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NUTRIENTS OTHER THAN NPK FOR CEREALS: A REVIEW

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NUTRIENTS OTHER THAN NPK FOR CEREALS: A REVIEW

by

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CONTENTS

GLOSSARY

B	-	Boron
Ca	-	Calcium
Chelate	-	Organic chemical compound
EDTA	-	Ethylene diamine tetraacetic acid
Fe	-	Iron
K	-	Potassium
Ligands	-	In a complex ion, the ions surrounding the central ion
MAFF	-	Ministry of Agriculture, Fisheries and Food
Mg	-	Magnesium
Mn	-	Manganese
Mo	-	Molybdenum
N	-	Nitrogen
P	-	Phosphorus
S	-	Sulphur
Soil Association	-	A group of soils developed on similar parent materials
Soil Series	-	Soils with a similar type and arrangement of horizons developed on similar parent materials
Soil type	-	The physical characteristics of a soil profile in terms of texture, depth, stoniness and drainage status
Zn	-	Zinc

ABSTRACT

The elements which are essential for plant growth are classified into two groups, according to the relative amounts (kg/ha or g/ha respectively) required by crops:

- Major nutrients: nitrogen (N), phosphorus (P), potassium (K), sulphur (S), magnesium (Mg), calcium (Ca), and chlorine (Cl)
- Trace elements or micronutrients: boron (B), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo) and zinc (Zn).

Balanced crop nutrition, with an adequate supply of all the essential plant nutrients, is crucial for optimum yield and quality of cereals. Inorganic NPK and, increasingly S fertiliser inputs, represent a significant proportion of the variable costs for cereal production and, to help ensure their efficient use, the availability of other nutrients must not be a limiting factor. Previous HGCA-funded reviews have covered both copper deficiency and sulphur nutrition in cereal crops, but little attention has been given to other non-NPK nutrients in recent years. This review draws together and updates existing information on the incidence, diagnosis and treatment of deficiencies of nutrients other than NPK in cereals, including the effects of deficiency on grain yield and quality. The soil chemistry and role in plants of these nutrients are also summarised.

Research studies have shown that deficiencies of Mg, Mn, S and, very rarely Zn, can occur in cereal crops, and are usually associated with specific soil types. Each deficiency produces characteristic symptoms in cereal crops and different cereal types can vary in their susceptibility to a particular deficiency. However, any inputs of these nutrients must be targeted according to deficiency risk, and not applied simply as insurance dressings, to ensure their cost effective use. Cereals are not susceptible to deficiencies of the other non-NPK nutrients (B, Cl, Fe, Mo) under UK growing conditions.

Cereals may show visual, and often transient symptoms of **magnesium** deficiency but seldom give a yield response to magnesium applications, unless soil reserves of Mg are very low. The latter situation is most likely to occur in sandy soils where sugar beet or potatoes are not grown in the rotation. This deficiency can, however, be induced on a wide range of soils under conditions of crop stress caused by poor soil structure, restricted rooting and/or drought. Treatment is very rarely necessary, unless symptoms persist, in which case a foliar Mg spray should be applied. The soil magnesium status should be maintained above Index 0 in arable rotations to avoid any risk of Mg deficiency limiting cereal yields. Magnesium application is very unlikely to improve grain quality on non-deficient soils.

Sulphur deficiency in cereals has increased over the last decade because of the continuing decline in the atmospheric deposition of S, due to restrictions on sulphur dioxide emissions from industrial sources. The occurrence of S deficiency is variable and depends on the interaction between crop N and S supply during the growing season. Grain yield responses have ranged from 4 to 40% across deficient sites in the UK and have sometimes occurred in the absence of any visual response to S application. Conversely, yield responses to applied S are not always obtained where deficiency symptoms appear in the untreated crop. Leaf analysis between flag leaf emergence and mid flowering (GS39-65), also grain analysis, can be used to assess crop S status and whether S is required for subsequent cereal crops. Soil analysis does not, however, reliably predict S deficiency in cereals. Currently, cereal crops grown on well drained sandy or shallow soils in areas where atmospheric deposition is less than 20 kg S/ha/year, are likely to need sulphur. Sulphur deficiency will gradually become more widespread and may occur on a wider range of soil types. Modelling predictions suggest that 30-40% of the UK land area may currently be at some risk of S deficiency for cereals and that this proportion will increase to about 50% by 2003. Sulphur deficiency is best prevented by a spring application of 10-20 kg/ha S as a water soluble sulphate fertiliser. The development of plant diagnostic techniques for earlier identification of S deficiency during the growing season will enable more effective corective treatment of deficiency in the growing crop.

Loaf volume, as a measure of breadmaking quality in wheat, is reduced by S deficiency and may sometimes be increased, without any response in grain yield, by S application. There is little information on whether malting quality in barley is affected by low S (relative to N) in the grain. Further work is also needed on S availability from organic manures and on effective options for late foliar S applications.

Soil data indicate that up to 5% of the cereal growing area in England and Wales, and 30% in Scotland may be deficient in **copper**. This deficiency usually occurs on sandy, shallow chalk and peaty soils; sometimes the deficiency is sub-clinical, where yield is reduced without any apparent symptoms. Soil analysis is particularly useful for identifying Cu deficiency, while plant or grain analysis is less reliable. Copper treatment, to prevent deficiency, is normally applied as a foliar spray of inorganic or chelated Cu in the spring. A large soil dressing of copper oxychloride or copper sulphate, prior to sowing, is an alternative treatment option where a deficiency has previously been identified. In practice this method is rarely used as it is less convenient than using annual foliar sprays. A single soil application has an appreciable residual value, which lasts for at least five years, but probably needs an additional foliar Cu spray in the first season following its application, to be fully effective. More information is needed on the extent of sub-clinical deficiency.

Manganese deficiency is the most common trace element deficiency in cereals and 15-20% of the total cereal area is usually treated with Mn each year. Soil applications of Mn are generally ineffective, as the applied Mn rapidly changes into less available forms. Deficiencies are best prevented or, where Mn deficiency only occurs infrequently, corrected by foliar spraying with manganese sulphate or a proprietary chelated or inorganic Mn product in the spring. Autumn, as well as spring treatment, may be necessary on very deficient soils. Manganese seed dressings, combined with subsequent foliar sprays, may also be useful for very deficient sites where deficiency may develop while there is still very little plant cover for foliar uptake. Take-all disease in cereals does not appear to be exacerbated by Mn deficiency under UK conditions, which is in contrast to findings in Australia and America, but increased mildew incidence is often associated with deficient plants. Treatment strategies for controlling Mn deficiency require further development.

Zinc deficiency has occasionally been recorded in barley crops grown on sandy soils with high pH and P status in Ireland and Scotland, but has not so far been encountered in England and Wales. The average annual rate of Zn deposition from the atmosphere exceeds crop removal of Zn, even in high yielding crops, although there is little information on the actual availability of this deposited source of Zn to crops. However, a re-assessment of the Zn status of crops grown on sandy soils in areas with below average Zn deposition would identify whether there is any potential risk of deficiency. Foliar spraying with zinc sulphate, or a proprietary chelated or inorganic Zn product, in the spring is recommended for the treatment of Zn deficiency.

