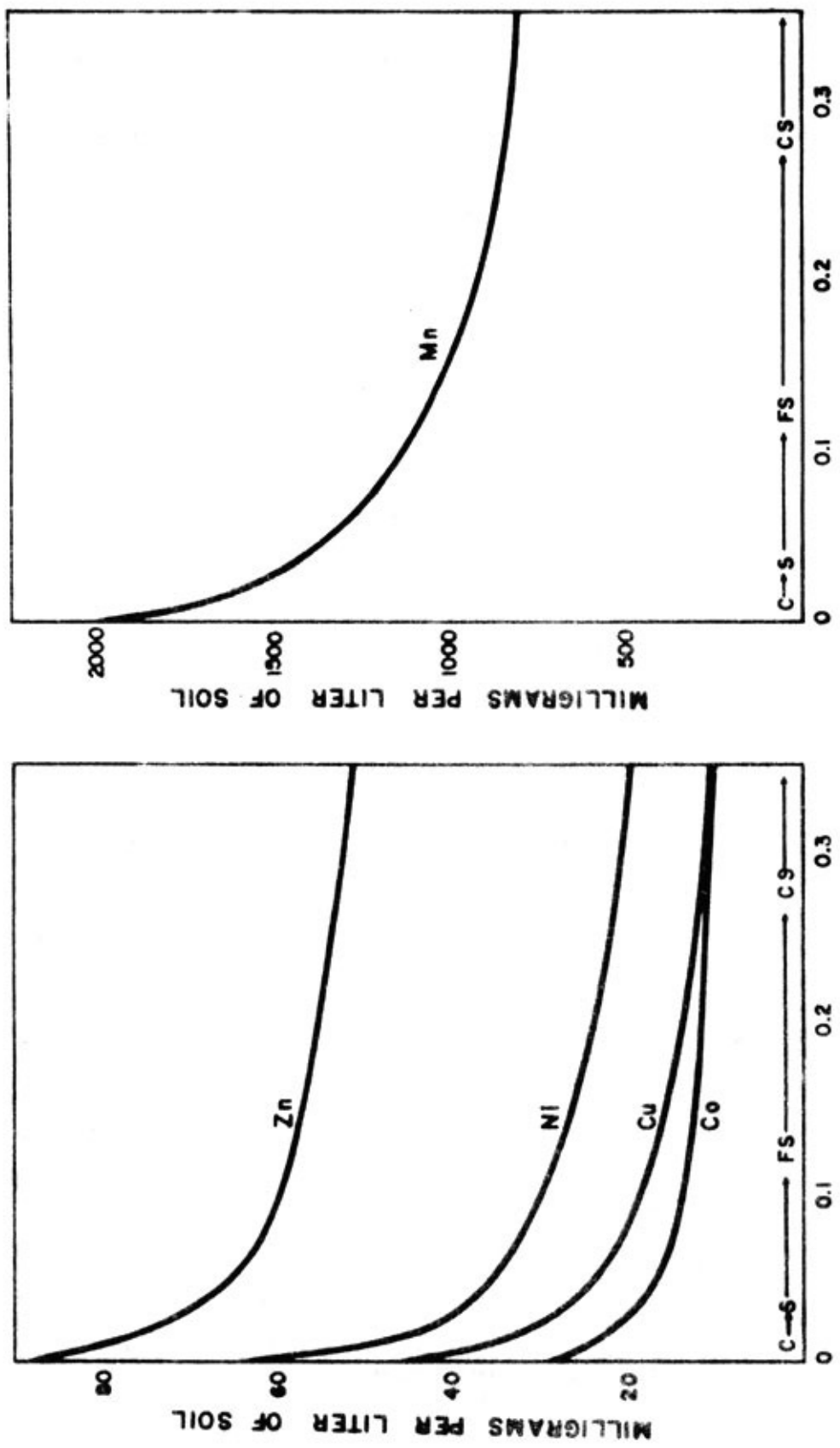
between five elements in material of 160 samples of Finnish mineral soils is shown in Fig.2 (327). The correlations for the given regressions were highly significant while that for the sixth trace element analyzed, lead, was obscured - perhaps owing to its more irregular existence in easily weathered 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 analyzed 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 density	Trace element content as expressed		
		on weight basis ppm	on volume basis mg/litre of soil	on volume basis 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





WEIGHTED MEAN DIAMETER OF PARTICLES (mm)

Fig. 2. 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 mg/l = 1 ppm if the volume weight of soil is 1.0).

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.

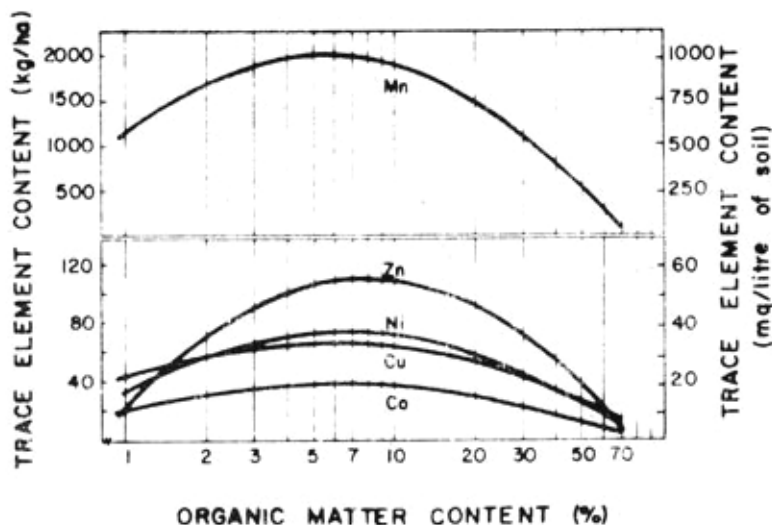


Fig. 3. Relations between the total content of five trace elements and organic matter content of Finnish soils. For all regressions the correlations were highly significant (327).

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 *et al.* (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.

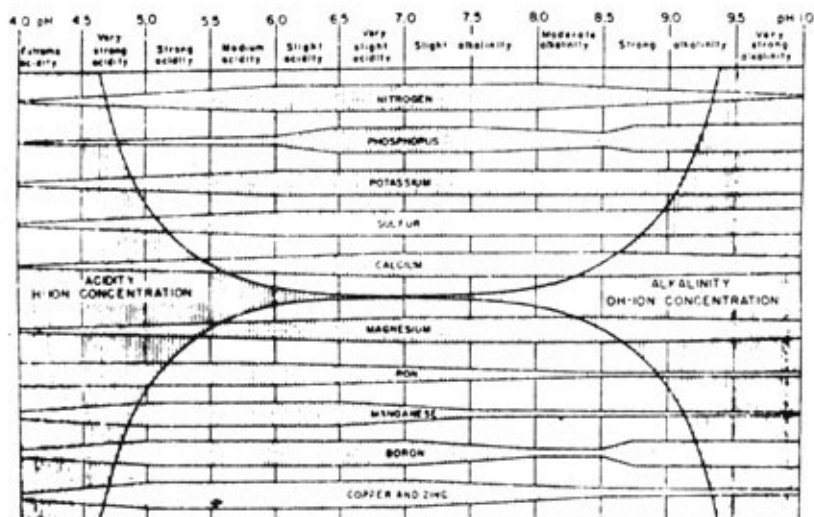


Fig. 4. The availability of plant nutrients in relation to soil pH (367).

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

Soil treatment	Soil pH	Element content (ppm in Oven Dry materials)							
		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 CaCO <sub>3</sub> /ha	6.1	0.19	1.34	1.54	112	0.18	1.40	1.48	41
27.1 tons CaCO <sub>3</sub> /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 FAO 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.

Table 6. 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 element	Soil group			
	Fine mineral soils		Coarse mineral soils	
No. of samples	60		49	
WMDP* (mm)	0.017		0.223	
	Total	Soluble	Total	Soluble
Cobalt (mg/l)	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 between 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 soil organic matter 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 absorption 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 *et al.* (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.

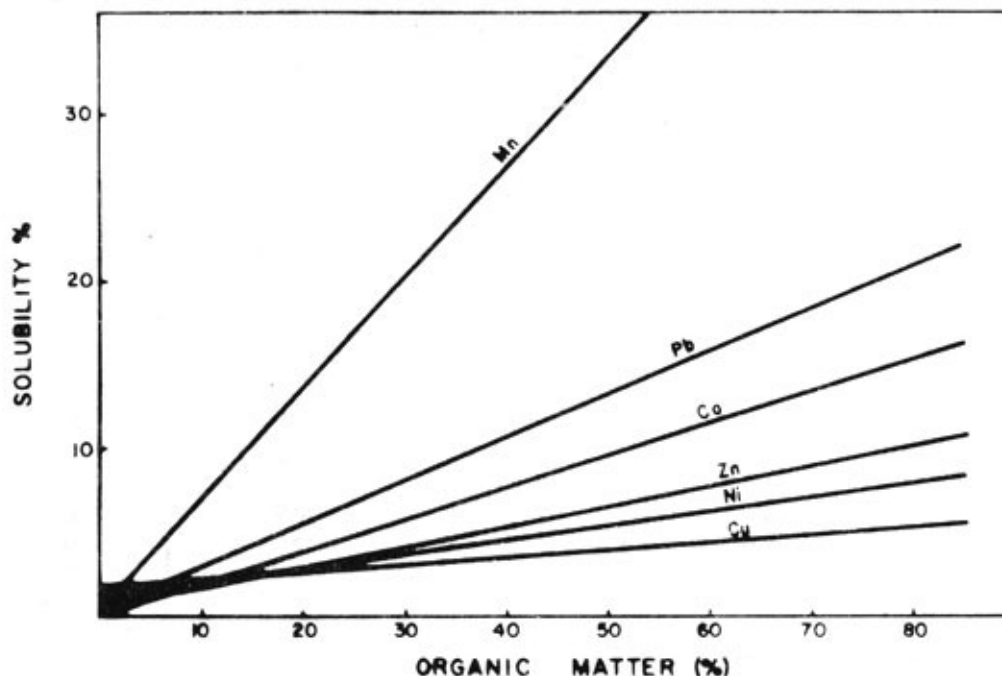


Fig. 5. Relations between the relative solubility (acid ammonium acetate) of six trace elements and organic matter content of soils (328).

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 oxidation-reduction 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), Hoagson (168) and Grable (139) and for individual trace elements these subjects are further discussed in Chapter III.

Plants are the source of trace elements for animals. 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 deficiency when grown on deficient soils. Wallace (389) mentions sugarbeet, mangold, globe beet, apple, sweet cherry and raspberry 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 *Agrostis tenuis* (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 extract 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 rumen 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  $^{75}\text{Se}$ , 34%;  $^{65}\text{Zn}$ , 14%;  $^{60}\text{Co}$ , 1%; and  $^{54}\text{Mn}$ , 0.4%.



### III. REVIEW ON INDIVIDUAL TRACE ELEMENTS

#### 1. Boron (B)

It is apparent that B is essential for all higher plants even though the need for it varies considerably with species. First indications of its beneficial influence on plant growth were observed by Bertrand (41) in 1903, who also recommended the use of B in commercial fertilizers as a supplement to N, P and K. The yield increasing effects of B on wheat, oats and radish as well as its toxic properties in relatively low concentrations were reported by Agulhon (3) in 1910. The essential role of B as a plant nutrient was fully confirmed somewhat later (43, 240, 337, 395). In 1931, it was found that the "heart rot" of sugar beets was caused by B deficiency since when (66), other B-deficiency diseases affecting a large variety of crops have been discovered and B can now be considered as one of the most important agricultural trace elements.

Despite considerable work carried out on B nutrition of plants over the past 60 years, the specific functions of B in plant nutrition are still largely unknown.

It is associated with meristematic activity, auxin, cell wall, protein and pectin metabolism, maintaining correct water relations within the plant, sugar translocation, fruiting processes and phenolase inhibition. It has been reported that its function in primordial and meristematic tissue was at the cell maturation stage. Whether it is required after cell expansion is still unproved. Differences in requirements may be related to the production of secondary meristem in some plants (163, 317).

B seems to be closely related to some function that Ca performs in the plant. If the Ca-B balance becomes disturbed because of a deficiency of B, characteristic B deficiency symptoms become evident. If the balance becomes upset due to a shortage of Ca or an excess of B, symptoms of B toxicity are likely to result (342).

It has also been suggested that B is necessary for the lignin polymerization process and since there is an association between flavonoid content and lignin production, it may be closely associated with the biosynthesis of flavonoids (298). The results of a study (401) concerning the influence of B shortage on the vegetative growth and yield of legumes showed that B is primarily needed to maintain the apical growing points and is directly associated with the process of cell division. It was also established that the vegetative yield does not depend directly on B supply except over a narrow range, e.g. the yield of beans (*Phaseolus vulgaris*) reached a maximum at the 0.05 ppm B level and was unaffected by further increases up to 2.5 ppm.

With the exception of a suggestion that boron deficiency may be connected to many allergic conditions in man and animals (5) no function for this element in the animal body has so far been revealed and there is no evidence of the essentiality of B for animals, although it has been known to occur regularly in animal tissues since 1912 (44). Muscle tissue and most of the organs of the body, other than the skeleton, contain only 0.5-1 ppm B in dry tissue or less, while several times higher B concentrations in bones have been reported (6, 127). While the average daily intake of B by human adults from ordinary diets ranges from about 10 to 20 mg, those of grazing animals are more variable depending on the soil type and plant species consumed, but are invariably much higher per unit of body weight (200, 373). Gastrointestinal and pulmonary disorders in lambs have been reported from high-boron solonchak and solonchak soils where the B contents of water (0.2-2.2 mg/litre) are also exceptionally high (289). In general, the B in food is rapidly absorbed and excreted, largely in the urine (200, 282).

The average B content of the earth's crust has been estimated to be about 10 ppm (Table 2). Even though B may exist as an impurity in many rocks and minerals most of the B in soils is present in the form of tourmaline (Table 3 and 4), a highly insoluble

borosilicate containing about three percent B. The total content of B in soils range usually from about 2 to more than 100 ppm, averaging about 30-40 ppm (179, 180, 258, 351, 400). Plant availability of soil B is closely correlated to the amount of B removed from soil by extraction with boiling water. The amounts range from less than 0.15 to over 50 ppm, the majority of soils having values less than 3 ppm. In soils of humid temperate regions values from 0.2 to 1.5 are frequent while soils of arid and semi-arid areas may contain 10 to 40 ppm or more of hot water-soluble B. The deficiency limit may be in the range of 0.5 ppm depending on the conditions and time of extraction and on soil factors such as pH and organic matter status (62, 180).