Deficiency risks at field level should initially be assessed from a knowledge of soil types and past incidence of observed symptoms or confirmed deficiencies in susceptible crops. Soil analysis will accurately predict the likelihood of Cu or Zn deficiency on candidate soil types. Leaf analysis can be used to diagnose or confirm whether visual crop symptoms or a suspected latent deficiency are caused by Mg, Mn, S or Zn deficiency. Where a particular deficiency problem is clearly identified, an appropriate amount and form of the specific element should be applied as a preventative or corrective treatment.

Trace element inputs from atmospheric deposition can be significant, especially near the coast and in areas of industrial activity. Organic manures, where used in arable rotations, will also add small amounts of these nutrients and contribute to the net balance of trace element reserves in soils. High yielding crops do not necessarily need trace element (Cu, Mn, Zn) applications, despite their greater nutrient demand, as such crops are more efficient at obtaining these nutrients from soil reserves. Greater mobilisation of these trace elements occurs in the rooting zone of high yielding crops.

There is no clear evidence at present to suggest that sub-clinical deficiencies are now occurring on a wider range of soil types than those where treatment would conventionally be recommended. Information on the Cu, Mn and Zn nutrition of current cereal cultivars is, however, very limited and the risk of sub-clinical deficiencies on marginal soil types should be further investigated. There is also very little information on whether applying combinations of trace elements together can have any beneficial effect on grain yield and quality.

A survey of the main commercial analytical laboratories and product supply companies in the UK showed that a wide range of deficiency threshold levels are used for some nutrients to interpret soil and plant analyses. Greater standardisation of crop and soil sampling procedures, analytical methods and associated interpretative guidelines on deficiency thresholds would help to improve the accuracy of diagnosing nutrient deficiencies in cereal crops.

Future research priorities and technology transfer requirements for the major and trace elements covered by this review are identified.

1. INTRODUCTION

Cereal yields in the UK have increased steadily over the past thirty years, resulting in higher nutrient offtakes in harvested crops. The total cereal area in the UK was 3.4 million hectares, representing 18% of the total agricultural area, and produced 22.4 million tonnes of grain (Anon. 1998). Crop nutrient requirements depend on the type of cereal grown, as well as on soil fertility status. The cereal market is dominated by wheat (60%) and barley (37% of the total cereal area), which gave average yields of 7.55 and 5.21 t/ha respectively in 1998. Nearly all of the remaining cereal area is occupied by oats. Milling wheats for breadmaking (Group 1 and Group 2 varieties; Anon. 1998a) were grown on 26% of the wheat area, while 61% of the barley area was grown for malting in 1998.

Balanced crop nutrition, with an adequate supply of all the essential plant nutrients, is crucial for optimum yield and quality of cereals. As well as nitrogen (N), phosphorus (P) and potassium (K), there are a number of other nutrients which are essential for plant growth and can be divided into:

- Other major nutrients: calcium (Ca), chlorine (Cl), magnesium (Mg) and sulphur (S)
- Trace or micronutrients: boron (B), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo) and zinc (Zn).

Adequate availability of all of these other essential nutrients is vital for ensuring that crops utilise NPK fertiliser inputs efficiently. The use of organic manures has declined on arable farms and high cereal yields are now achieved and maintained by the application of inorganic fertilisers. Unless S-containing fertilisers are applied, S supplies from the soil are largely dependent on atmospheric deposition of S. Soil Mg reserves depend on soil texture and whether Mg fertiliser is applied for crops in the rotation which are sensitive to Mg deficiency. The ability of soils in continuous arable production to supply the trace element demands of crops has also become more important, although atmospheric inputs of trace elements can be significant, especially near the coast and in areas of industrial activity (Archer, 1985). Data on the total and extractable trace element status of UK soils have been produced both by McGrath & Loveland (1992), as a Geochemical Atlas, and by Archer & Hodgson (1987).

Deficiencies of several of the essential non-NPK nutrients are known to affect cereals grown on certain soil types in the UK. Agronomic inputs of these nutrients must, however, be targeted according to deficiency risk, rather than applied as insurance dressings, to ensure their cost effectiveness; both unnecessary applications and failure to treat potential deficiencies will result in financial loss. Accurate prediction or diagnosis of nutrient deficiencies is therefore important to ensure that all fertiliser inputs are used economically and sensibly. The development of remote sensing techniques to measure key agricultural crop parameters as an aid to crop management decisions, may in future enable the early detection of nutrient deficiencies and hence better targeting of remedial treatments (Dampney *et al*., 1998).

Apart from sulphur, treatment recommendations for these nutrients are based largely on older trials work with lower yielding varieties, which were often sited on soils with moderate to severe deficiency risk. High yielding crops are not necessarily more prone to trace element deficiencies than lower yielding crops (Sinclair *et al*., 1990a). It has, however, been suggested that yield responses to trace element applications are now occurring in the absence of visual symptoms in cereals, due to sub-clinical deficiencies on marginal soil types and/or high yielding crops. There is only limited independent experiment data to verify whether sub-clinical deficiencies are developing in situations where treatment would not conventionally be recommended. Also, most previous studies concentrated mainly on single nutrient effects, rather than treatments testing combined applications of these nutrients, which may have some interactive benefits.

This review summarises existing information on the incidence, diagnosis and treatment of deficiencies of nutrients other than NPK in cereals, also the effects of deficiency on grain yield and quality. The soil chemistry and plant physiology of these nutrients are also briefly outlined. Data on the nutritive value and chemical composition, including mineral elements, of cereal grains have been compiled by MAFF (1990). Topics requiring further R and D are identified and appropriate studies are recommended for developing and improving decision support systems which would identify crop and soil requirements for applications of these major and micronutrients, to ensure their effective use for UK cereal crop production.

2. THE SUPPLY OF TRACE ELEMENTS IN SOIL SOLUTION

There are a number of generally accepted features of trace element chemistry which are common to all crops:

- Trace elements are required by crops in only small amounts compared to the major nutrients. Plant uptake is usually measured in g/ha rather than kg/ha.
- Trace elements contents of different soils vary depending on the parent material from which they were formed but are usually lowest in soils derived from acid igneous rocks and sands.
- Soil solution concentrations of trace elements are primarily determined by the ease of weathering of the primary minerals of which they are a part but are subsequently modified by a number of soil and crop factors: soil pH, organic matter, surface absorption, microbial activity, crop rooting density, nutrient uptake and release of organic substances from plant roots.
- The availability of most trace elements decreases at higher soil pH levels. Low temperatures and other factors that affect root growth an activity, such as waterlogging or soil compaction, will also reduce trace element and other nutrient uptake.
- Trace element and other nutrient deficiencies are referred to as 'clinical' when specific symptoms appear in a crop or 'sub-clinical' (latent or hidden) when no symptoms develop but the crop responds to trace element fertilisation. Crop symptoms may persist (acute deficiency) or disappear naturally (transient deficiency) and can be confused with one another and with those caused by drought, severe frost or herbicide damage.
- It is common practice in the U.K. to identify critical concentrations of trace elements in plants and soils associated with clinical deficiency. However yield loss can still occur above such critical concentrations and in mainland Europe, threshold plant concentrations for deficiency are those below which less than 90% crop yield is achieved. Such values are obtained not by appearance of deficiency symptoms but by assessment of crop performance on different soil types.
- It is generally accepted that advisory recommendations should be based on the principle that an application of a trace element fertiliser is required only where a specific deficiency has been identified by soil and/or plant analysis.

The requirements of cereals for individual trace elements are outlined in more detail in subsequent chapters of this review. This section reports the results of studies which investigated the soil solution supply of copper, manganese and zinc, the three trace elements which may cause deficiencies in cereal crops, and their implications for crop nutrient requirements.

2.1 Copper, Manganese and Zinc in Soil Solution

The supply of Cu, Mn and Zn to plant roots is not merely a function of the total or extractable amount of the particular nutrient in the soil, but also of the rate of replenishment of the soil solution by the nutrient pool as well as the volume of soil exploited by the root system. Plants obtain these nutrients largely if not exclusively by uptake from solution. However, data relating to their concentrations in soil solutions are extremely limited. There are various reasons for this. In general it has been difficult to isolate the soil solution in a form which relates closely to that which occurs in undisturbed soil. Secondly, the concentrations of Cu, Mn and Zn present in soil solutions are low and have, as a consequence, posed difficulties in analysis.

Substantial increases in the concentrations of Cu, Mn and Zn in soil solution have been observed in the rooting regions of barley plants both in pots (Nielsen, 1976) and in field experiments (Linehan *et al*., 1985). These field observations were extended by Linehan et al. (1989) who carried out experiments on 9 sites in North-East Scotland over a number of seasons between 1983 and 1985 and comparisons were made between the rooting zone of spring sown barley and autumn sown barley and between these and adjacent uncropped soil. Information on EDTA extractable Cu, Mn and Zn, soil texture and pH from these sites are given in Table 1, which forms the basis of discussion in the following sections.

Table 1. Site identification and soil characteristics for soil solution studies

Site	Soil Association [1]	Grid ref.	Texture [2]	EDTA [3] Cu	Mn	Zn	pH [4]	Year of expt
				(mg/kg)				
A	Boyndie	NJ 609622	Sandy loam	3.8	287	2.8	5.8	1984
B	Stonehaven	N0 840727	Sandy silt loam	14.0	150	21.5	6.2	1984
C	Stonehaven	NO 841729	Sandy silt loam	9.5	107	14.9	5.9	1984
D	Stonehaven	NO 583804	Sandy silt loam	3.1	250	5.4	6.3	1984
E	Corby	NJ 934157	Sandy loam	15.4	20	9.0	6.5-6.6	1983-85
F	Boyndie	NH 653633	Loamy sand	2.4	22	2.3	6.6	1984
G	Boyndie	NJ 653635	Loamy sand	3.5	26	3.6	6.5	1984
H	Countesswells	NJ 750096	Sandy loam	1.6	34	2.2	6.5	1984/85
I	Countesswells	NJ 750098	Sandy loam	0.7	20	1.6	6.4	1985

1 - Glentworth and Muir (1963); 2 - MAFF (1984); 3 - MLURI/SAC (1985); 4 - pH of 1:1 soil:water prior to seed sowing
Source: Linehan et al. (1989)

There are well established observations that symptoms of Cu deficiency are usually not evident before the end of tillering, while Mn and Zn deficiency symptoms occur in field crops early in the growing season but frequently disappear by mid-season (Withers & Sinclair, 1995; Pumphrey & Koehler, 1959; Linehan & Sinclair, 1985). The latter authors reported that as the rhizosphere of spring barley developed then increases in Mn and Zn concentrations in soil solution occurred, producing maxima in early to mid summer. These changes were not related to pH changes. Nutrient uptake depends on the concentration of nutrients in soil solution but plant content depends on the growth rate of the plant as well. Linehan & Sinclair (1985) showed that, in spring barley, Mn deficiency may develop in early growth stages when demand is high but supply from the soil solution is relatively low. As mobilisation in the soil solution progresses, supply meets demand and the crop "grows away" from deficiency (see Fig.1). Because of the interaction between growth rate and supply it may be that only the most extreme situations will be demonstrated by soil testing and that more moderate deficiencies might require plant tissue analysis.