When reviewing the trace element problems of European soils Ryan *et al.* (315) stated that instances of low soil values for B were reported from almost all countries. Its deficiency is most often associated with soils of high base status derived from calcareous parent materials and with coarse textured, leached soils. It occurs under extreme climatic conditions ranging from semi-arid in Greece to humid in Ireland. In Great Britain B deficiency occurs most often on light textured, sandy soils low in organic matter, and is more common in dry summers and on limed and heavily fertilized fields (175). In the United States B deficiencies have also been reported from each state in one or more crops; e.g. Alfalfa has been found to be growing on B-deficient soils in 38 states and in Wisconsin alone about 60 percent of its 2.5 million acres of alfalfa have been estimated to be deficient in B (317). In the more humid regions of the U.S.A., B deficiency occurs most often on sandy and highly weathered soils, where the available B is readily leached from the soil (39, 272).

Whetstone *et al.* (400) point out three large regions in the United States in which the soils seem likely to be deficient in B. The first runs along the Atlantic coast from Maine to Florida, and westward approximately to the Appalachian mountains and then along the Gulf Coast to Texas; the soils are largely Red and Yellow Podzolic and Podzols, and have sandy top soils and are rather acid; they owe their low soluble B content mainly to leaching. Across northern Michigan, Wisconsin and Minnesota there is another broad strip of Podzols and the third area is in the states of the Pacific coast and the Pacific Northwest, where the parent material is evidently low in B. The greater part of the old Cotton Belt has also been designated as an area in which B deficiency will become more widespread in the near future (107) because of highly calcareous soils and due to the continuing increase in the use of agricultural lime on already heavily limed soils causing a decrease in solubility and availability of B.

Toxicity of B has been reported in Germany from areas where excessive B has been applied in fertilizers, and in Israel in waterlogged bog soils, in Cyprus in Alluvial and Red Mediterranean soils which have been irrigated with waters enriched with B (315), while in the U.S.A. in desert and semi-arid regions certain soils and irrigation waters may contain toxic concentrations of B (404). One ppm in irrigation water is injurious to some plants and 4 ppm is injurious to most dicotyledons (238). Irrigation waters containing 2 ppm B are reported to be undesirable, e.g. sea water contains more than twice this amount (262). Natural B toxicity is relatively rare except in arid regions and toxicity from added B is more likely on acid, sandy soils, even on those previously B-deficient. An example of this was reported from the United States, where during the World War I high concentrations of B containing substitutes from western salines were used to replace German potash and caused considerable injury to potato and other crops (171, 400).

Since the commonly employed salts of B are water-soluble it seems apparent that toxic soil levels of B, resulting from over-application are quite readily leached from the majority of soils and, therefore, rarely persist for more than one season (168, 294).

B occurs in soils in both organic and inorganic forms. Total B may be concentrated in either surface or lower horizons, but water-soluble B occurs usually in the surface of well drained soils. In poorly drained soils concentrations of soluble B in lower horizons have been observed (83, 149, etc.). In general, B is more mobile in soils than are other trace elements, especially in coarse textured soils. Winsor (407) for example, found that

B added in herbicidal amounts was lost from the surface eight inches of a sandy loam within six months. The presence of high pH and high clay content, however, may seriously reduce the movement of B in soil profiles (107, 319, 400, etc.) since B is firmly held by clays and its fixation usually increases with rising soil pH.

As mentioned before, liming of acid soils thus raising the soil pH, causes a decrease in the availability of B. Whether this decrease is due to the rising pH only, or due to an effect of Ca ions on the absorption of B, or both, has not been agreed. Several investigators have pointed out that both Ca and K influence the uptake of B. A possible explanation is that Ca from limestone combines with soluble B to form highly insoluble calcium metaborate and thus reduces the availability of B. Addition of K, on the other hand, should increase the availability of B in the soil due to the formation of potassium tetraborate of high solubility (107). However, at high pH values K has also been found to depress the solubility of B (280) so crops receiving heavy K fertilization have a higher B requirement, and unless this can be met from the soil, B deficiency may result (410). Therefore, in some states in the U.S.A. B is added to the K fertilizers to meet this extra need (326). It is apparent that when B is deficient, both applied K and Ca aggravate the lack, but when B is present in excess, K aggravates the injury but Ca decreases it (191, 244). There is also a possible interaction between P and B in soils; for example, addition of 1 000 kg calcium hydrogen phosphate per hectare was found to decrease the B content of sour-orange leaves from 34 to 22 ppm on a loamy fine sand and from 67 to 41 ppm on a sandy loam soil (51). The possible role of Ca in this case was not explained. There are also indications that excess Al may decrease the uptake of B by plants (128).

A considerable proportion of B is held in the soils organic matter from which it is gradually released by soil microorganisms. These also compete with plants in utilizing the available B, transforming it into organic forms from which B is again released and oxidized to various inorganic forms upon the death of micro-organisms. During drought periods, when the microbial activity is slow, and there is less breakdown of organic matter, B deficiencies have been observed to be more frequent than during periods of adequate moisture supply. Thus irrigation increases the availability of B (107, 183, 317). Because of the fixation of B by soil organic matter, greater amounts of applied B are required to produce B toxicity in plants growing on soils rich in organic matter than on low organic matter soils (293).

Light is another factor which may affect the uptake of B by plants; for instance, the results of MacVicar and Struckmeyer (237) indicate that soyabean plants growing in pot cultures in long-day conditions on a B deficient soil showed B deficiency symptoms earlier and more severely than those subjected to short-day photoperiod. Some plants like beans, buckwheat and cocklebur are more sensitive to changes in photoperiod, developing B deficiency more readily under long-day conditions, while in other plants such as tomatoes or sunflower the duration of the daylight does not alter their mineral requirements.

Plants are extremely variable both in B requirements and in B uptake. In general the B contents of root crops and legumes are the highest followed by fruits and vegetables, while cereals and hays are poorest in B (32, 202). A comparison of some crops grown on the same soil is given in Table 7.

Typical B contents of healthy and B-deficient plants were reviewed for a number of crops by Brandenburg and Koronowski (68); for example, the B contents of healthy sugar-beets on a dry basis were 25-40 ppm in leaves and 15 ppm in roots; the figures for B-deficient plants were 13-20 and 13 ppm respectively. Healthy mangel-wurzel contained 20-46 ppm in leaves and 17 in roots (B-def. 7-18 and 16 ppm resp.); turnips 30-40 ppm in leaves and 18-22 in roots (B-def. 9-20 and 8-15 ppm resp.); potato leaves 14-30 ppm (B-def. 4 ppm); lucerne 20-29 ppm (B-def. 7-19 ppm); apple 20-25 ppm in leaves and 16-26 in fruit (B-def. 12-16 and 2-6 ppm resp.); tobacco leaves 16-50 ppm (B-def. 4 ppm); celery leaves 26-38 and tubers 19-29 ppm (B-def. 15 and 13 ppm resp.).

**Table 7.** Boron content of some common plants (ppm in dry matter) grown on the same soil (46, 47).

Barley	2.3	Potato	13.9	Soyabean	37.2
Rye	3.1	Tomato	15.0	Lentil	41.4
Wheat	3.3	Pea	21.7	Turnip	49.2
Onion	4.3	White Mustard	22.2	Black Mustard	53.3
Maize	5.0	Carrot	25.0	Radish	64.5
Flax	7.1	Tobacco	25.0	Beets	75.6
Spinach	10.4	Lucerne	25.0	Dandelion	80.0
Celery	11.9	Cabbage	37.1	Poppy	94.7

The optimum level of B in rutabaga (*Brassica napobrassica*) leaf tissue was in the range of 24 to 45 ppm (146) corresponding to 1.1-1.8 ppm hot water soluble B in the soil. The B content of 0.7-0.8 ppm in the soil produced only moderate brown-heart disorder, but 0.6 ppm in the soil and 6 ppm in rutabaga leaf tissue were related to severe brown heart condition. This indicates only a narrow range of B required to produce moderate and severe brown heart disorder. Eaton (112) and Wilcox (404) also reported that B is toxic to many plant species in a concentration not much greater than that required to prevent deficiencies and to support maximum growth. Because of this narrow margin problems associated with the presence of excess B in the soil exist in some areas, both in crops and apparently also in grazing stock (289).

As with other trace elements the amounts of B absorbed by different plants of the same species may differ considerably, even when they are growing near one another in the same habitat. Lounamaa (229), for example, pointed out that the B content in the ash of the leaves and twigs of birch (*Betula verrucosa*) growing in the same habitat ranged from 300 to 3 000 ppm.

As could be expected, an increase in the B concentration of the medium brings about an increase in the B content of the plant. The data of McIlrath and de Bruyn (244), for example, show that increasing the B supply from 0 to 50 ppm increased the B content of shoots of Siberian millet from 29 to 1166 ppm at a low (40 ppm) Ca supply level and from 14 to 760 ppm at a high (480 ppm) Ca supply level. For the same reason significantly higher B contents were found in cabbages grown in urban than in rural areas (292).

Disorders in plants due to B deficiency have been described for more than 50 plant species including blueberries, cabbage, carrots, cauliflower, celery, citrus, corn, cotton, fruit trees, grapes, different legumes, lettuce, nut trees, onions, peppers, potatoes, radishes, rutabagas, spinach, sugar and table beets, sugarcane, tobacco, tomato, turnips etc. The B requirements of small grain crops, most pasture grasses and sorghum are so low that B deficiency symptoms hardly ever develop in field conditions.

The symptoms vary widely between species of plants and are often given descriptive names such as "heart rot" of beets, "cracked stem" of celery, "internal cork" or "drought spot" of apples, "yellow top" of alfalfa, "brown rot" of swedes, "brown heart" or "water core" of turnips, "top sickness" of tobacco and many others.

The common symptoms of B deficiency are the brown spots in the interiors of root crops, splitting of stems of kale and kohlrabi, yellowing of the leaves of alfa-alfa, red leaves on Ladino clover, discoloration of the curd of cauliflower, black areas inside the stalks of cabbage, cracked stems in celery, death of growing points of lettuce, yellowing and curling of tomato leaves, internal cork and malformation of apples, dieback, rosetting and malformation of fruit of citrus and unrolled leaves of corn. Detailed descriptions of B deficiency and toxicity symptoms for a number of crops can be obtained from several sources (68, 164, 341, 347, 391).

The annual removal of B from the soil by different plants varies considerably with soil B contents, plant species and yield levels. As reviewed by Arent (15) a 33 ton/ha crop of lucerne removes 500-600 grammes of B/ha, sugarbeets (40 tons/ha) remove 300-500 g/ha, turnip (60 tons/ha) 200-240 g/ha, potatoes (20 tons/ha) 40-102 g/ha and cereals (2 000 kg/ha) only 20 to 40 grammes of B per hectare.

The B content of common fertilizers is generally low. Out of the several hundreds of N, P and K fertilizers listed by Swaine (352) the majority contain less than 20 ppm of B and about two thirds less than 50 ppm. Most of the lowest as well as the highest B values are found in N fertilizers. The reported B contents of farmyard manure vary from less than 1 to about 8 ppm, averaging about 2-4 ppm, which corresponds 2-4 grammes of B per tonne of fresh material. Most values for liquid manure range from about 2 to 6 ppm in fresh material.

It is obvious that the removal of B from soils by crops will not have been compensated for by using common NPK fertilizers. For example, an application of 1 000 kg/ha of NPK fertilizers containing 20 ppm B, would only bring 20 g B/ha to the soil for replacement of the 20 to 600 g/ha (see above) annually removed by different crops. Even this small amount may still be diminished by leaching and other losses. Therefore, in the more intensive farming areas, as well as on B-deficient soils elsewhere, it is necessary to include some borated fertilizers in fertilizing practice, especially for B-responsive crops such as legume, root, tuber and cotton crops.

The most commonly used B fertilizer is borax (sodium tetraborate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) containing 11.3% B. It is also produced as a slowly soluble, fritted boron, containing about 6% B, and for spray application there are highly soluble forms such as Solubor ( $\text{NaB}_5\text{O}_2 \cdot 5\text{H}_2\text{O}$ , cont. 20.5% sol. B) and Boric acid ( $\text{H}_3\text{BO}_3$ , cont. 17.5% sol. B). Other products are Kernit ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ ), Colemanit ( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ ), Calciumtaborate  $\text{Ca}(\text{BO}_2)_2 \cdot 2\text{H}_2\text{O}$ , cont. 6.5% sol. B), Pandermit ( $\text{Ca}_2\text{B}_5\text{O}_9\text{OH} \cdot 3\text{H}_2\text{O}$ ) and slightly soluble Boracit and Howalit (68,317).

Marked increases in the yields of a considerable variety of crops have been obtained by applying B-fertilizers. A striking example of this is from Germany where on B deficient soils over 90 percent increases in sugarbeet yield with a simultaneous increase in the sugar content of the beets by an application of 20 kg borax per hectare have been reported (67). Because the range between required amounts and amounts that are toxic to plants is very narrow, B fertilizers must be applied with greater caution than is required for other plant nutrients.

Liberal application of B may result in the death of plants and therefore boron compounds have also been used as weed killers. Since the B requirements of various plants differ widely, the recommendations for different crops vary accordingly. Highest doses (from 1 to 3-4 kg B/ha or about 9 times this amount as borax) are generally recommended for alfalfa, beets, celery, sugarbeets and turnips growing on B deficient soils.

For rutabaga, potatoes, cauliflower, carrots, radishes and tomatoes the recommendations usually range from 1 to 2-3 kg B/ha. Somewhat less is recommended for broccoli, lettuce, mangels, cabbage, corn, grapes and strawberries, and less than 1 kg B/ha for sweet potatoes, cotton, tobacco and groundnuts. About half of the above doses are sufficient if applied as foliar spray or drilled.

Soils with a high exchange capacity and (or) neutral or alkaline reaction may be fertilized with larger quantities than those of low exchange capacity, low Ca saturation and low pH. The texture and organic matter content of soils also influence the amount that should be applied to a given soil; e.g. Purvis (293) states that while 11.2 kg/ha (10 lb/acre) of borax is sufficient for celery on the light sandy soils of Florida, 112 kg/ha (100 lb/acre) may be required for the same crop on Michigan peat soils.

Since there appears to be little accumulation of applied B in most soils, annual application of B may have to be made on deficient soils. However, in some cases the residual effects of B application may last for several years, for instance, Tähtinen (355) found that the rates of B application were still clearly reflected both in the B contents of plants and in the contents of water-soluble B in the soil four to six years after its application.

## 2. Chlorine (Cl)

In spite of the suggestion by Nobbe and Siegert (275) over a hundred years ago that Cl is an essential element for the normal growth of buckwheat, this element has only recently been accepted as an essential plant nutrient. This has been mainly because of its ubiquitous existence in nature in relation to low requirements and difficulties in producing absolutely Cl-free experimental conditions. Most of the Cl deficiency cases have been reported from pot experiments and relatively few Cl responses from field conditions. Plants responding to Cl include buckwheat, tomatoes, tobacco, cotton, maize, barley, peas, lucerne, lettuce, cabbage, potatoes and carrots (81, 190, 363, 372).

Although Cl deficiency symptoms seldom develop in field conditions, potassium chloride has often been reported to be superior to potassium sulphate insofar as yields are concerned, because the chloride fertilized plants tend to maintain a higher moisture content in their leaves and appear to have somewhat greater resistance to drought. Sometimes chloride has been found to lower the quality of certain crops, notably tobacco and potatoes (29). Symptoms of Cl deficiency in tomatoes include wilting of the leaflet tips and progressive chlorosis of the leaves followed by bronzing and necrosis. The early symptoms in sugarbeet resemble those of Mn-interveinal chlorosis on the blades of the younger leaves. Later, flat depressions form in the interveinal areas causing the veins to have a distinct raised appearance. Descriptions in more detail have been given, e.g. by Broyer *et al.* (81) and by Ulrich and Ohki (372). There is an almost complete lack of knowledge about the role of Cl in plant physiology.

Cl is usually found in soils in highly soluble forms and is subject to losses by leaching. Deficiency however develops only in extreme conditions, but leaching, e.g. from sandy hill soils, may cause accumulation of Cl in adjoining depression areas. Seashore soils in humid regions and saline soils in arid regions often contain toxic amounts of Cl. For instance, soils prevalent in Japan contain relatively large amounts of Cl apparently due to the fact that Japan is surrounded by seas (413). White alkali soils contain a high proportion of chlorides and sulphates of sodium.

Plants receive measurable quantities of Cl (NaCl) in the rain. At Rothamsted an annual average of 16 lb/ac was reported (314) but in areas of high rainfall and near seashores the amounts are much higher. Cl is not intentionally applied to soil by fertilization but almost all fertilizers contain at least traces of Cl and in some, e.g. ammonium and potassium chlorides, considerable amounts of it are added to soils.

Plants tend to absorb large amounts of Cl if it is available and their Cl content varies from trace-level up to several percent. In pastures it is often around one percent, but may vary from 0.2 to 1.5 percent (349). Cl is essential for animals for the production of hydrochloric acid needed in digestion and sodium chloride is usually included in their diet to meet these requirements.

### 3. Cobalt (Co)

The essentiality of Co for higher green plants has not yet been definitely established even though responses of non-leguminous plants to Co have been reported (405). Co is required by Rhizobia for nitrogen fixation and thus indirectly by leguminous plants. Also some species of nitrogen fixing blue-green algae need Co for their normal growth (4, 170, 231). In blue-green algae Co deficiency results in reduced growth and chlorosis. In nitrogen fixation by Rhizobia, Co plays a part in the formation of vitamin B<sub>12</sub>, which is required for the formation of leghaemoglobin needed for N fixation.

Co deficiency in ruminants is relatively widespread, resulting in loss of appetite, progressive emaciation, retarded sexual development, muscular atrophy or anaemia. Sometimes the only symptom may be very slow growth or none at all. Sheep are usually affected more than cattle and young stock more than old. It has been shown that vitamin B<sub>12</sub> is synthesized in the rumen by micro-organisms, hence the ruminants special requirements for dietary Co. In non-ruminants the vitamin B<sub>12</sub> complex must already be present in the diet (281). Several sources (287, 373, 374) give detailed descriptions of Co deficiency diseases, often known by local names such as "coast disease" in South Australia, "pining" in Scotland, "bush-sickness" in New Zealand, "Nakuruitis" in Kenya, "salt sick" in Florida, and "wasting disease" or "enzootic marasmus" in Western Australia.

The average content of Co in the lithosphere has been estimated to be about 40 ppm (Table 2) and the total Co content of soils is usually in the range of 1-40 ppm, but values up to 800-1000 ppm have been reported from areas where Co minerals are present (9, 154, 351). Many pasture soils in different parts of the world are known to have too low a Co content for sheep or cattle. Owing to differences in availability from soil to soil there is apparently no direct correlation between the total Co content of soils and of the herbage. However, many instances of Co deficiency have been reported from soils of 2-5 ppm or less of total Co (29, 346, 349, 414). The amount of Co extracted from Scottish arable soils by 2.5 percent acetic acid varies from less than 0.05 ppm in very deficient sand to over 1 ppm in many soils derived from basic igneous rocks. The level of deficiency lies at about 0.25 ppm in mineral soils of an average pH range from 5 to 6, but other factors are involved and must be considered in interpreting the analytical results (258).

While Co deficiency is not limited to any particular type of soil or parent rock, many incidences in Great Britain and Ireland are associated with calcareous sands, old red sandstone and granite (281). Similar relationships have been reported from other European countries, (e.g. Austria, Greece and western Germany) and in addition Co deficiency has often been observed to occur in areas of podzols or podsolized soils (Poland, Spain, Scotland, Ireland, western Germany, England and Wales), of light sandy soils or other coarse textured soils (Netherlands, Norway, Finland, Israel, Sweden) and of peat soils (Ireland, Finland, Poland). In the Netherlands especially, sands with low organic matter and low clay content and in Sweden all soils, except clays, may be susceptible to Co deficiency (315, 390).

As for other trace elements such soil factors as texture, pH and soil moisture content are related to the amounts of Co in soils and to its availability to plants. As mentioned above, Co deficiency often occurs on coarse textured soils and correlations between the Co content of soils and their textures have been reported. In 160 Finnish soils the total content of Co significantly decreased with coarser textured soils (Fig. 2). A similar relationship existed between the content of Co soluble in acid ammonium acetate and texture, but since the relative solubility was not found to be affected by texture, the latter relation was considered to be due mainly to the former (328). Similarly, a linear positive relationship between the Co and the clay contents of 32 Pakistani soils has been reported (386) and in another study the clay fraction of a soil was found to contain up to seven times as much Co as the sand (167).

The acidity of the soil can influence the solubility of Co and its uptake by plants. Within a pH range from 4 to 7 a significant decrease in soluble Co with increasing pH has been reported, this relation being more prominent in organic and in coarse mineral soils than in fine mineral soils (328). Thus, liming the soils may cause a considerable decrease in the uptake of Co by plants (see Table 5). There are, however, more indications that with very heavy liming of acid soils the solubility of Co may begin to increase after reaching pH 7 (412) and that liming does not alter the uptake of natural Co but greatly reduces that of added Co (34). In general, Co is poorly absorbed by plants from calcareous soils.

The amount of extractable Co and its uptake by plants from poorly drained soils has been found to be greater than from well drained soils (258, 259, 353). Kubota *et al.* (210) obtained similar results with two well-drained Brown Podzolic soils but found no moisture effects on Co uptake by plants on two Nevada soils, namely an excessively drained Brown soil and a poorly drained Wiesenboden, both on granitic alluvial pan. The reasons for this are not clear and Bear (28) states that oxidation-reduction effects are unlikely to play much part in the chemistry of soil Co.

Soil Co has been found to be rather closely related to some other elements in soil, particularly to Ni (235, 239) and Fe (208). Application of cobalt chloride to soil has also been found to increase the uptake of Mo by herbage (263) and increases in the plant uptake of Co were observed when  $\text{FeCl}_2$ ,  $\text{AlCl}_3$ , and  $\text{CaCl}_2$  were added to the soil (132).

An average content of Co in mixed pasture herbage, 0.11 ppm in dry matter, was reported by Mitchell (261) and mean contents of 0.10, 0.20 and 0.26 in hay and meadow hay by Zacherl *et al.* (415), Schiller *et al.* (321) and Kocalkowski *et al.* (204). The Co content of grasses is generally somewhat lower and that of legumes higher than average (13, 29, 113, 122, 123, 213, 303). Therefore, Co deficiency in animals is less likely to develop if legumes are contained in the forage. Cereal grains, particularly maize, are poor sources of Co, with concentrations usually lying within the range 0.01 to 0.06 ppm Co. Wheat bran typically contains 0.12 to 0.16 ppm and leguminous seed and oilseed meals 0.2 to 0.3 ppm Co (374).

Where the Co content of forage is less than 0.1 ppm lambs and calves are likely to respond to Co dosing. If the content is less than 0.07 ppm and is maintained at this low level for some months, Co deficiency is inevitable (13, 29, 358, 374). For cattle the Co requirement is somewhat lower, for instance in Ireland the Co deficiency in cattle appears to be confined to areas where Co levels in herbage are less than 0.04 ppm (281). Co is toxic when fed in excessive amounts. For dairy cattle the tolerance has been reported to be somewhat in excess of 50 mg of Co per 100 lb of body weight (110 mg/100 kg), an amount considerably exceeding the requirement (198, 333). Co toxicity is not a practical problem under pastoral conditions.

The level of available Co in most soils, and hence the uptake by plants, can readily be raised by the application of Co-containing fertilizers. For example, data from Mitchell *et al.* (263) showed that an application of 2 lb cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) per acre increased the Co content of herbage from 0.07-0.08 ppm level to about 0.2 ppm; with 11.2 kg/ha (10 lb/acre) the content was increased to about 0.8 ppm and with 89.60 kg/ha (80 lb/acre) to 3 ppm (1 lb/acre = 1.12 kg/ha). The normal rate of cobalt salt application to pasture land is very small. If applied annually, 2 to 4 ounces cobalt sulphate per acre (140-280 grammes/ha) is sufficient, and a single application of 20 ounces per acre every three or four years will maintain satisfactory Co concentration in herbage. An example of the residual effect of Co fertilization was reported by Rossiter *et al.* (312) who found that single applications of 4 and 8 ounces of cobalt sulphate increased the Co content of pasture herbage from 0.04 to 0.19 and 0.39 ppm in the first year, but by the second year the concentrations had fallen to 0.10 and 0.16 ppm, respectively. There are some differences in opinion as to whether it is better to apply Co to the soil or whether it should be given directly to livestock. In Ireland applications of cobaltized superphosphate to soil and the administration of a pellet composed of cobaltic oxide have both given highly satisfactory



results (281). In some cases Co fertilization has also produced yield increases in leguminous pastures through the stimulus given to the nitrogen-fixing rhizobia (290). On highly alkaline soils the application of Co containing fertilizer may remain ineffective.

Common mineral fertilizer materials usually contain only traces or a few ppm Co as impurities and can seldom be expected to remedy Co deficiency in soils. Nitrogen and potash fertilizers, in general, are lower in Co (mostly 0-1ppm) than phosphates (usually 0-5 ppm). The Co content of farmyard manure varies from about 0.2 to 6 ppm in dry matter and that of liquid manure from 0.001 to 0.02 ppm in fresh material or from 0.04 to about 2 ppm in dry matter (352).

#### 4. Copper (Cu)

Although the presence of Cu in plant and animal tissues was known well over a century ago, convincing evidence of its essentiality for animal nutrition was presented first in 1928 (152) and for the normal growth of higher plants in 1931 (228, 336).

The average occurrence of Cu in the earth's crust has been estimated to be 70 ppm (Table 2) and its total content in soils ranges usually from about 2 to 100 ppm but, occasionally, values up to 5 000 ppm or more have been reported from soils of Cu-rich areas usually located near ore deposits (174, 230, 257, 383). The total Cu content of a soil is often related to the origin of its parent material and its resistance to weathering and, therefore, indirectly to soil texture (see Table 4 and Fig. 2 and related text). For the relation between total soil Cu and soil organic matter content see Fig. 3 and the related text.

In addition to the total content of Cu in soil the soluble amounts are dependent on several other soil factors controlling the relative solubility of Cu in different conditions. Such factors as soil organic matter, pH, reduction-oxidation, seasonal variation and interaction with other elements should be mentioned.

Cu occurs in soils principally as  $Cu^{+2}$  ions adsorbed by clay minerals or tied up by organic matter. It is known that Cu can readily combine with any free complexing agent that may be available and that organic matter has a large capacity to combine strongly with Cu. Several theories on the forms of binding have been presented. It is also obvious that not only the quantity but also the quality of soil organic matter affects its ability to complex the Cu ion, making these relations more obscure.

The fixation of Cu by organic matter has often been considered the main cause of Cu deficiency in organic soils (e.g. 183, 354). However, this view was not supported by the results of Scharrer and Schaumlöffel (320), who showed that Cu, when added in small amounts, was more readily available in soils rich in organic matter than in mineral soils. Also Svanberg (350) found that Cu may be effectively fixed in peat soils, but states that plants obviously have a power of taking up this element from organic compounds. When the effects of several partial soil factors (including total Cu content, pH and organic matter content) on the soluble amounts of Cu in over 200 soils were analyzed by means of multiple regressions (328), significant positive correlations were found with total Cu and significant negative correlations with soil pH in most soil groups: but organic matter was in significant negative correlation with soluble Cu only in one out of five soil subgroups, namely on organic soil. One of the reasons for the lack of soluble Cu/O.M. correlation in other soil groups is the obvious increase of total Cu with organic matter up to 5-7 percent O.M. level (see Fig. 3) followed by a decrease in organic soils. Even in these soils the negative correlation between soluble amounts of Cu and O.M. is weakened by the slightly increasing relative solubility of Cu with increasing O.M. content (see Fig. 5). Although Cu may occur in soils in both mono- and divalent forms the effect of oxidation-reduction on its availability is generally considered smaller and less clear than, for instance, that of Fe and Mn. Fresh supplies of readily oxidizable organic matter have been said to contribute to maintaining Cu availability (249) and again responses to Cu may be larger in hot, dry summers than in cool, moist ones (151).

On the basis of the results quoted above (and keeping in mind the obscuration often caused by the different ways of expressing the results, see p. 6) it may be concluded that, in spite of the relatively strong fixation of Cu by organic matter (apparently much stronger than for other trace elements), the basic reason for the commonly existing Cu deficiency in organic soils in most cases is due to the low total Cu contents of these soils rather than to Cu fixation alone.