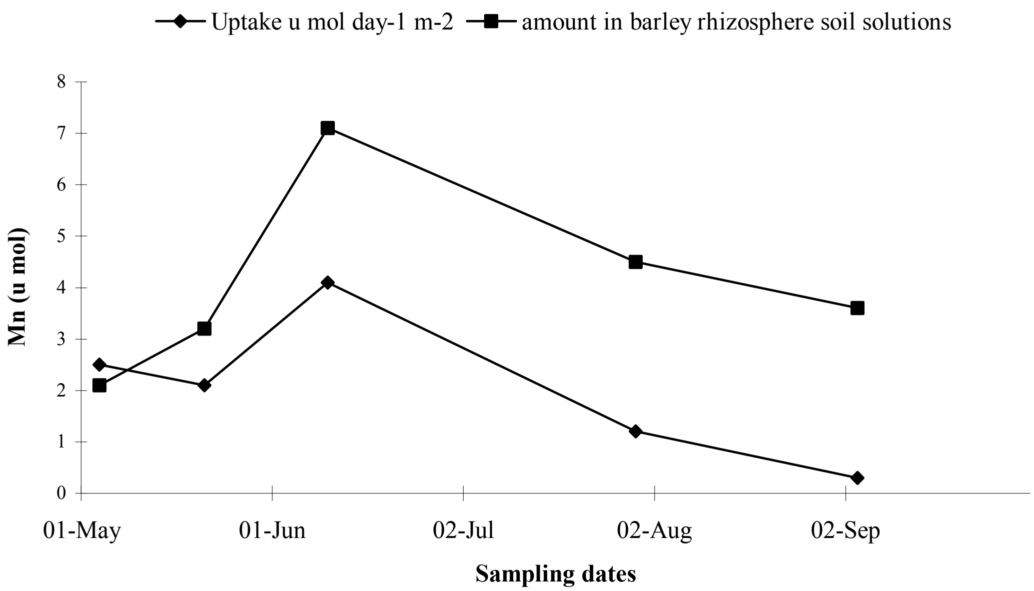

Figure 1. Manganese in soil and plant through the growing season

Autumn-sown cereals start into active growth much earlier in spring than is the case for spring-sown crops. They are often actively growing before the spring crops are sown. As a result their demand for Mn, Zn and, less so Cu inevitably occurs much earlier in the season. This was demonstrated in adjacent fields of the same soil parent material by Linehan *et al*. (1989) at sites H and I (Table 1). The demand for these nutrients is not only much higher in the autumn-sown crop but also occurs much earlier in the year, as illustrated in Fig. 2a for Mn and Zn. Maximum offtake of Mn and Zn by the autumn-sown crop occurred in mid-May, and early July for the spring-sown crop. For the autumn-sown crop the maximum Mn and Zn concentration in root-zone soil solution occurred in early May whilst that for the spring-sown crop occurred in early July (Fig. 2b). Equivalent data for Cu, showing similar effects, were presented by Sinclair & Withers (1995) in their review of Cu deficiency in cereals. The requirement for Cu is relatively low in the early part of the season, when there is sufficient Cu mobilisation to meet this demand, which would explain why Cu deficiency is seldom seen before the end of tillering. Bearing in mind that the concentrations of Cu, Mn and Zn occurring in the root-zone results from the balance between uptake and mobilisation, these are the patterns one might expect from the differing patterns of plant growth and nutrient uptake. It is thus apparent that substantial mobilisation occurs in the root-zone of autumn-sown winter barley much earlier in the year than for the spring-sown crop. Because soil and climate were removed as variables in this experiment this seems to be further clear evidence for the involvement of the growing plant and its related rhizosphere micro-organisms in the mobilisation of Cu, Mn and Zn.

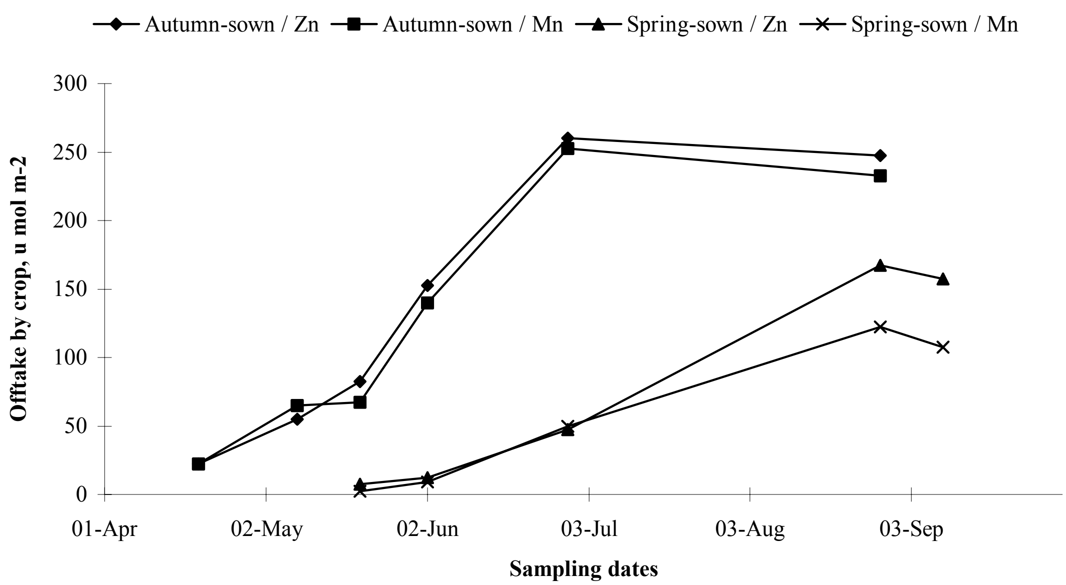

Figure 2a. Mn and Zn offtakes by spring-sown and aurumn sown barley

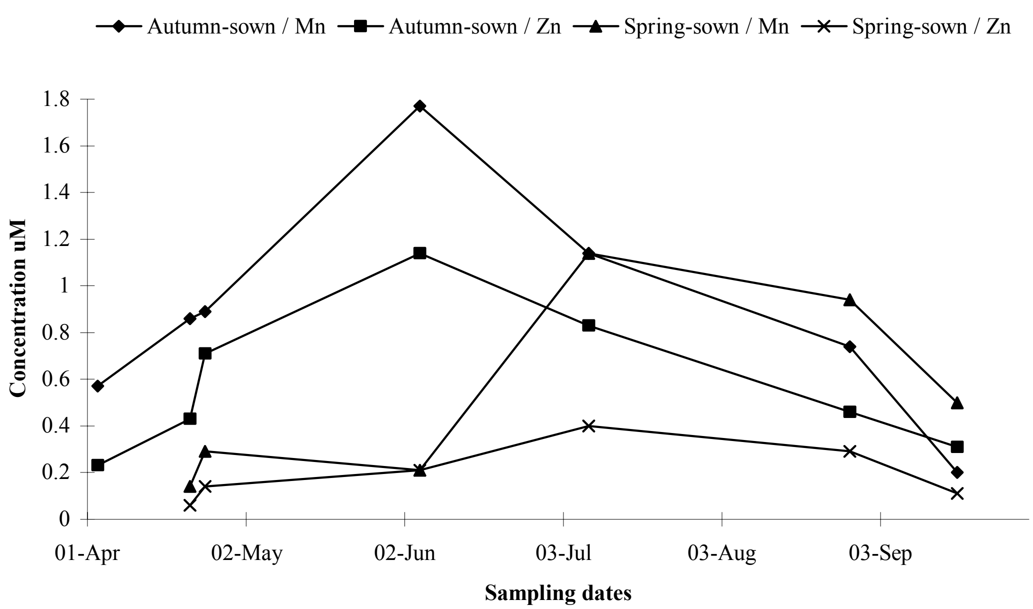

Figure 2b. Mn and Zn concentrations (uM) in soil solutions from root-zones of spring-sown and autumn-sown barley

2.2 Effect of soil pH

On some occasions, two peaks in concentration for Mn or Zn were observed (Linehan *et al*., 1989). A dramatic increase in Mn concentration occurred in late April followed by a drop in early May in the root-zone of spring barley at site G (Table 1). A second peak in concentration occurred in early June followed by a progressive drop through the rest of the season. The initial peak in Mn occurred at the same time as a transient drop in soil pH to a value of 5.3. pH is the parameter most widely accepted as exerting a controlling influence on the plant availability of micronutrient actions (Sanders, 1983; Jeffrey & Uren, 1983; Petrie & Jackson, 1984). Soil acidification results in substantial mobilisation of Mn and Zn (Sims, 1996). The pH drop in the root-zone observed at site G resulted from the combined drilling of ammonium nitrate with the seed. Such fertiliser induced acidification of soil is well established (Smiley, 1974) as is the related mobilisation of Mn (Goldberg *et al*., 1983 and Holmes *et al*., 1983). As the transient pH drop disappeared, Mn concentration dropped from its high value of 5.5µM to a value of only 2.2µM in late May. Despite the fact that pH then rose very slightly toward neutrality, Mn concentration again increased to produce a second peak of 4.0µM in mid June. This second non pH induced peak was regarded as corresponding to the single peak seen previously on sites where fertiliser was broadcast at seed sowing so that no sharp pH drop occurred.