The role of soil pH as a factor affecting the solubility or availability of Cu to plants is not very clear even though most results indicate that the solubility of Cu in the soil decreases slightly over the range from acid toward the neutral and alkaline pH ranges. It is apparent, however, that pH has less influence on the solubility of Cu than on that of Mn, Mo or Zn. A quite substantial decrease in exchangeable Cu with increasing pH in sandy soils in Florida was found by Peech (286), and reduced Cu toxicity with increasing pH has been reported elsewhere (101, 309). No differences in the uptake of Cu by plants with variations in soil pH, however, were observed by French *et al.* (129) and, similarly, no relation between Cu deficiency and soil pH could be established when analyzing the results of over 600 Cu trials in Sweden, where Cu deficiency is common (234). Partial explanations of the different findings above may be that the amounts of Cu extracted by chemical solvents vary more with soil pH than the amounts removed by plants (168), and that the selectivity of certain cation exchange sites for small quantities of Cu may obscure the pH effect; while, when present in large quantities, some of the Cu will occur in nonselective exchange sites and the release to the soil solution will then be increased at low pH values (52). Furthermore, at high pH, the excess Cu may be changed to mineral forms of low solubility.

Interactions between Cu and other elements in soils have been pointed out by several investigators. Excess Cu has been noted to induce Fe deficiency in citrus (308). An antagonistic interaction between Cu and P was reported by Johansson (187) who found that building up the P status by P fertilization on poor soils with a potential lack of Cu, can cause an acute Cu deficiency. This was most likely to happen on light soils poor in nutrients and the risk became greater with increasing O.M. content (See also Table 8 on page 37). Similarly in Ireland, on cutaway peat, Cu deficiency was accentuated by N fertilization so wheat yields on plots receiving 500 kg/ha nitrogenous fertilizers and no Cu failed completely, however symptoms of N deficiency were also obvious in all plots treated with Cu but no N (121). The residual effect of a copper sulphate dressing as low as 8 kg/ha was sufficient to ensure good growth on this soil. On the other hand, Cu dressing stimulated nitrogen mineralization and nitrification on a sandy loam receiving 200 ppm N as dried blood (297). A possible interaction between the need for Zn and for Cu was reported in soils where low Cu dressings only are required, and where the crops respond to Zn only if Cu is also given, but not if it is withheld (232). Some of the above interactions may be explained on the basis of two limiting factors.

Organic soils have often been found deficient in Cu, apparently because of their low total Cu content and partly due to their high capacity to fix Cu, as discussed before. This is especially true in the northern countries where, for example in northern Sweden, half the organic soils, but only one fifth of the mineral soils, have been estimated to be Cu deficient (2). In the United States Cu deficiency in field crops occurs mainly on organic soils including peat and muck (38) and similarly in Finland the deficiency of Cu has been found to be associated usually with peat soils or coarse mineral soils (356). There the average total contents of Cu in fine mineral, coarse mineral and organic soils were reported to be 33, 16 and 14 mg and soluble contents (acid amm. acetate) 0.61, 0.29 and 0.19 mg per litre of soil, respectively (328). Also Ryal *et al.* (315) when summarizing the occurrence of Cu deficiency by country and soil, state that Cu deficiency is most common in peats and podsolized soils in zones of high precipitation. It is also associated with granite, calcareous sandstone basalt, red sandstone and carboniferous limestone parent materials. Furthermore, in their list of Cu deficient soils, peats or peaty soils are mentioned in 11 out of 14 countries, podzols or podsolized soils in nine countries and in cases where soil texture is specially pointed out reference is always made to sands or coarse textured soils.

The methods used for analyzing soluble soil Cu vary greatly in extracting power. One of the basic reasons for the heterogeneity of methods is apparently the tendency of Cu to form rather stable chelates and complexes with soil organic matter. The weakest extractants include various electrolyte solutions; chelating agents are somewhat stronger and the most effective extractants are strong mineral acids. *Øien and Semb (277)* when comparing three methods found that extraction with 0.02 M EDTA solution or 0.043 N nitric acid a somewhat better estimate of available Cu status of Norwegian soils than did a concentrated nitric and perchloric acid digestion. The small fraction of Cu (generally less than 1 mg/litre of soil) extracted from Finnish soils with slightly acid ammonium acetate (pH 4.65) solution apparently represents relatively well the available Cu fraction in these acid soils since it was significantly correlated to the Cu content of timothy grown on 216 sites. The lack of correlation found in the subgroup of organogenic (>15% O.M.) soils was attributed to Cu-organic matter bonds which were too strong for the weak extractant used (330).

Cu plays a role in plant growth as an enzyme activator or as a part of many oxidizing enzymes such as mono- and polyphenol oxidase (tyrosinase), laccase and ascorbic acid oxidase, which function in respiration. It is also important in protein metabolism and may be associated with chlorophyll formation. Several sources give detailed information about these functions (e.g. 98, 108, 164, 267, 347).

The content of Cu in most normal plants is usually within the range from 5 to 25 ppm, but varies with plant parts and species, state of maturity, soils etc. *Bear (29)* gives average Cu contents varying from 12 to 20 ppm for rye, vetch, carrot tops, bean tops and ryegrass. In flue-cured tobacco a range of 15 to 21 ppm Cu has been reported (91), but the content in the leaves was found to be several times higher than in the stalks (243). For cabbage and lettuce, contents ranging from 0.4 to 48 and from 3 to 60 ppm, respectively, have been reported (30). *Beeson et al. (33)* found the Cu content of 17 grass species grown together on a sandy loam soil ranged from 4.5 to 21 ppm. The average Cu contents of timothy were reported by *Zacherl et al. (415)*, *Schiller et al. (321)* and *Lakanen (213)* as 6.9, 6.4 and 6.3 ppm, respectively. In the last mentioned study the range was from 1.9 to 12.5 ppm, and in 30 percent of the samples, the Cu content was less than 5 ppm. Somewhat lower Cu contents of hay ranging from 0.8 to 10.4 (aver. 3.8) ppm have been reported from Poland (136). In citrus leaves a satisfactory Cu range was tentatively considered to be 5 to 16 ppm (194, 306). If the content is less than about 4 ppm, visible deficiency symptoms, lowering of production or some effect on fruit quality may be expected. The lower limit of "excess" (not toxic) was estimated to be about 17 ppm, but the flexibility of such limits was emphasized. It has also been stated (363) that the amount of Cu present in a plant in relation to amounts of other heavy metals is perhaps of greater importance to proper plant functioning than the absolute amount of Cu per se.

Disorders in plants due to Cu deficiency are called by a variety of names such as "reclamation disease" in oats and other cereals, "exanthema", "red rust", "ammoniation", "dieback" or "peach leaf condition" in fruit trees, etc. The symptoms vary with the crops; for example, in small grains the deficiency is characterized by loss of colour in the younger leaves, followed by breaking of the leaves and eventual dying of the leaf tips. In more severe cases the leaves become shivered, twisted and broken and the plant dies (207). In legumes leaves may wilt and wither without chlorosis and excessive leaf shedding occurring (272). In forage grasses, entire plants become stunted and yellow in colour, followed by necrosis of growing points and the tips of the younger leaves (409). There are considerable differences among plant species in their sensitivity to Cu deficiency. For example, symptoms of deficiency have not been observed in tobacco under field conditions (246) but oats and wheat apparently would be good indicator crops for anticipating Cu deficiency (409). Detailed descriptions of Cu deficiency symptoms in a number of crops including various grain crops, legumes and forage grasses, fruit and nut trees and vegetables etc. are given in "Hunger Signs in Crops" (341) and "Handbuch der Pflanzenkrankheiten" (323).

Like other trace elements, Cu is toxic to plants if it exists in any but small concentrations. Although cases of Cu toxicity have been reported, it seems not to be

widespread and apparently is only of local importance, mainly in areas affected by Cu pollution from mining or as a result of accumulated spray residues (211, 309, 413).

Excessive amounts of Cu may depress the activity of iron and Hewitt (162) found that it led to chlorosis of the leaves of tomato and sugarbeet resembling that produced by iron deficiency. The addition of calcium phosphate to the soil has been found to reduce the uptake of Cu by sour orange, probably due to the formation of insoluble Cu phosphates (51).

Cu deficiencies in animals occur in all continents under a wide variety of climatic conditions and are more common in grazing animals than in pigs or poultry which usually receive adequate amounts in their diets. Simple Cu deficiency usually occurs when the Cu content of forage is about 5 ppm or less on a dry basis. "Conditioned" Cu deficiencies, which are more common, may occur at higher Cu levels and may be due to several complicating factors such as high Mo levels or high Mo plus inorganic sulphate limiting the utilization of Cu by the animals (see also III 8. Mo, p.35). The symptoms of Cu deficiency vary with animal species but are often characterized by a form of anaemia, depressed growth, bone disorders, depigmentation of hair or wool, abnormal wool growth, lowered fertility and nervous disorders in lambs or kids of deficient mothers (373, 374, 377).

Cu poisoning in farm animals may occur both under natural conditions when the Cu contents of the soils and the pastures are high and it may be produced by treatments for Cu deficiency diseases or by the increasing use of Cu compounds in agriculture. Cu toxicity symptoms may also occur with normal Cu levels in forage if coupled with complicating factors such as abnormally low levels of Mo in forage or associated with liver damage caused by the plant Heliotropium europeum. Sheep are generally less tolerant of high dietary intakes of Cu than are cattle or other species. The functions of Cu in the nutritional physiology of animals as well as the symptoms of both its deficiency, toxicity and the curing of these conditions, have been excellently described by Underwood (373, 374).

Cu deficiency is usually corrected by applying copper salts to the soil or by spraying soluble or slightly soluble copper solutions on the plants. Copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) is most commonly used for both purposes but other products, such as copper oxide and copper ammonium phosphate, can be used and chelated copper compounds are also commercially available.

Where copper sulphate is applied to the soil the normal rates range usually from 5 to 20 kg of the material per hectare. Peat soils may require somewhat larger amounts than sandy soils of low buffer capacity. In general, caution should be exercised when applying Cu since it is not readily lost from the soil and yearly additions may accumulate to produce toxicity.

Copper sulphate, when used alone, is a poor foliar fungicide, but when combined with lime to produce Bordeaux mixture, both tenacity to the host plant surface and long term effectiveness against fungi are greatly increased, and toxicity to the host is reduced (268). It is apparent that Cu deficiency has often been unintentionally prevented when controlling plant diseases with Cu-containing materials such as the above, but Cu toxicity has also been caused by fungicide treatments as reported for instance from the vine-producing areas of the South-West and South-East regions of France (100, 138).

The Cu content of common commercial nitrogenous fertilizers is generally very low. In the extensive review by Swaine (352), the Cu content of about half the analyzed samples of N-fertilizers fell within the range 0-1 ppm and about three-quarters contained less than 10 ppm. Only occasionally values up to 50 ppm or more were listed. In potassium fertilizers about one-third of the samples listed had a Cu content of 1 ppm or less and about half contained less than 10 ppm. Some values up to 1000 ppm or more were registered for certain potassium salts and wood ashes. Phosphatic fertilizers contained generally more Cu than the other two types. About half of the Cu values were within the range 0 to 15 ppm, but values up to 50 ppm were quite common, and in about one-fifth of the several hundreds of analyses recorded the Cu content exceeded 50 ppm. For certain phosphatic rock and guano materials values up to 1000 ppm or more were given. In the U.S.A. fertilizers

enriched with Cu contained on the average 0.36 percent Cu in 1964 (375). Farmyard manure usually contains 5 to 15 grammes Cu per ton (35) or 10 to 50 ppm in dry material (352). For liquid manure values from 0.01 to 0.4 ppm Cu in fresh material have been reported (352).

## 5. Iodine (I)

Traces of I are found in almost all living tissues. It is not known to be needed by plants but is essential for animals and has a long history in human and veterinary medicine. Its importance as a trace element is that a certain level must be maintained in the thyroid glands of mammals to prevent the development of I deficiency symptoms such as enlarged thyroid known as goitre. Among trace element deficiencies one of the most widespread is that of I.

The average content of I in magmatic rocks of the upper lithosphere is about 0.3 ppm, in ocean water about 0.05 ppm and in soils about 2 ppm, ranging usually from about 0.6 to 8 ppm but exceptional values up to 70 ppm may exist (137, 258). Because the solubility of most I compounds is high, the appreciably higher concentrations of I in soils than in rocks, from which the soils are derived, cannot be explained without taking into consideration external sources of I. The additional I in soils is likely to be air-borne oceanic from rain and snow or carried by oceanic winds in a gaseous state or adsorbed on floating particles of dust. It has been estimated that 22 to 50 mg of I per acre will fall annually in the rain on the Atlantic coast, while only 0.7 mg per acre will fall in the Great Lakes Region of North America (161). Thus, the annual precipitation and distance from the sea are important factors determining the I content of soils. This explains the lower I content of inland soils than coastal soils. For the same reason soils in areas recently subjected to glaciation and exposed to air-borne oceanic I replenishment for only a relatively short period, usually have low I contents.

The above factors are in close agreement with the geographical distribution of goitre areas found in a number of countries in Europe, North America and elsewhere (137). This is apparently because, due to the high solubility of most I compounds, the plant uptake closely follows the soil I content even though there are differences between the plant species.

The I content of plants usually varies within the range 0.1 to 1 ppm in dry matter, but higher values, up to 4-5 ppm, have often been reported and some of the plants growing in seawater may contain several hundred ppm. The critical deficiency limit reported in literature seems to lie around 0.05-0.07 ppm in dry matter. In mammals most of the body I (70-80%) is concentrated in the thyroid gland although the mass of the thyroid is usually only about 0.2% of the whole body (373).

Visible evidence of I deficiency occurs most frequently in newborn farm animals in goitrous areas. Besides the enlargement of the thyroid gland, the symptoms often include stillborn or nonviable and hairless calves. Also foals are frequently born dead or, if alive, are weak and unable to stand, have a high pulse rate and breathing difficulties. In sheep, an enlarged thyroid gland is the most characteristic symptom. Lambs are frequently dead at birth or die soon afterwards. In swine, hairlessness of newborn pigs is a usual symptom of I deficiency. The amounts of I required by farm animals are small and goitre and related I deficiency symptoms are easily prevented by supplying I in the form of iodized salt in the diet.

The I content of common fertilizers varies usually from traces to about 20 ppm but contents up to a few hundred ppm may be found in phosphate rocks and Chilean nitrates and several thousands of ppm in organic manures containing seaweeds (352).

## 6. Iron (Fe)

As far as the occurrence of Fe in the earth's crust and soils is concerned, it can be considered as a major element since it ranks third in abundance (about 5 percent) among the mineral elements in the earth's crust after silicon and aluminium, and soils rarely contain less than one percent Fe. In plant nutrition Fe acts as a trace element and its content in plants is often exceeded by those of other trace elements such as B, Mn, Se or Zn. In soils the trace element characteristics of Fe are due to its low solubility and its low availability to plants.

The essentiality of Fe was definitely established long ago for both plants and animals. It has a long history as a therapeutic agent in human medicine from ancient Greek and Roman times. Anaemia was treated with dilute Fe salt solutions even in Roman times, although its relation to blood formation did not become known until the 17th century, following the findings of two English physicians, Sydenham and Willis (326, 373). The importance of Fe as a plant nutrient became evident after Gris (143, 144) had shown the beneficial effect of the application of Fe salts to chlorotic plants. Fe deficiency, in fact, is the first nutrient deficiency in plants ever to be reported. About two decades later it was established by German scientists that Fe is a component of chlorophyll (221).

The total Fe contents of temperate soils usually vary from about 1 to 5 percent. An average estimate of 3.8 percent was given by Winogradow (406). Values lower than one percent are usually found in acid coarse textured soils, in peat soils and in the leached A horizon of podsolized soils. In most soils, Fe is bound mainly in the clay and silt fractions (266). Since Fe is also likely to be concentrated due to soil development processes, values up to 10 percent are not so rare and Fe contents up to 50 percent or more have been reported for Latosols and Laterites (e.g. 216, 332) which, therefore, resemble low-grade iron ores. High stability of soil aggregates and high soil porosity are often associated with high iron oxide contents. Some Fe may be lost from soils through removal by crops, leaching and by erosion but because of the high total contents and since it is required only in minute amounts, losses are likely to be insignificant compared to those of other trace elements. The total amount of Fe in soils is generally a very poor indicator of its availability to plants and deficiencies primarily due to low total content are rare. The availability of Fe is of prime concern. However, Fe deficiencies, where low total Fe is an apparent reason, have been reported especially in plants grown on acid, raised swamp (Hochmoore) soils. These peat soils which, in general, are low in all nutrients (see p.9) also contain very small amounts of total Fe; this is because of their considerable thickness which prevents the surface horizons from having contact with the Fe (and other nutrients) containing ground waters. In addition, a considerable portion of the low total Fe may be bound as highly insoluble Fe humates, bringing the available Fe to a minimum and resulting in its deficiency (69, 114, 318, 327).

Values of readily soluble Fe in soils varying from 1-5 ppm up to 1000 ppm or more have been reported (1, 24, 214, 329, etc.). The amounts obtained with different extraction techniques, however, are hardly comparable; for example, Lakanen and Erviö (214) comparing eight extractants found more than 100-fold differences between the extraction powers of the methods tested. In general, 1 N ammonium acetate (pH 7), acid ammonium acetate (pH 4.65), and acetic acid (pH 2.5) showed the lowest extraction power and extractants containing EDTA the highest. The results obtained with EDTA solutions were also better correlated with the Fe taken up by plants, even though these correlations were less significant than those for other trace elements. It should be mentioned that, for example in the United States, no generally acceptable chemical method for determining plant available Fe has been officially approved (39). For some methods, however, clear guidelines for interpretation have been established. An example of these is the DTPA extraction method of Lindsay and Norvell (227) according to which the Colorado State University Soil Testing Service is using the following interpretation on Colorado soils where the total Fe content varies from 0.26 to 6.75% and the DTPA extractable Fe from 1.5 to 160 ppm (126): 0.0-2.0 ppm = low, 2.0-4.5 ppm = marginal and above 4.5 ppm = adequate.

Fe deficiency problems are most often associated with soils derived from calcareous materials. In Europe, as summarized by Ryan *et al.* (315), Fe deficiencies were recorded on the following soils: calcareous soils on chalk and marl formations in England and Wales, Xerorendzinas and calcareous "Raw Soils" in Cyprus, Rendzinas and Brown Calcareous soils in France, Rendzinas and Brown Forest soils in Greece, over-irrigated calcareous soils in Israel, clay soils in Netherlands, swamp soils in Norway, sandy podzolic soils and peats in Poland, Brown and Red Calcareous and calcareous alluvial soils in Portugal, Sierozems, Reddish Brown and Alluvial soils in Spain and Rendzinas, Brown Forest and Gray-Brown Podzolic soils in Sweden. In the same report Fe toxicity problems were recorded only in Spain on acid soils derived from granite.

Iron plays an important role in soil chemistry being involved in numerous reactions affecting the chemical and physical properties of soils. Due to its interaction with other elements, it may considerably affect the availability of micro- as well as macro-nutrients. The availability of Fe to plants is greatly affected by various soil properties and also by interaction with other elements. Some of these are briefly discussed here.

The amount of plant available Fe in soils depends largely on soil pH and redox potential. In acid soils Fe is usually in ferrous forms which are available to plants, but in neutral or alkaline soils it is oxidized to ferric iron which may be so insoluble that plants have difficulty in absorbing enough, e.g. at pH 7, the solubility of  $Fe^3$  is only  $10^{-17}$  moles per litre while that of  $Fe^2$  is  $10^{-4}$  (141). Increasing oxidation potential leads to the oxidation of Fe from ferrous to ferric forms and, therefore, decreases its availability. The oxidation potential increases with increasing pH and with increasing aeration, so that the reaction  $Fe^2 \leftrightarrow Fe^3$  due to both of these factors is likely to proceed toward  $Fe^3$  and to decreasing Fe availability. Improvements in soil structure may have a similar influence (99, 264, 403). Increasing acidity as well as depletion in soil structure are likely to cause a reaction toward the reduction of iron. Therefore, the portion of ferrous Fe of the total Fe usually increases toward the lower soil horizons due to the decreasing aeration. In poorly drained soils the reduction of ferric to ferrous iron may be effected by decomposing organic matter, and some wet soils may contain so much ferrous iron at low pH values that they are toxic to plant roots (29).

Although the deficiency of Fe may occur on both acid and alkaline soils, it is perhaps most common on calcareous soils as a lime induced Fe chlorosis. In addition to high pH decreasing the Fe availability, high concentrations of calcium in soil solutions may not only decrease the uptake of Fe on these soils, but there is also evidence of inactivation of Fe within the plant due to abundance of Ca or Ca + P (79, 80, 242, 252, 278, 357, 361). Fe deficiency has been induced through both high Ca and P applications, but also through K deficiency. In all cases the deficiency could be corrected with potassium application (58).

Low oxygen content of soils has been found in some cases to be related to Fe deficiency. The reason for this might be the increased carbon dioxide content of the soil (21, 131, 393) which, with soil water, may form bicarbonate ions in a calcareous medium. These ions may indirectly decrease the availability of Fe by increasing the solubility of calcium phosphates and thus the concentrations of calcium and phosphate ions, leading to decreased availability of Fe in the medium or inactivation within the plant (77, 251, 252, 279). The appearance of Fe deficiency symptoms in soils of high moisture content, especially if in combination with low temperatures, has been attributed to an increasing  $CO_2$  content in soil water with decreasing temperature (104).

Several authors have reported anomalies in Fe uptake caused by high contents in soils of heavy metals such as Mn and Cu. There is a clearcut antagonism between Fe and Mn, which can influence the mineral composition of the plant to a very considerable extent. Evidence has been presented that the Fe/Mn ratio affects the growth and the condition of the plant more than the absolute concentrations of these nutrients. For example, in the extensive studies of Somers and Shive (335) with soybeans, the growth and condition of plants were normal when this ratio was approximately within the range of 1.5 to 2.6; but when the ratio

of soluble Fe to soluble Mn in the plant leaves was outside this range pathological symptoms tended to develop. Above the ratio of 2.6 symptoms of Mn deficiency and/or excess of Fe were likely to develop. If the ratio fell below 1.5 symptoms of Fe deficiency and/or Mn excess were obvious. The development of these symptoms was highly dependent on the ratio in the substrate but almost independent of the actual Fe and Mn amounts. The above conclusions have received only partial support from many subsequent investigators; e.g. Weinstein and Robbins (398) did not find that high Fe concentrations induced symptoms of Mn deficiency but that high Mn concentrations did induce chlorosis indicative of Fe deficiency. Twyman (370) did not consider the Fe/Mn ratio very significant in determining Mn deficiency or toxicity but thought that the ratio might be important in the metabolism of healthy plants as a factor in determining growth and yield. Mn induced Fe deficiencies have been reported from many countries and on several plants due to both high Mn content of soils and to applied Mn. Cu-induced Fe deficiency has been reported, on vine cultures, due to continuous use of Cu containing plant protection materials accumulating in the humus-rich surface horizons (102, 130) and severe Fe deficiencies in citrus on acid soils due to Cu and Mn containing plant protection materials together with high P fertilization. These soils may contain about 785 kg/ha (700 lb/acre) of Cu and Mn while the contents in similar virgin soils are only 5.6 to 11.2 kg Cu and 34.6 to 44.8 kg Mn per hectare (5 to 10 lb Cu and 30 to 40 lb Mn per acre) (169, 222, 307). It is possible that the effect of Mn, and perhaps Cu, on Fe is that Fe is oxidized from the ferrous to the more insoluble ferric form (359). Other heavy metal cations have also been found to influence the uptake of Fe.

Compared to the abundant occurrence of Fe in soils, its content in plants is low, although, in most cases it is higher than that of other trace elements. The Fe content of normal plant tissue ranges from around 25 to more than 500 ppm, dry weight, depending on plant part and species. Some vegetable species such as spinach, lettuce, kohlrabi, broccoli and green cabbage are rich in Fe, containing 100 to 800 ppm in dry matter. Leguminous plants usually contain more Fe than grasses. Fe contents in timothy varying from 25 to 262 ppm (aver. 81 ppm) were reported by Lakanen (213), but values less than 50 ppm were rare. Both higher and lower contents have been reported elsewhere (122, 313). Fe contents may vary from 20 to 740 ppm in the leaves of fruit trees and from 50 to 420 in those of deciduous and coniferous ones (147, 201). Due to the partial mobility of Fe in plants there are considerable differences in its content in the different parts of the plant. In corn Fe may be precipitated in or near the stalk nodes of the plant and may be prevented from translocating to the leaves where it is needed, thus causing the plant to suffer from deficiency (317).

A distinction may be made between the total Fe in plants and soluble, available or active Fe. The total Fe in plants used for food is less important for nutritional purposes than the percentage of ionizable or nutritionally available Fe. The available Fe in plant tissue may range from 20 to 100% of the total Fe (317). Sometimes the Fe that is proportional to chlorophyll in the plant is called active, and enough active Fe for normal chlorophyll development is present only after a certain minimal amount of residual Fe exists in the leaf (169).

In the nutrition of chlorophyll-containing plants, Fe has a multiple role. It is a tightly bound component in a wide group of haemo-proteins, which include the cytochrome system, catalase, peroxidase and haemoglobin. Their distribution in plant tissues and cell fractions is quite varied. Deficiency of Fe suppresses cell division and leaf primordia production. Iron may be involved in some reaction of photosynthesis but its role in chlorophyll synthesis is still unsolved although correlation has been found to exist between the chlorophyll content of leaves and their Fe content (163, 182). Fe can be considered to be at least moderately mobile in plants (70, 76).

The most characteristic effect of Fe deficiency on plants is the failure to produce chlorophyll in young leaves and therefore the main visual symptom of the deficiency is a chlorotic mottling of the leaf. The first symptoms occur in the younger leaves within the interveinal areas. When the deficiency persists, the affected areas become lighter in colour and spread to include the leaf veins. In severe cases all the green colour of the leaf may be lost and the entire leaf may turn yellow or almost white.



Detailed descriptions of the deficiency symptoms for a number of crops including various legumes, vegetables, fruit trees, nut trees, root crops, grain crops, etc. can be obtained from several sources (e.g. 68, 341).

Fe plays a vital role in the life processes of animals as it is a constituent of a haeme group which makes up about 4 percent of the haemoglobin molecule. In the absence of an adequate amount of Fe the formation of red blood cells is reduced resulting in anaemia. However, among farm animals, pigs are the only species in which Fe deficiency presents a practical problem and even in this species the deficiency is confined to the early part of the suckling period and to animals reared under restricted conditions. In grazing stock uncomplicated Fe deficiency has not been clearly demonstrated under naturally occurring conditions (373).

The main problem in correcting Fe deficiencies in plants is to make the soil Fe more available or to add Fe to soil or to plants in available forms. Increasing the availability of the native soil Fe by proper soil management including moisture control for accumulating ferrous Fe in wet or waterlogged soils, or acidifying alkaline soils by ammonium sulphate or sulphur applications, is apparently of less value than correcting Fe deficiencies by applications of iron salts. Ferrous sulphate has been the most commonly used salt for many years. It is water soluble and may be used as a foliar spray or it may be applied directly to the soil. It is not recommended as a soil treatment for chlorosis on alkaline, heavily limed or calcareous soils because the soluble ferrous sulphate quickly ionizes in the soil, becomes bound to other ions and loses its effectiveness. Soil applications may also be economically impractical because of the large amounts required. For example, to correct Fe deficiency in sorghum, one to three foliage sprays with ferrous sulphate solution have been shown to be more effective and more economical than soil treatments. (206, 408). Solutions containing 1-4% ferrous sulphate at rates of about 200 to 1 000 litres per hectare have been used. Since hard or alkaline water may cause iron precipitation, rain water is preferable or, if not available, it may be necessary to add 0.2-0.5 ml sulphuric acid per litre in order to keep the iron in solution. It should be sprayed immediately to avoid conversion to the insoluble ferric hydroxide.

In some cases both the application of iron sulphate as a fertilizer material or as foliar sprays has given unsatisfactory results, for example, in correcting Fe deficiency in citrus. Pressure injections of ferrous sulphate into trees may be more effective but not practical because recovery is only temporary and is followed by injury to treated trees (305, 339). Perhaps the most effective way to remedy Fe chlorosis is by using iron chelates either as soil dressings or as foliar sprays. Chelates have been used to correct trace element deficiencies only during the last 20 years, i.e. since the introduction of ferric potassium ethylenediamine tetraacetate (EDTA) by Jacobson (181) in 1951 for maintaining iron supply in nutrient solutions and, after the first practical application of the synthetic Fe-EDTA chelate by Stewart and Leonard (344, 345) in the same year, to correct Cu-induced Fe deficiency in citrus on acid sandy soils in Florida. Since then, tremendous advances have been made in the use of chelating agents, not only with Fe, but also with other trace elements that are deficient. The term chelate is derived from the Greek word "Chela" (a claw) because these organic compounds can combine with metal ions in such a way that the metal is clutched between the pincers of the organic molecule, in two or more positions, thus resembling a claw. Chelates are highly stable and although some of the Fe chelates, for example, are quite soluble, the iron does not ionize or precipitate in the soil, but is held in a soluble complex form which is available for root absorption. In chelates the iron is protected from fixation and the chelating molecule including the iron may enter the plant and be transported to the leaves. The chelated metals are only slowly exchangeable with other cations but highly water soluble chelates may be subject to some loss by leaching and may also be decomposed by microbial activity.