The pattern of changing Cu concentration at this same site (site G) was entirely different from that for Mn. Cu concentrations increased progressively to a maximum value in mid July (Linehan *et al*.,1989). The distinction between Mn and Cu, especially during the early part of the season, corresponds with the findings of earlier workers that, whilst Mn and Zn are mobilised into soil solution by acid pH, Cu is much less affected (Sanders, 1983; Jeffrey & Uren, 1983). These differences in behaviour must relate to differences in the immobile forms of the metals in soil. Substantial amounts of Mn and Zn probably occur in ionic form (Sanders & Kherbawy, 1987) held absorbed onto charged inorganic surfaces in the soil whilst Cu is thought to be complexed by small organic ligands and held on charged organic surfaces (Sanders, 1983).

2.3 Rate of replenishment of the soil solution with Cu, Mn and Zn in relation to crop demand

Plant roots release organic substances capable of complexing micronutrient cations although these ligands may have a rather transient existence because rhizosphere micro-organisms utilise them as carbon sources. Despite their individual short lives such ligands might, if produced continuously, play a significant role in micronutrient mobilisation. On the basis of a review of earlier work Gardner *et al*. (1983) concluded that it was unlikely that soil micro-organisms would secrete compounds able to release significant quantities of nutrients for plant uptake. This conclusion was based on macronutrients which, because of the quantities needed by plants, would require large amounts of active compounds to mobilise them in significant quantities. Plant requirements for Cu, Mn and Zn are much smaller. The release by micro-organisms of relatively small amounts of chelating ligands could thus mobilise nutritionally significant quantities of these elements. Differences in the extent and nature of exudation by plant roots might explain observations that cereal cultivars differ in their sensitivity to Mn deficiency (Nyborg, 1970). Varietal susceptibility to Cu or Mn deficiency has not been researched in the UK but breeding varieties less susceptible to these deficiencies may be worthwhile in the sustainable farming systems of the future.

Survival of micronutrients in the soil solution depends on their sequestration by soluble organic ligands (Merckx *et al*., 1986). Sinclair et al. (1990b) extended this observation by calculating the rates of replenishment of the soil solution with Cu, Mn and Zn in relation to crop demand. Measurements were made on a commercial crop of winter wheat (cv. Fenman) grown on till derived from Lower Old Red Sandstone. Dry matter accumulation, root length, uptake of Cu, Mn and Zn, and concentrations of these elements in soil solution were measured on 9 occasions from early May until harvest in early September.

The nutrient inflow rates (I) between each sampling were calculated as

$$I = (U_n - U_{n-1}) / (t_n - t_{n-1}) \quad x \quad 0.5 (L_n + L_{n-1})$$

where U is the cumulative uptake of Cu, Mn and Zn in above-ground plant samples, t is time, L is root length in soil of 0 to 150 mm depth and n is the sample chronosequence number (Mengel and Barber, 1974).

The size of the reservoir of each element in the soil solution was calculated from the concentration of Mn and Zn in the soil solution, the bulk density and moisture content of the soil and the volume of soil in the root-zone. This was taken as 50% of the total soil volume to a depth of 150 mm. This latter parameter was based on the assumption that the zone of influence of the root extended 3.5 mm from a root. Whilst no measurements have been made for field grown wheat it seems likely from work on other plants (Smith *et al*., 1986) that this is a minimum value for a plant approaching maturity. Sinclair *et al*. (1990b) calculated the period of time required to deplete the soil solution of Mn and Zn (T) as:

$$T = \frac{C \times \left(d \, \frac{100}{100 - m}\right)^{-1} \times D \times V_f}{L \times I} \quad \text{days}$$

where C is the concentration of Cu, Mn and Zn in the soil solution in mol L^{-1}. D is the depth of sampling in mm, d is the soil dry bulk density (g cm^{-3}), m is the moisture content of the fresh soil (%), L is the length of root (mm^{-2}), I is the calculated inflow rate (mol m $root^{-1}$ day^{-1}) and V_f is the volume fraction of the soil in the root zone, assumed to equal 0.5.

The inflow of Cu, Mn and Zn, calculated for above-ground material only, was at a maximum in July at 0.43×10^{-9}, 11.6×10^{-9} and 1.6×10^{-9} mol m $root^{-1}$ day^{-1} for Cu, Mn and Zn respectively (Sinclair *et al*., 1990b). It is already clear that mobilisation within the root-zone provides a reservoir of soluble Cu, Mn and Zn available for uptake by the crop. From the values calculated for this reserve and from the inflow rates the time required for depletion of the reserve was calculated by Sinclair *et al*. (1990b), assuming no other changes (Table 2).

Table 2. Length of time (days) required for crop uptake to deplete the soil solution of Mn and Zn at 4 dates.

Element	8 May	21 May	4 June	3 July
Cu	121.0	9.6	0.8	1.6
Mn	12.6	7.6	4.4	0.8
Zn	20.9	1.8	3.4	1.7

It is clear from the data shown in 2 that these three elements in the soil solution are depleted more rapidly between 8th and 21st May in this experiment, than would be expected from inflow rates. Later in the season calculated inflow rates were such that they could only be sustained by continuous and rapid mobilisation from insoluble forms. Thus, although depletion rates are driven by nutrient uptakes generated by crop growth, they will be modified and limited by the balance between mobilisation and immobilisation within the root-zone which depends on microbial activity controlling the flux of organic ligands.

3. MAGNESIUM

Recent estimates suggest that foliar Mg sprays are applied to approximately 3-5% of the UK cereals area each year, but very little or no Mg-containing fertilisers are applied as soil dressings specifically for cereal crops. However, some Mg is applied to a small proportion of the cereal area each year as magnesian limestone.

3.1 Function and uptake

Function

Magnesium is a major element which is an essential component of chlorophyll and is involved in a number of enzyme-driven plant physiological processes including phosphorylation, assimilation of carbon dioxide and protein synthesis. About 10 per cent of the magnesium in plant leaves is associated with chlorophyll, the remainder is present in various forms, either in the ionic state or bound in complexes with organic constituents.

Uptake

In common with other major nutrients, magnesium uptake reaches a maximum at soft dough stage in cereal crops. Cereals have relatively low magnesium concentrations, typically ranging from 0.1 to 0.2% in leaves, which tend to decrease as the season progresses. This variation reflects both the ability of different soils to supply Mg and the large influence that plant rooting density and seasonal weather patterns exert on Mg uptake by the plant. The uptake of Mg at the root surface is also highly dependent on concentrations of other cations (calcium, potassium and ammonium) in the soil solution and when these are in plentiful supply, especially K, the uptake of Mg is poor (Mengel & Kirkby, 1987). Magnesium uptake is enhanced by some anions such as nitrate and phosphate. Magnesium is very mobile within the plant, and, during reproductive stages of growth, Mg moves readily within leaves and to the developing grain. Magnesium enrichment of the grain occurs towards the ripening stage, so that ripe cereal grain contains about 0.12% Mg, while the Mg content of the straw can be as low as 0.05%. The amounts of Mg removed in grain and straw at harvest are typically 1.2 kg and 0.8 kg per tonne (fresh material) respectively and, in the majority of soil types, soil Mg reserves will gradually become depleted unless Mg is applied at some stage in the crop rotation.