Chelates are usually not toxic to plants, 1000 kg/ha having been tried without ill effects (183) and in mammals EDTA is effective for detoxicating poisonous metals such as lead, which are then excreted as non-toxic chelates (89).

EDTA is probably the best known iron chelate and it has been found to be very stable and effective in acid conditions but in alkaline, clayey soils, often having an excess of lime, EDTA is not sufficiently stable. Under alkaline conditions Fe - APCA (amino polycarboxylic acid), DTPA (diethylenetriaminepenta acetic acid) and EDDHA (ethylenediamine di-o-hydroxyphenylacetic acid) are more suitable for use. The relative effectiveness of four iron chelates in making Fe available at pH 7 is reported as follows: APCA>DTPA>HEEDTA>EDTA (317, 376,).

The amounts of chelates to be used depend on the crop as well as on the soil and the severity of the deficiency. In one case Fe deficiency in citrus was corrected in six weeks after the application of 6 grammes Fe as Fe-EDTA per tree. The usual recommendation, depending on the size of trees is 10 to 20 grammes Fe per tree but in some calcareous soils applications of 100 or sometimes 300-600 grammes have been necessary, which may not be economical (223, 344, 345). For field crops typical applications vary from about  $\frac{1}{2}$  to 1 kg Fe per hectare. Residual effects have been reported of Fe chelates from one to three years after the application, depending on the amount applied, severity of the deficiency, soil properties, etc. (215, 224).

For foliar spray applications, solutions containing 0.1 to 0.2 percent of Fe-chelates have been used. Often two to four treatments with some 8 to 20 day intervals are required. These can also be combined with plant protection treatments providing the resulting solution is not alkaline in reaction. In general, results obtained with chelate sprays have not been as satisfactory as by soil treatment, perhaps due to the decomposition of chelates by sunlight. Although chelates are favoured for supplying soil Fe to many crops, on some, e.g. turf, they have not been better or longer lasting than foliar sprays of the cheaper iron sulphate (238, 317).

## 7. Manganese (Mn)

Bertrand (40) was apparently the first to claim that Mn was associated with an oxidizing enzyme, laccase, in the plant, and concluded later, in 1905, that Mn was an essential element for normal plant growth, which view was later substantiated by numerous other investigators. Toxicity effects of Mn on cereals were already reported in 1902 by Aso (18) and later by others on numerous other crops. Bertrand and Javillier (44) showed in 1911 that Mn is required for sporulation in Aspergillus niger, and since then its essentiality for many other microorganisms has been established. Even though the Mn requirements of man have not been definitely established, small amounts of it have been found essential for the nutrition of domestic animals, especially poultry and pigs.

Mn in soils originates primarily from the decomposition of ferromagnesian rocks. The average content in the lithosphere is 1000 ppm (Table 2) and the total quantities present in soils vary from less than 100 to several thousand ppm (Fig. 1). The total Mn content of the soil, however, cannot be considered as an indication of the availability of this element to plants because of a number of factors affecting the uptake. For example, in the study of Hoyt and Nyborg (172) total Mn gave a poorer estimate of plant available Mn than any of the eight other methods used for determining extractable Mn.

Among the factors affecting Mn availability soil pH and the oxidation reduction conditions may be the most important (see p. 10 and 13) since the forms in which Mn occurs in soils are strongly related to these factors. Russell (314) states that plants can certainly use divalent and almost certainly cannot use tetravalent Mn, while their ability to take up any appreciable proportion of Mn in trivalent form is quite unknown. Thus, in practice the problem is to maintain a reasonable, but not excessive concentration of divalent Mn in the soil. Some results, however, indicate that higher oxides of Mn and unavailable Mn are not necessarily synonymous, as is commonly assumed (283, 284). A dynamic equilibrium is believed to exist between the Mn forms so that the tetravalent form is most likely to occur in alkaline soils, the trivalent form is presumably favoured by soil pH values near neutrality and the divalent form is found in acid soils (62, 218, 363).

There are indications that Mn oxidation in soils near neutrality is largely microbiological and that a number of soil bacteria and fungi which are effective in oxidizing Mn, have been identified (74, 295), while in alkaline soils, above pH 8, nonbiological oxidation is more marked. Although the reduction of oxidized Mn to a more soluble form, brought about by the addition of certain reducing compounds, soil sterilization, or flooding, is usually accompanied by decreasing pH, the soil pH may be only an indirect factor affecting the Mn availability.

Several field experiments have shown that the relationship between the availability of Mn and soil pH, and pH values around 6 - 6.5 appear to be critical, the lower values favouring reduction and higher values oxidation (62). In Norway no response to Mn fertilization was observed in soils with pH values below 6.3 (324) and significant negative correlations have been found to exist between soil pH and exchangeable Mn in Punjabi and West Bengali soils (22, 300), and between pH and ammonium acetate-extractable Mn in Indiana soils (362). Similar results have been presented from a number of locations and therefore it is obvious that Mn deficiency is usually associated with alkaline or neutral soils and its toxicity with acid soils. Liming of soils decreases the availability of Mn (see Table 5) and in several cases it has been reported to cause deficiency (315).

Among the other factors affecting the availability of Mn to plants is the organic matter of soils. In many countries, including Switzerland, Sweden, Norway, Greece, Ireland and England, the deficiency of Mn has been found to be associated with peats, particularly those overlying calcareous materials (315). The presence of considerable organic matter in soils frequently results in the appearance of deficiency symptoms at a lower pH than in soils with a lower humus content. This has led to the assumption that certain types of organic matter will form insoluble complexes with divalent Mn (363) or result from biochemical action (57). On the other hand, higher oxides of Mn do not commonly occur in organic soils (157) and addition of organic matter to soils with a low content of it has been found to increase the availability of Mn (90). With increasing soil organic matter reducible Mn is reported to increase (22, 88), as well as the exchangeable Mn (93) and the relative solubility of Mn (Fig. 5). It seems, therefore, that Mn deficiency found in organic soils is associated with a low total Mn supply in these soils rather than with low availability due to organic bindings (see also p. 7-8 and Fig. 3).

As with many other trace elements, both total and soluble contents of soil Mn seem to decrease from finer to coarser textured mineral soils (see Fig. 2 and Table 6); sands in addition to peat and other soils derived from calcareous materials are often associated with Mn deficiency in many European countries (315).

Mn interacts with other elements in plants and soils and its interrelation with Fe seems to be of particular importance since both elements are greatly affected by soil oxidation-reduction conditions and microbiological activity. Increased Fe supply can decrease uptake of Mn and vice versa, but Mn deficiency is not necessarily synonymous with excess of Fe (139, 382). Also Co may decrease the availability of Mn, particularly where the soils are repeatedly fertilized with Co. This may have an important bearing on the availability of Mn under certain conditions, such as in the sandy soils of South Australia, where the total Mn in the soils is commonly as low as 5 ppm and the soils are also deficient in Co (245).

Mn has several functions in plants. It is essential in photosynthesis and acts as a catalytic agent in nitrate reduction where it may be replaced by Fe. It is a constituent of some respiratory enzymes and of some enzymes responsible for protein synthesis. As an activator in enzyme systems of the carboxylic acid cycle and carbohydrate metabolism it may be replaced by Mg. Many of the functions of Mn are obscure and difficult to interpret. Reviews of Mn functions in plants have been presented, e.g. by Hewitt (164) and Nason and McElroy (267).

Symptoms of Mn deficiency have been described in many agricultural or horticultural crops such as oats, rye, wheat, rice, maize, peas, soya beans, potatoes, tomatoes, cotton,

tobacco, sugarbeet, tea, sugar-cane, pineapples, pecan, peaches, spinach and citrus, and in a number of forest trees. Among grain crops, oats are the most sensitive to Mn deficiency, called "grey speck", and are therefore likely indicators of the deficiency in any area. In some crops the malformation caused by Mn deficiency is sometimes referred to as "marsh spot" (peas), "streak disease" or "pahala blight" (sugar-cane), "speckled yellows" (sugarbeet), "yellow disease" (spinach), and "mouse ear" (pecan).

Mn deficiency symptoms often include pale green to yellow discoloration or chlorotic spots of dead tissue between the green veins of young leaves. Sometimes the chlorotic patterns resemble those of iron or magnesium deficiency. For detailed descriptions of symptoms in a number of crops, see "Hunger Signs in Crops" (341) or "Handbuck der Pflanzenkrankheiten" (205).

Values from 25 to 50 ppm of easily reducible Mn have been mentioned as representing the limit below which symptoms of Mn deficiency are likely to develop, while soils containing 100 ppm or more of easily reducible Mn are able to support a normal crop (87, 325). The concentration of Mn in the tissue of plants showing deficiency symptoms varies with the species. In sugar-cane the range showing deficiency symptoms is usually from 1 to 10 ppm in blades while the normal concentration is usually from 20 to 400 ppm. The critical level varies with the Fe/Mn ratio and can be below 10 ppm if the ratio remains above 1. In soybeans deficiency symptoms are apparent if the above ground parts of the plant contain less than 15 ppm Mn and in sugarbeet and citrus the symptoms may appear with as high as 20 ppm Mn in blades (194, 272, 306, 322).

Mn toxicity symptoms are likely to develop in acid soils where the availability of this element is at a maximum, as described on previous pages. Cases of toxicity have been reported, e.g. on barley, lucerne, tobacco, soybean, swede and cotton. The symptoms, which are usually most prominent on young plants, differ among species, but a brown spotting of leaves is frequently observed. Sometimes excess Mn produces symptoms of iron deficiency (52). There is considerable variation among the plant species and varieties in their tolerance to excess Mn. Relatively tolerant types include sugarbeet, oats, rye, celery and broad beans. Barley, potatoes and red clover are intermediate in tolerance and French beans, swede and many other brassicas, excluding rape, are highly susceptible to Mn toxicity. The difference in tolerance is partly related to the uptake of Mn, which is relatively low in beet and oats, and partly to actual differences in tolerance (164). For example, in some varieties of Lolium perenne tolerance to Mn seems to be associated with low root cation exchange capacities (384). Mn toxicity, in general, can be suspected if more than 1 000 ppm Mn is present in plant dry matter (28) but in field grown tobacco, for example, symptoms of Mn toxicity have been reported at leaf concentrations of 387 to 585 ppm in conditions where the pH of soil was lowered from 5.2 to 4.5 by a heavy ammonium nitrate application (402). In another case, abnormal or "black" tobacco contained 1152 ppm Mn, whereas the content in normal leaf was 360 ppm (217); and in solution cultures typical Mn toxicity symptoms occurred when the tissue concentration reached about 3000 ppm (166). Poor lucerne growth in the Goulburn district of Australia was shown to be associated with high Mn levels (300-900 ppm) exceeding the normal level for lucerne (about 175 ppm) by 2-5 times. It was concluded that the Mn toxicity was induced by large, previous superphosphate applications which lowered the soil pH (125). Mn toxicity in citrus, similarly induced by heavy use of ammonium sulphate, was also reported from Australia (14). Extremely high concentrations of Mn have been reported, 3400 ppm in the seed of lupinus albus (134) and 11,300 ppm in leaves of field-grown potato plants (150). Autoclaving the soil has been reported as causing Mn toxicity symptoms in groundnuts due to two mechanisms: the direct release of Mn complexed with the organic fraction of the soil, and the killing of micro-organisms that normally transform available Mn into higher oxides (64).

The Mn requirements of farm animals vary with species, age, reproduction functions, etc. and depend also on the chemical form of Mn in diet as well as on the nature of the rest of the diet. In general the requirements of birds are very much higher than those of mammals. For example, some experiments suggest that the requirement of pigs is less than

12 ppm for growth but over 12 ppm for normal reproduction (199); for heifers approximately 10 ppm is required for normal growth (36) but considerably less for young calves (155). Underwood (373) when reviewing widely the functions of Mn in animal nutrition gave an approximate value of 40 ppm Mn for the minimum requirement of poultry. He also referred to studies showing that hens can tolerate 1000 ppm Mn without ill-effects, while 500 ppm in the diet of growing pigs retarded growth and depressed appetite.

Since in most cases, abnormal Mn conditions are associated with extremes in soil pH, the correction of these disorders often includes liming or acidification of soil. Liming reduces the solubility of soil Mn and soils should be limed to a pH of at least 5.5 to correct Mn toxicity. Phosphate may be beneficial on soils where soluble Mn has reached levels that are toxic because less soluble manganese phosphates are formed (158, 392). Messing (250) observed that application of superphosphate to soil with pH values less than 5 generally raised the soil pH and decreased the water-soluble and exchangeable Mn, and at pH values above 5.5 superphosphate generally lowered the soil pH and increased the concentration of water-soluble and exchangeable Mn.

In correcting Mn deficiency in the field, the most commonly adopted practice is perhaps the addition of soluble manganese salts, such as manganese sulphate (cont. 26% Mn), to soil at the rate of 30 to 100 kg/ha. Other Mn fertilizers are manganous oxide containing 48 or 65% Mn and manganese ammonium phosphate. Mn added to calcareous soil may be converted to unavailable forms within a few days (e.g. 163, 387) and, therefore, manganese sulphate is sometimes mixed with 2-3 times its weight of sulphate of ammonia or with an equal weight of sulphur to speed up its effect and to obtain more lasting effects through lowering the soil pH. Finely ground elemental sulphur and ammonium sulphate have also been used alone for this purpose. Mn is also available in chelated forms.

Spraying a weak manganese sulphate solution (e.g. 5-10 kg Mn SO<sub>4</sub> in 800-1000 litres of water per hectare) on the foliage of the crop has been successful especially in cases where application to soil would be ineffective or would act too slowly. With foliar spraying the symptoms of Mn deficiency usually begin to disappear within a few days.

Producing anaerobic conditions through flooding and thereby reducing oxidized Mn to a more available form has only a limited practical application in the correction of Mn deficiency in plants.

Commonly used nitrogen fertilizers reviewed by Swaine (352) usually contained very little Mn among impurities. The same is true also for most potash fertilizers, but in phosphate fertilizers the Mn content is generally higher, often a few hundred ppm but, in basic slag it may be up to 10,000-50,000 ppm. The Mn content of farmyard manure usually ranges between 30 and 300 ppm in dry matter. In the United States of America, in 1964, fertilizers enriched with Mn contained 0.63 percent Mn on the average (375).