The absence of widespread magnesium deficiency on chalk soils, despite often low extractable soil Mg levels, suggests that the calcium/magnesium interaction is not as dominating as the potassium/magnesium interaction. An application of ammonium-nitrogen to crops suffering from magnesium deficiency can temporarily intensify the symptoms, but when the ammonium-nitrogen has been converted to nitrate, the plant is then better able to use the available magnesium. Crops are more likely to show symptoms of magnesium deficiency when there is poor nitrogen uptake (Archer, 1985).

3.2 Deficiency

Soil factors

Only a small proportion for the total soil content of Mg is available for plant uptake, availability of supply being dictated by the amount of exchangeable Mg held on soil particles. there is very little release of Mg from soil organic matter. An absolute shortage of Mg is most likely to be found on sandy soils with low cation exchange capacity, especially where the latter is dominated by other cations (i.e. very acid or alkaline soils) and Mg is subject to leaching loss. On heavier soils, weathering of soil minerals is sufficient to maintain a satisfactory pool of exchangeable Mg and solution concentrations are relatively high.

Data from the Representative Soil Sampling Scheme (Skinner *et al*., 1992) showed that only 3% of arable fields) in England and Wales were deficient (Index 0, <26 mg/litre Mg; Anon., 1994) in Mg. Results from the National Soil Inventory for England and Wales show a median value of 98 mg/litre (Index 2) for extractable magnesium concentration in topsoils (McGrath & Loveland, 1992). These results indicate that most arable soils have an adequate magnesium status for cereal cropping. Some Mg, on average about 4 kg/ha/year (Anon., 1998b), is supplied from rainfall and other forms of atmospheric deposition, this input can be as high as 10 kg/ha/year near to coastlines.

Symptoms of magnesium deficiency, where they occur in cereals, are much more likely to have been induced by poor soil conditions or other factors which restrict root development and magnesium uptake, rather than an absolute shortage of magnesium in the soil. Soil compaction and surface capping, also root damage due to pest attack e.g. cereal cyst eelworm or disease infection e.g. take-all, may induce magnesium deficiency.

Symptoms

Although cereal crops are much less susceptible to magnesium deficiency, compared with sugar beet and potatoes, deficiency symptoms are fairly common in cereals, particularly in spring, and are mainly caused by adverse soil and weather conditions. Spring cereals develop marked symptoms of magnesium deficiency if very cold dry conditions prevail early in the season; the appearance of these latter symptoms usually coincides with a delay in the emergence of secondary roots. Although visual symptoms may be very marked, even prolonged deficiency usually has only a small effect on plant growth and yield is only slightly affected.

Magnesium deficiency causes leaf chlorosis, because of the association of this element with chlorophyll. Symptoms appear initially in the older leaves. In oats, dark-green spots show in a regular pattern between the veins on a pale yellowish green background, producing a 'beading' effect which is best seen when a blade is held up to the light. When the deficiency is severe, irregular whitish necrotic strips develop between the veins. the 'beading' is less marked in wheat and is difficult to detect in barley. Tips and leaves of the latter become yellow or orange and in severe cases older leaves wither. These symptoms should not be confused with the chlorotic 'beading', distributed irregularly over the leaves of some varieties of wheat, that is due to a physiological cause apparently unconnected with magnesium deficiency.

Symptoms are often transient on soils of adequate Mg status and usually coincide with periods of rapid growth as Mg is transported from older leaves to younger, expanding leaves. Under these conditions Mg fertilisation via foliar sprays is unlikely to be worthwhile (Archer, 1985).

3.3 Yield response

Compared with other nutrients, relatively few experiments have been carried out to test the yield response of cereals to magnesium applications. However, results from both earlier and more recent trials have shown that yield responses to magnesium fertilisers are rare. Slight symptoms of magnesium deficiency produce no measurable effects on yield and even severe symptoms may only cause moderate yield reductions. As cereals have a relatively small demand for Mg, high yields can be obtained with a relatively low intake of Mg.

ADAS experiments in south-east England compared different forms of soil - applied magnesium at one, sandy loam site in 1961 and 1962, cropped with winter wheat followed by spring barley, and at two loamy sand sides in 1962 which were cropped with spring barley (Charlesworth, 1967). All three sites had low soil magnesium status prior to treatment applications. Deficiency symptoms were obvious in the winter wheat, but not in the spring barley test crop. However, the yield responses obtained from magnesium in the wheat crop were not statistically significant, but one site gave a significant yield increase of 0.5 t/ha (+17%) from the lowest rate (63 kg/ha) only of calcined magnesite which was tested at that particular site. For all the cereal test crops, increases in leaf and/or available soil magnesium cereals reflected the relative solubilities of the magnesium forms applied.

Experiments in Scotland during the 1960s on soils with low magnesium status showed a significant yield increase of 0.16-0.3 t/ha (4-8%) in oats at one site, but no significant responses in barley at two other sites (Reith, 1967).

ADAS experiments between 1983 and 1988 at two barley and two winter wheat sites on shallow chalk soils with low to moderate (20-30 mg/litre, Index 0-1) soil Mg status in Berkshire and Hampshire tested foliar sprays of Epsom salts, at 20-30 kg/ha during early stem extension, and/or soil applications of kieserite at 50-100 kg/ha. One winter wheat site also tested calcined magnesite, applied at 100 kg/ha. None of the sites showed any response in grain yield from foliar or soil applied Mg (Chalmers, unpublished).

There has been considerable commercial pressure in past years to apply minor and trace elements in situations where responses would not normally be expected. ADAS Crop Centre federated trials on winter wheat in 1990/91 at six such sites, ranging in texture from sandy loam to silty clay loam, tested a range of foliar treatments containing magnesium, sulphur, manganese or other micronutrients which were mostly applied as single timings at either GS31 or GS39. No deficiency symptoms were observed at any site and there were no benefits in either grain yield or quality from any of the micronutrient applications (Grylls, unpublished). Untreated yields at individual sites ranged from 7.6 to 9.3t/ha. A more limited range of treatments, testing foliar sulphur and trace element 'cocktail' treatments applied at GS31 or as GS31+GS59 splits, at four sites on medium and heavy textured soils in 1990, had also shown no significant treatment effects on winter wheat yields, which ranged from 8.3 to 8.6 t/ha across sites and treatments.

ADAS Crop Centre trials on winter wheat at two sites in 1994 and one site in 1995, on medium or heavy textured soils, tested applications of magnesium, also copper, manganese and sulphur either singly or as different combinations. None of the sites showed a significant yield benefit from any of the treatments (Simpson, pers.comm.).

A three year study from 1995 to 1997 in the ARC Northern Region studied the yield response of winter wheat (cv Hereward) to a foliar Mg spray, also to separate foliar applications of boron or manganese at the same sites. In 1995 leaf tissue samples were taken at GS30, just prior to product applications, for analyses (Table 3). Leaf analysis indicated a low, but not deficient magnesium content at the time of tissue sampling, while boron and manganese concentrations were adequate. Neither Mg or any other element application produced a significant yield response.

Table 3. Nutrient concentrations in Untreated plants and treatment yields, 1995 ARC site

Product Application	Leaf Tissue (Untreated, GS30)	Yield (t/ha)	% of Untreated
Untreated		6.67	
Magnesium (5l/ha)	0.13%	6.61	99.1
Manganese (2.25l/ha)	53ppm	6.63	99.4
Boron (5l/ha)	5.9ppm	6.80	101.9
CV 3.83%	LSD 0.44t/ha		

In 1996 the experiment monitoring was extended to cover several sampling dates of both soil and plant tissue element contents. In each case the analyses given are those of the untreated crop (Table 4). The April tissue analysis indicated a marginally deficient magnesium, and low manganese status. The sequential analysis also revealed some considerable temporal variation between sampling dates for Mg. None of the nutrient applications gave a significant yield response.

Table 4. Plant and soil nutrient concentrations in Untreated plots and treatment yields, 1996 ARC site

Product	Soil Analysis		Tissue Analysis			Yield	% of
Application	9 May	18 June	9 April	9 May	20 June	(t/ha)	Untreated
Untreated						9.14	-
Magnesium (5.0 l/ha)	81	112	0.10	0.15	0.24	9.30	101.8
Manganese (2.25 l/ha)	172	190	29	33	42	9.32	102.0
Boron (5.0 l/ha)	1.0	1.0	8	3.5	7.7	9.20	100.7
Copper (0.5 l/ha)	10.6	14	10	34.7	6.2	8.89	97.3
CV 3.18%	LSD 0.52t/ha						

Soil and plant tissue samples were taken for analysis (again presented as untreated crop) on five and seven occasions respectively at the site in 1997 (5). Soil and leaf analyses suggested a satisfactory nutrient status for both Mg and the other elements, although leaf nutrient concentrations tended to vary considerably between sampling dates.

Table 5. Plant and soil nutrient concentrations in Untreated plots, 1997 ARC site

Sampling date	Mg	Mn	B	Cu
Soil Analysis (ppm, 0-30cm)				
8/11/96	46	578	1	4.7
12/2/97	40	-	1.2	6.4
14/3/97	40	527	1	6.4
8/4/97	37	542	1.1	6.9
6/5/97	47	464	1.4	6.3
Leaf Analysis	%	ppm	ppm	ppm
3/12/96	0.12	66	2.7	0.3
28/1/97	0.15	172	5.2	9.1
12/2/97	0.14	103	7.4	11
14/3/97	0.11	68	2.8	7.4
8/4/97	0.11	57	1.3	6.4
6/5/97	0.11	43	3.7	7.2
3/6/97	0.17	97	9.2	3.7

None of the element applications produced a significant yield response (Table 6).

Table 6. Effect of nutrient applications on winter wheat grain yield, 1997 ARC site

Treatment	Yield (t/ha)	% of Untreated
Untreated	7.99	100
Manganese (2.25l/ha)	7.89	98.7
Boron (5.0l/ha)	8.02	100.4
Magnesium (5.0l/ha)	8.17	102.2
Copper (0.5l/ha)	7.83	98.0
CV 3.07%	LSD 0.44t/ha	

3.4 Grain quality

In Germany, foliar applications of Epsom salts (as Bittersalz) between ear emergence and end of flowering (GS60-69) have been commonly used on cereals, with the aim of improving grain weight and hence yield, even on soils with high magnesium status. This supplementary input of magnesium during the grain fill period may reduce the amount of magnesium translocated from flag leaves and other parts of the plant to the grain, which would help to maintain photosynthetic activity, particularly in dry conditions when further magnesium uptake from the soil will be restricted. Commercial trials have apparently given worthwhile yield increases to such applications of Epsom salts in Germany. However, the S content, present as sulphate, of Epsom salts may be a contributory factor to any yield response obtained from late foliar applications.

A trial in 1990 on shallow chalk with a satisfactory magnesium status (Index 2) in the topsoil at ADAS Bridgets, Hampshire showed increases in leaf and grain magnesium concentrations, but no significant effects on either grain yield or quality, from foliar applications of 25kg/ha of Epsom salts at GS59 and/or GS69 (Froment, unpublished).

3.5 Diagnosis and treatment

Soil and leaf analysis, also examination of soil physical conditions, should be used to confirm a visual diagnosis of suspected Mg deficiency.

Leaf and soil analysis

In the UK, a leaf Mg concentration of less than 0.1% (DM basis) is considered to be deficient for cereals. Scott & Robson (1991) found, using solution culture, that deficiency symptoms occurred in wheat if the leaf tissue contained <0.12% Mg, irrespective of leaf age. The minimum Mg concentration, both in whole shoots and the youngest enlarged leaf blade, which still gave maximum short weight was about 0.09%. Deficiency symptoms were apparent on young leaves before any reduction in shoot weight was detected.

Soil analysis, along with examination of the soil structure and crop root development will identify whether a deficiency of Mg in the growing crop has been caused by a deficiency in the soil and/or restricted root activity due to poor soil or weather conditions. An absolute deficiency (less than 20-25 mg/litre, Index 0) of Mg for cereal cropping is usually confined to light sandy soils, which have inherently low Mg reserves and are more prone to Mg leaching, and is a less frequent cause of deficiency symptoms than those produced by adverse soil conditions. Magnesium deficiency induced by over-use of potassium is seldom encountered in arable rotations. The effect of an imbalance is not likely to be very great unless the ratio of available K:Mg is well above 5:1.

Treatment

Symptoms of magnesium deficiency caused by adverse soil conditions cannot be cured by treatment with magnesian compounds, though a temporary improvement in the colour of the crop can sometimes by achieved by the use of foliar sprays. Severe Mg deficiency is possible where prolonged stress conditions coincide with a low Mg content in the soil and, although very seldom seen, are conditions under which a yield penalty can be expected.

Magnesium fertiliser can be applied to soil either as magnesium limestone or as magnesium sulphate (Kieserite) to correct a soil deficiency of Mg. Magnesium limestone is not recommended where soil pHs are already adequate for plant growth at pH 6.5 or more. Currently recommended inputs of K fertiliser to satisfy the maintenance requirements of cereal crops (35-90 kg/ha) are not sufficient to significantly antagonise the uptake of Mg on most soils. Residues from magnesium applications for potatoes or sugar beet, where these crops are grown in the rotation will meet the requirements on subsequent cereal crops (Anon., 1994). Otherwise, magnesium fertiliser for cereals is only likely to be justified if the soil is at index 0 (less than 26 mg/litre) and, in this situation, 85 kg/ha MgO should be applied every three or four years.