## 8. Molybdenum (Mo)

The essentiality of Mo was established fairly recently. Bortels (60) showed its importance on the growth of *Azotobacter* in 1930 and was apparently the first to observe a response to Mo applied to field plots of leguminous crops. Later he showed (61) that Mo played a similar role in nitrogen fixation by blue-green algae, but that in these functions Mo could be partially replaced by vanadium. The occurrence of Mo in low concentrations in a wide range of plant and animal tissues was known for some time before its essentiality for higher plants was shown by Arnon and Stout (16) in 1939. Animal disorders due to Mo arise from excess and seem to be related to Cu and S metabolism but its essentiality for animal nutrition has not yet been fully established. In spite of some indications that very low Mo concentrations (0.03 ppm or less) in pasture are associated with the occurrence of renal xanthine calculi in sheep (17), this condition can hardly be attributed to lack of Mo alone since similar concentrations of it exist in other parts of the world without any evidence of this disorder (374).

Mo is present in the earth's crust and soils in extremely small quantities. Its average abundance in the earth's crust has been estimated to be 2.3 ppm (137), in igneous rocks it is about 1.5 ppm, and in sedimentary rocks 0.2-3 ppm (63). The total Mo content of soils usually varies from 0.2 to 5 ppm, averaging about 2 ppm (351) but values of more than 200 ppm may occur, especially near molybdenite mines (229, 258). Mo in soil is largely unavailable, for up to 90 percent of the total Mo may be present in the mineral form and values usually less than 0.2 ppm have been reported for soluble Mo when using common chemical extracting solutions such as neutral or acid ammonium acetate, acetic acid, hydrochloric acid, sulphuric acid, ammonium oxalate or Tamm's acid oxalate etc. It has been suggested that soil pH should be taken into account when interpreting the analytical results for available Mo. Davies (96), using acid oxalate as the extractant, considered the response level to be 0.2 ppm Mo in soils at pH 5 but only 0.05 ppm in soils at pH 6.5 level. Several investigators have pointed out the complications involved in determining the minute quantities of Mo present in soils and plants.

The reactions of Mo in soils are not well understood. It is believed to occur in soils as the oxides  $\text{MoO}_3$ ,  $\text{Mo}_2\text{O}_5$  and  $\text{MoO}_2$ . The two reduced oxides are not available to plants but may slowly transform to  $\text{MoO}_3$ , which in turn is slowly converted to soluble molybdates, apparently the primary Mo sources for plants. This reaction is favoured by an alkaline medium and may explain the increasing availability of Mo with increasing soil pH. In acid soils the presence of Fe and Al oxides may lead to formation of unavailable Fe and Al molybdates (10, 192, 193, 363).

Attention has been called to the analogy between the reactions of Mo and P in acid soils (193), but as stated by Hodgson (168), there is no such analogy in alkaline soils where P is precipitated by Ca whereas the solubility of Mo continues to increase. Since oxidation of the lower oxides tends to increase the availability of Mo, it would seem logical that Mo would be more available in well drained than in poorly drained soils. Some results, however, suggest the opposite. Kubota *et al.* (210) reported that wet soil conditions increased the Mo in soil solution and Mo uptake by clover. Forages produced on poorly drained soils have been found to contain toxic amounts of Mo in certain areas (209) and on some soils with high water table, low levels of Cu coupled with high levels of Mo are believed to cause Mo poisoning of cattle (185).

Soil pH is apparently the principal regulator of the solubility of Mo. Unlike other trace elements (Mn, Co, B, Ni, Fe, Cu, Zn) Mo becomes increasingly available with increasing pH (see Table 5). It has been suggested that the poor growth of legumes on acid soils could be due to too low an availability of Mo to meet the need of such crops (29). The addition of calcium carbonate to an acid soil with pH 4.7 increased the Mo content of plants on it from 7.4 to 23.2 ppm in one case (26) and in another a tenfold increase in uptake was mentioned when raising the soil pH from 5 to 7, although it was suggested that above pH 8 liming restricts uptake and that at equal levels of water-soluble Mo less is taken up at high pH. In acid soils the addition of phosphate may increase Mo uptake while the opposite seems to be true in alkaline soils (Table 8).

When reviewing trace element problems in relation to soil units Ryan *et al.* (315) state that there is an apparent association between an excess of Mo and heavy textured soils that are generally hydromorphic and derived from calcareous materials, while Mo deficiency problems occur over so wide a range of Great Soil Groups that little correlation can be made. However, deficiency is most commonly associated with acidic soils.

Mo is required by plants in only small amounts and an excess may cause toxicity to grazing animals. The Mo contents of plants vary considerably according to the species, plant parts, climatic conditions, stage of maturity and soils etc., ranging from less than 0.1 to over 200 ppm in dry matter, but are for the most part within the range 1 to 10 ppm. Apparently owing to the interaction between the above mentioned and other factors it is difficult to establish any clearcut normal value for Mo contents of different plants. For example, Beck (31) found that the average Mo content of 110 pasture grasses from different areas in

**Table 8.** The effect of phosphate application on the contents of three trace elements in tomato leaves grown in pots of three soils (85).

Phosphate added per pot	Olivenhain loamy sand pH 4.6				Encondido silt loam pH 5.7				Moreno sandy loam pH 7.6					
	Shoot weight gramme	ppm in D.M.		Cu/Mo ratio	Shoot weight gramme	ppm in D.M.		Cu/Mo ratio	Shoot weight gramme	ppm in D.M.		Cu/Mo ratio		
		Cu	Mo			Cu	Mo			Cu	Mo		Cu	Mo
2	47	4.5	0.57	147	7.9	12.3	0.98	30	12.5	27	8.0	3.08	30	2.6
10	52	3.5	0.50	34	7.0	8.9	1.68	21	5.3	37	9.0	2.57	21	3.5
26	55	3.1	0.85	28	3.6	4.3	1.94	21	2.2	43	7.1	2.02	18	3.5
50	61	3.3	0.94	26	3.5	4.8	2.00	19	2.4	54	7.5	1.67	15	4.5

D.M. = dry matter

Heavy phosphate applications do not only increase the Mo uptake in acid soils but also decrease that of Cu, thus disturbing the Cu/Mo ratio. This may induce Cu deficiency in grazing animals especially in conditions where the animals' diet contains high levels of Mo.

Western Australia (0.87 ppm on dry basis ranging from 0.1 to 3.8) was several times higher than that of subterranean clover from the same areas (average 0.16, range 0.03-0.62 ppm). Similar results have been recorded from other parts of the world, but on the other hand, Barshad (25) concluded that legumes have a greater capacity to accumulate Mo than plants of some other families, and Lewis (225) reported values from 4 to 18 ppm Mo in the dry matter of timothy, meadow fescue, cocksfoot, meadow grasses (*P. trivialis* and *pratensis*) and rye grasses (*Lolium perenne* and *L. italicum*) from Teart pastures (Mo toxic) in Somerset, England, while the corresponding figures for wild white and red clovers ranged from 57 to 109 ppm. The highest Mo contents of clover were usually found in the middle of the growing season (July-August), while for most grasses the seasonal variation was not as obvious. In legumes Mo seems to concentrate mainly in seed; for instance, in soybean the Mo content in seed, 3.2 ppm on dry basis, was five times as high as that in the leaf, 0.5 ppm (364). These contents were increased to about 12 and 4.6 ppm respectively, by an application of 2.5 kg/ha sodium molybdate. For wheat the figures were the opposite, grain contained less Mo than the leaf, about 0.5 and 0.9 ppm before and 1.4 and 4.4 ppm after Mo application, respectively.

It is apparent that no definite, general limits for the Mo content of plants indicating its deficiency or toxicity can be assessed. From the values given in literature it seems that a response of many plants to Mo can be expected if the content is less than 0.1-0.5 ppm, while for some plants (e.g. tobacco and sugar-cane) the requirements are so low that Mo deficiency rarely develops under field conditions (246, 322, 343). Mo deficiency in citrus, called "yellow-spot", was relatively widespread in Florida on acid soils but has become rare since liming was adopted as a general practice (194). Cereals appear to be rather insensitive to Mo deficiency and Kranz and Melsted (207), when reviewing nutrient deficiencies in maize, sorghum and small grains, noted no reports of Mo deficiency in these crops in the U.S.A., but mentioned cases in field grown maize, wheat and oats in New Zealand.

It is obvious that Mo plays a much more important role in the production of forage crops than other crops because of its essentiality to nitrogen fixing nodule bacteria and also due to its toxic effects on animals. Mo deficiency has been diagnosed on many legume species, e.g. lucerne, soybeans, clover and peas. Grasses in general are more adept at satisfying their Mo requirement from soils low in available Mo than are the legumes and other broad leaved plants (189), and, therefore, deficiency of Mo in grasses seldom occurs under field conditions (409).

The symptoms of Mo deficiency vary from species to species but chlorosis, either partial producing spotting or mottling, or general over the whole leaf is usual. Wilting of the margins of the leaves may follow and lower leaves die and drop prematurely. Several sources (e.g. 205, 341, 347, 391) give detailed descriptions of Mo deficiency in a number of plants. No injury to most plants is reported even where the Mo concentration exceeds 100 ppm.

Healthy plants usually have a content of 1 to 5 ppm, but if the content exceeds 20 ppm signs of toxicity in grazing animals become apparent. The latter figure, however, depends largely on the Cu content of plants and on animal species. Mo toxicity in cattle may occur even at 3 to 7 ppm Mo level, if the herbage is deficient in copper and contains only 3 to 5 ppm Cu, but where the Cu content of herbage is about 10 ppm, then about 20 ppm Mo must be present before toxic effects are produced. Inorganic sulphate also has a protective action against high intake of Mo (374). Among farm animals, cattle are the least tolerant, sheep and poultry intermediate and horses and pigs the most tolerant. Underwood (373, 374) has described at length the symptoms of Mo toxicity in animals as well as its role in animal nutrition.

Treatments of Mo deficient soils usually involve liming and, amongst others, Parker and Harris (285) found yield responses from applications of two tons of limestone equivalent to applications of 0.2 lb Mo per acre (about 5 tons and 0.2 kg/ha, respectively) on an



acid soil with pH 5.6. The application of Mo further increased the protein content of the seed on a limed soil. In many Mo deficient soils liming will release adequate quantities of this nutrient. Where it is necessary to supply Mo salts, e.g. to forage crops, rates of application should be kept quite low, ounces rather than pounds, and treatments should be repeated at infrequent intervals, since the absorption of Mo increases with an increase in the level of its supply and may result in Mo toxicity or interfere with Cu metabolism in grazing animals (8, 97, 348). In peat soils 3 kg  $\text{Na}_2\text{MoO}_4$  per hectare has been reported to increase the Mo content in white clover up to the limit of toxicity to animals (165). One to three ounces per acre (70 to 210 grammes/ha) of Mo salts are usually recommended to correct the deficiency. This can be applied to soil directly mixed with fertilizers, by coating seeds, e.g. with sodium molybdate powder, or by spraying plants with a solution. In some experiments carried out for controlling Mo deficiency in alfalfa, semi-wet treatment of the seed with 100 mg Mo/ha proved slightly more effective than foliar application with the same dose (173).

Correction of excessive concentrations of Mo in plants growing on Mo-toxic soils may be more difficult than the correction of its deficiency. The use of sulphate or manganese fertilizers may help to reduce Mo uptake (188). Copper applications to alkaline soils with a high content of available Mo may not decrease the Mo concentration in forage but, as mentioned before, the protective effect of Cu as well as that of inorganic sulphate against high intakes of Mo is well established for all animal species. These relations have been excellently reviewed by Underwood (374). If the areas producing Mo toxic crops are identified, blending these crops with those from low-Mo areas and supplying the animals with adequate Cu may be sufficient to prevent Mo toxicity in animals.

The concentration of Mo in most nitrogen and potassium fertilizers reviewed by Swaine (352) was less than 0.2 ppm, but generally somewhat higher in phosphatic fertilizers, varying from traces to a few ppm with occasional values of 20 ppm or more. It has been stated (11) that most evidence indicates that Mo is rarely present in significant amounts in the fertilizers generally used, and that soluble Mo in N and P fertilizers and liming materials is inadequate for legumes (119). The Mo content of farm manures varies widely depending on the feed, bedding, animal species and stage of decomposition. A range from about 0.5 to 5 grammes (0.001 to 0.011 lb) per ton has been reported (35).

## 9. Selenium (Se)

Se is not an essential element for plant growth but it has an important role in agricultural production in localized areas throughout the world. This is not merely due to its recently discovered essentiality for animals but mainly to its toxicity. Although it has been known for well over a hundred years that Se is toxic for animals, such naturally occurring diseases as "alkali disease" and "blind staggers" were first identified as Se poisoning during the 1930 decade.

The average Se content of the earth's crust is about 0.1 ppm (Table 1) but in soils it is usually higher, varying normally within the range 0.1 - 2 ppm (351, 396). Some soils derived from Cretaceous shales and other sedimentary rocks contain abnormally high amounts of Se varying from 1 to 10 ppm. Most of the Se-toxic areas are located in the semi-arid regions of Israel, Australia and America for example but extremely toxic values, up to 1200 ppm, have also been reported from an area of relatively high rainfall in Ireland (124). It is apparent that in semi-arid regions the limited rainfall prevents removal of Se in drainage waters causing accumulation in situ, while in high rainfall areas the high Se accumulation in low-lying valley soils of impeded drainage is due to leaching of soluble selenium from higher lying soils. Many seleniferous soils in U.S.A. are derived from glacial, lacustrine and recent alluvial materials, and in Ireland from glacial drift on limestone with associated shale beds (351).

As with the total Se content of soils, the Se content of plants also depends largely on the form of Se in the soil. Insoluble basic iron selenides are not absorbed by ordinary crop plants while soluble selenates and selenites, as well as organic forms of Se, are highly available to all plants. Since the proportion of these forms varies greatly in different soils, the total content of Se is not always a reliable index of toxicity (373).

Considerable differences occur in the absorption of Se from soil by plants, depending on the plant species. Miller and Byers (253) divided plants into three categories on the basis of their capacity to absorb Se: (1) Plants showing a limited tolerance and absorbing only small amounts (up to 5 ppm); (2) those absorbing moderate amounts (up to about 30 ppm) without harm to themselves; and (3) those absorbing Se up to several thousand ppm and accumulating it in their tissues. Most grasses and garden vegetables were included in the first, all cereals in the second, and certain species of Astragalus, Stanleya, Oenopsis and Xylorrhiza in the third category. Plants in the last group are often called Se accumulators and used as indicators of Se toxic soils since they seldom grow outside seleniferous areas. These plants seem to need Se and since they can also use forms of Se not available for regular plants, they can convert Se to organic forms which will be more available to following plant generations.

Treatments of seleniferous soils have not been very successful. They usually contain so much native sulphate that gypsum treatment, based on ion competition, is ineffective. If too much Se is added to a soil, the condition may be corrected by gypsum or barium chloride. Barium selenate is supposed to be highly insoluble and unavailable to plants (363).

The first symptoms of Se poisoning in cattle and horses include the loss of long hair accompanied or followed by soreness of the feet. Further signs are dullness and lack of vitality, emaciation and roughness of coat, stiffness, cirrhosis of the liver, anaemia and, in the final stages of acute Se poisoning, "blind staggers" when animals suffer from blindness, abdominal pain, salivation, grating of the teeth and partial paralysis. Respiratory disturbance may lead to death, but it may also result from starvation and thirst due to lack of appetite, lameness, pain and unwillingness to move (373). Several sources (287, 288, 373, 374, etc.) give detailed information of the symptoms in different animal species and their treatment.

Se is an essential element for animals, a deficiency of which produces muscular dystrophy and allied diseases. It is functionally related to vitamin E. Several soils, especially in New Zealand but also elsewhere, have been found Se deficient (12, 95, 395). In New Zealand, where 274 Co-Se trials were carried out on all classes of soil, there was response to Se in 43% of the S. Island and in 14% of the N. Island trials (153). Almost all the responses occurred on slightly weathered sand or silt soils. There are also indications that soils on parent materials derived from greywacke, mica schist, non-basic aeolian sands and rhyolitic ash are involved (178). Increases in liveweight of lambs of up to three kg in 12 weeks after drenching with 5 mg Se monthly were reported from New Zealand (176, 396), mainly on soils of less than 0.45 ppm total Se, which is considered as a critical response level. However, on some organic soils with over 1 ppm Se, responses were obtained as well. This was assumed to be due to the presence of Se in a reducing environment as relatively insoluble selenite. Another explanation may be that, if the values were given on volume basis (e.g. mg/litre instead of ppm), the Se content of these organic soils might have turned out to be even lower than those in most of the Se deficient mineral soils in the trials (see p. 6 and 8).

Some Se may be added to soil by fertilizers and soil amendments. Many limestones and phosphate rocks contain less than 1 ppm Se, but certain types may have higher contents. Other fertilizers usually contain up to a few ppm and some sulphate containing fertilizers may have higher contents especially if the sulphuric acid is made from pyrite (352).

## 10. Zinc (Zn)

The beneficial effect of Zn on the growth of *Aspergillus niger* was already observed a hundred years ago by Raulin (302). Its essentiality for higher plants was indicated by Mazé in 1914 (240) but was first fully recognized in 1926 (337) even though the use of Zn salts as fertilizer material for field crops was recommended as early as 1912 by Javillier (184). First signs of the importance of Zn for higher animals were from the year 1919 (71) but full proof of its essential role in animal nutrition was obtained some 15 years later (366).

The Zn content of the lithosphere has been estimated to be about 80 ppm (Table 2) and in soils its total content reported usually ranges from 10 to 300 ppm with occasional lower and higher values. The total content of Zn in soils, however, has often been found to be an unreliable index of Zn status of soils because of several factors affecting its availability to plants. Zn deficiency is found in a wide range of soil textures but most often in sandy soils. This may be due to the same reason as for many other trace elements, i.e. that most Zn containing rock and minerals are easily weathered (see Table 4) and thus likely to form fine textured soils. Zn is accumulated in surface soils where it is absorbed by clay particles and organic matter. Removal of surface soil, e.g. by erosion, may lead to Zn deficiency in soils low in its content.

Zn is generally more available in acid than in alkaline soils, the range of least availability being about pH 6.0 - 7.0. Viets *et al.* (381) found that the Zn uptake of plants decreased to about one half when the pH of the soil was increased from 5 to 7. At high pH the formation of insoluble calcium zincates is favoured and Zn may be less available. Therefore liming of acid soils decreases the availability of Zn and may produce Zn deficiency (360). On the other hand, Zn toxicity may result if soils are acidified to increase the availability of other elements or when Zn fertilization is continued over a long period with Zn rich materials such as sewage sludges (28, 183). In soils of sodium alkalinity the availability of Zn may increase with increasing pH due to the formation of relatively soluble sodium zincates (28). In several studies, however, no apparent connection between the soil pH and Zn uptake by plants could be established (363).

There are indications that Zn deficiency is more pronounced in cool and wet weather than in warm and dry weather. An example of this is from California, where winter grown sweet-corn showed severe Zn deficiency on soils where no such deficiency occurred when the same crop was grown in summer (378). In some cases the soil temperature - Zn uptake interaction seems to concern only the uptake of applied but not the native soil Zn (236) while in others no light or temperature dependency on Zn absorption could be noted (301). Alternate wetting and drying has been reported to cause more Zn to become associated with the soil O.M., whereas keeping the soil moist causes more Zn to become fixed on the inorganic soil fractions (118).

Zn deficiency on high phosphate soils or accentuated by heavy or excessive phosphate fertilization has been reported (53, 54, 75, 82, 115, 197, 360, 394). In some cases the Zn content of beans was reduced by 20-30% and that of maize by 30-50% by a 375 kg P/ha application. This Zn-P interaction does not appear to be common to all soils (49, 56, 82) and the nature of the phosphate induced Zn deficiency is not known, but may be partly explained on the basis of two limiting factors (75).

In calcareous soils, such as rendzinas, variations in the calcium carbonate content have been found to have only a minor effect on Zn availability (270) whereas the mineralogical composition of these soils plays an important role in influencing both the total content and availability of Zn (269). Soils rich in montmorillonite may contain twice as much total Zn as attapulgitic soils but in the former soils, due to stronger Zn bounding to montmorillonite, the content of available Zn may be lower.

Especially in earlier literature the view was presented that the fixation of trace elements, including Zn, by organic matter might be strong enough to cause the deficiencies often found in organic soils. However, in peat soils, in spite of the high fixing capacity of organic matter, the trace elements are apparently less effectively bound than in mineral soils. This view is supported, e.g. by Dobrovolskii (105) who found that the maximum contents of water-soluble forms of almost all trace elements occur in the humus horizon and by Dolar (106) who states that Zn uptake is closely related to the organically bound soil reserves. Also Sorensen *et al.* (338) reported a positive correlation between extractable Zn and O.M. content ranging from 0.4 to 2.2 percent and Jensen and Lamm (186) and Sillanpää (328) found the relative solubility of Zn to be much higher in organic than in mineral soils (see Fig. 5). This may be partly due to the generally lower pH of organic soils.

Zn deficiency was recorded in a dozen European countries by Ryan *et al.* (315). The data was not sufficient to establish clear soil relationships, but in some countries the deficiency seems to be associated with Red Mediterranean, Reddish-Brown, Brownish-Yellow Sandy, some loess-derived, certain Alluvial and bog soils.

The content of Zn in plants normally ranges between 20 and 100 ppm of dry weight, but varies with plant species as well as with plant parts. The stage of maturity of the plant, the nature of the soil on which the plant has grown, the climatic conditions and, of course, Zn fertilization also affect the Zn content of plants.

Some plants seem to have a much stronger ability to extract Zn from soil than others, e.g. on the Zn deficient soils in Florida native weeds contained on the average 140 ppm of Zn, while crotalaria growing on the same soil as a cover crop only contained 4-11 ppm in the dry matter (310). Therefore, ploughing in native weeds was suggested as a means of preparing the land for maize. Lichens seem to be strong Zn collectors, their Zn content being 1,000-10,000 ppm of ash or 1.5-9 times higher than that of Mn and over 10 times higher than those of Cu and B, while in wild herbaceous flowering plants from the same areas the Zn content was usually 300-900 ppm of ash or only about one tenth of that of Mn (229).

The Zn content of the principal range grasses in a Zn deficient area in Guyana (British Guiana) was reported to vary from 18 to 42 ppm and the minimum Zn requirement of grazing cattle from 20 to 30 ppm (220). Pasture plants and forages growing on normal soils usually contain 30-100 ppm Zn (32). An average Zn content of 20 ppm in timothy has been reported from Sweden (196), 31 ppm from Finland (213) and 23, 31 and 38 ppm from middle European countries (204, 321, 415). The Zn content of alfalfa flour grown on neutral or alkaline Hungarian soils varied from 14 to 18 ppm and was found to be higher in the flour from the first cutting than from the later ones (291). Sugarbeet may respond to Zn application if the Zn content of the young, fully developed leaves is around 10 ppm of dry weight or less (55, 371), and in sugar-cane Zn deficiency symptoms are also likely to occur after leaf composition drops below 10 ppm (322). For dwarf beans and citrus the critical level is somewhat higher, about 20 ppm in the mature leaves (194, 306, 380). For tobacco the minimum requirement is less than 10 ppm in the tissue and perhaps for that reason there have been no confirmed cases of Zn deficiency in field grown tobacco (241). Maize is known to be very sensitive to lack of Zn. A concentration of 20 to 70 ppm in the ear leaf at silking was considered as an adequate level of Zn for maize by Barber and Olson (23).

The effects of soil and Zn fertilization may be quite substantial on the Zn content of plants. Bean tops and rye grown on Sassafras loam had Zn contents of 112 and 93 ppm respectively, while the Zn contents of the same plants grown on Collington loam were five times higher, 551 and 456 ppm respectively (29, 65). Application of Zn at the rate of 5.6 kg/ha (five lb/acre) has been reported to increase the Zn content of tobacco from 22 to 74 ppm (20). The Zn content of young oat plants grown in sand cultures was increased from 8 to 30 ppm by a 224 kg/ha application of zinc sulphate, but reduced from 20 to 5 ppm by an application of 2240 kg/ha of calcium carbonate. In the latter case the pH of the medium was increased from 5.9 to 7.9. In the same study an increase of phosphate dressing reduced the Zn content of oat plants from 30 to 17 ppm without any significant change in the

pH (Table 9). Similar effects from phosphate on the Zn uptake by young sour orange plants grown in field conditions and from iron on the Zn uptake of maize have also been recorded (51, 133).

Table 9. The influence of superphosphate application to the soil on the Zn and P content of oats (311).

Superphosphate applied kg/ha	Soil pH	Yield per pot grams D.M.	Zn ppm in D.M.	P % in D.M.
0	5.64	8.7	30.1	0.24
560	5.68	9.2	17.0	0.61
1 120	5.59	8.9	16.6	1.06
1 680	5.45	8.6	17.9	1.40

Zn functions in plants largely as a metal activator of enzymes. These functions have been widely reviewed, for instance by Stiles (347) and Hewitt (164). The deficiency of Zn produces changes in leaf morphology and in cell histology. Its symptoms have been recorded in more than two dozen crops including maize, sorghum, cotton, sunflower, buck-wheat, beans, peas, cocoa, apple, peach, pecan, citrus, sweet cherry, apricot, avocado, grapes, cabbage, carrots, celery, lettuce, onions, spinach, tomatoes, etc. Depending on the crop, the disorder is called by half a dozen different names, such as white bud (in maize and sorghum), little leaf or rosette (cotton and some fruit trees), mottle leaf or frenching (citrus) and sickle leaf (cocoa).

Zn deficiency symptoms in maize include chlorosis and the plants become stunted; also emerging leaves show yellow to white bleached bands in the lower part of the leaf (207). In cotton pronounced interveinal chlorosis and bronzing of leaves, which become brittle with upturned margins, arrested stalk elongation, delayed growth and fruiting and reduced yields are the general signs of Zn deficiency (27, 37, 107). In legumes typical symptoms include stunted growth and developing of brown spots with yellowing of the leaf tissue between the veins of lower leaves; dead tissue drops out of chlorotic areas (272). In vegetable crops the new leaves are abnormally small and mottled with yellow, or uniformly chlorotic (294). In fruit and nut trees Zn deficiency symptoms generally appear on the youngest leaves which become chlorotic, veins remaining green. Internodes are markedly shortened near the tip of the shoot producing rosettes of small chlorotic leaves. Older leaves may become bronzed and fall easily (84). Leaves irregular in colour pattern, reduced in size, pointed or very narrow, with a sharply contrasting pattern of bright yellow mottling on green background and small and pale fruits are typical symptoms of Zn deficiency in citrus (194). Detailed descriptions furnished with colour plates of Zn deficiency symptoms for the above mentioned crops, as well as others, can be obtained from several sources (e.g. 221, 341, 391).

A Zn dietary deficiency may occur in some farm animals, most often in pigs and poultry, seldom in cattle, but has not been found in sheep or man. Zn is relatively nontoxic to birds and mammals. The functions, requirements and symptoms of deficiency and toxicity of Zn in animals have been widely reviewed by Underwood (373, 374).

Zn content of normal or mixed mineral N, P and K fertilizers varies from traces to about 2000 ppm, the majority of fertilizers containing only a few ppm. In particular the Zn content of K-fertilizers seldom exceeds 1 ppm and that of N-fertilizers is usually less than 10 ppm with occasional values up to several hundred ppm. Phosphate fertilizers are usually richer in Zn and some organic fertilizer materials, like sewage sludges, may sometimes contain 10,000 ppm Zn or more (352). The Zn content of farmyard manure usually ranges

between 10 and 200 ppm in dry matter (35, 352). Zinc sulphate containing about 36 percent Zn is perhaps the most commonly used fertilizer for controlling Zn deficiency in plants. It is usually applied to the soil at a rate of 11.2 - 89.6 kg/ha (10 to 80 lb/acre) and can also be sprayed over vegetable, fruit and field crops. When applied as one percent spray or drilled in at 125 kg/ha (1 cwt/acre) wheat yields up to 35 percent higher have been obtained (110). Increases from 16 to 95 percent in potato yields were obtained with Zn application on some Colorado soils containing less than 4.8 ppm 0.1 N HCl - extractable Zn, while on soils containing more than 5.5 ppm Zn there was no response to it. Uptake of Zn was greater from soil-applied Zn EDTA than from soil-applied Zn SO<sub>4</sub>. Foliar sprays of either Zn SO<sub>4</sub> or Zn EDTA (0.5%) were effective in correcting Zn deficiency (334) but chelated sources of the element in fertilizers may be more effective than ionic sources and therefore are needed in lesser quantities (e.g. 8, 29, 334).

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