A laboratory incubation study by Heming & Hollis (1995) evaluated the effectiveness of kieserite granules, calcined magnesite as powder or granules and magnesium limestone as magnesium fertilisers. The results confirmed previous findings (Draycott *et al*., 1975) that kieserite is the most reliable product for raising low soil magnesium status. The limited study also showed that the lower recovery of magnesium from calcined magnesite in calcareous compared with non-calcareous soils appeared to be mostly due to particle size effects rather than soil pH, in contrast to the large effects of pH on magnesium availability previously reported by Draycott & Durrant (1972) for calcined magnesite. Bolton (1973) tested the effects of different forms of magnesium application to a sandy soil, on wheat as well as sugar beet and potato crops.

Soil applications of magnesian fertiliser are more reliable than foliar sprays of Mg obtaining a yield response on soils with low Mg status. However, Mg is very mobile within the plant and foliar sprays can rapidly relieve the visual symptoms where the deficiency is identified in the growing crop. In this situation, a foliar application of 20 kg/ha Epsom salts plus non ionic wetter may be worthwhile, if symptoms persist. Biosolids and livestock manures generally contain small to moderate amounts of total magnesium, relative to cereal crop requirements, and are a useful source of this nutrient (Nicholson *et al*., 1997).

4. SULPHUR

In areas of low S deposition, S deficiency is usually detected first on oilseed rape and has then developed on cereal crops a few years later. Yield responses in cereals to sulphur application were first obtained in the early and late 1980s in Scotland and England respectively. The incidence of S deficiency in cereals crops has increased since then as a result of the continuing decline in the atmospheric deposition of S. In 1998, about 15% of the total UK cereal area was treated with an S-containing fertiliser, at average rates of 11-15 kg/ha S (27-38 kg/ha SO_3) according to cereal type (Source: British Survey of Fertiliser Practice). This chapter summarises and updates information in the HGCA-funded review by Withers & Sinclair (1994) on the sulphur requirement of cereals.

4.1 Function and plant uptake

Function

Sulphur is an essential component of the amino acids cysteine and methionine and is required for a number of important enzyme reactions controlling metabolic and growth processes within plant cells (Mengel & Kirkby, 1987). Sulphur is taken up by plants in the form of SO_4-S, which is then activated by reaction with adenosine triphosphate (ATP) and reduced to sulphide form prior to the incorporation into cysteine. Cysteine provides the sulphydryl (S-H) group required to form the disulphide (S-S) link between protein chains (polypeptides) and the oxidation-reduction reactions associated with the S-H groups in cysteine are an essential part of cell enzyme activity. Cysteine-rich proteins and enzymes (e.g. ferredoxin and ribulose biphosphate dehydrogenase) play an active part in photosynthesis and assimilation of carbon dioxide in actively growing tissue. Methionine is considered to be the basic building block from which plant proteins are synthesised and the methyl group of methionine is involved in chlorophyll formation, as is visually apparent when S is in short supply. Sulphur is also a component of coenzyme A, which has an important role in fatty acid and lipid metabolism, and of the vitamins biotin and thiomine (Vitamin B).

Plant uptake

The amount of S in a cereal crop at harvest can range between 7 and 30 kg/ha, depending on both S supply and yield level, although most crops contain nearer to 15 kg/ha (Withers *et al*., 1997). The total crop requirement for S, however, may be larger than the offtake at harvest, as maximum S uptake in winter wheat occurs at, or shortly after, anthesis and declines thereafter (Gregory *et al*., 1979). Up to 50% of the total S taken up at anthesis may subsequently be lost by harvest, probably due to leaching losses from senescing leaf tissue and the translocation of S from the shoots and roots back to the soil. Data reported by Withers *et al*. (1997) from HGCA-funded experiments in 1993 and 1994 agree with this pattern of uptake. More detailed information on the pattern of S uptake, distribution and subsequent translocation within the plant during the growing season is reported by Withers & Sinclair (1994).

The relationship between grain yield and S uptake by the whole crop is less close in winter wheat than in oilseed rape but, as a general guide, winter wheat needs at least 2 kg/ha S per tonne of grain produced to ensure S sufficiency. Breadmaking varieties have approximately 10% greater S concentrations in grain than non-breadmaking varieties, as the former have higher grain protein concentrations, but grain N:S ratios are remarkably similar (McGrath *et al*., 1993; Zhao *et al*., 1995). Although breadmaking varieties contain more S in grain, the total S uptake is generally similar to that of non-breadmaking varieties, which tend to give higher yields (McGrath *et al*., 1995). Malting varieties of barley show similar grain S concentrations to feed varieties (Withers *et al*., 1997).

4.2 Soil and atmospheric sulphur supply

Supplies of S from the soil and the atmosphere used to be sufficient to meet the S demand of cereals grown on all soil types. However, coarse textured and shallow arable soils in areas of low S deposition within the UK now require S fertiliser inputs to prevent deficiency in cereals and other susceptible crops, because of depleted soil S reserves.

Atmospheric deposition

According to Unsworth & Fowler (1985), S is deposited from the atmosphere in gaseous form (dry deposition), in mists and fog (occult deposition) and in rain (wet deposition). In the major cereal growing areas of the UK, the majority of atmospheric S deposition is in the form of gaseous sulphur dioxide (SO_2), of which up to 50% may diffuse directly into the leaf through the stomata. The amount of dry S taken up at any given location depends on diurnal changes in the concentration of SO_2 in the atmosphere and the rate at which it is delivered to the leaf surface. In areas remote from industrial activity, where dry deposition of S is very low, wet deposition takes on greater significance.

Total emissions of sulphur dioxide in the UK have decreased steadily, from 6.4 to 3.2 million tonnes between 1970 and 1993, following international agreements on target reductions in emissions (DoE, 1995). By 1992, most of the UK was receiving less than 30 kg/ha S annually from atmospheric deposition, with most of southern England, also Wales, the Scottish Borders and all of Scotland., a significant proportion receiving less than 20 kg/ha and the East of Scotland, Devon, Cornwall and West Wales down to below 10 kg/ha (McGrath *et al*., 1996). Subsequent information suggests that most rural areas probably now receive a total of only 5-15 kg/ha S each year, because of further reductions in sulphur dioxide emissions from power stations (Campbell & Smith, 1996). Consequently, a significant percentage of arable land is now at risk from sulphur deficiency and this will increase as further reductions in emissions are achieved by 2003.

Mineralisation and immobilisation processes

The soil S supply depends on the amount of SO_4-S in solution and adsorbed onto soil surfaces, and on the microbial mineralisation, or hydrolysis by extracellular enzymes, of carbon (C)-bonded and ester-sulphate forms of S in the organic matter. Temperature, moisture, pH and substrate supply all have an important influence on S mineralisation. Mineralisation decreases markedly at temperatures below 10^{o}C, so it is very limited during much of the winter and early spring in UK soils. Laboratory incubation studies have indicated a wide range of mineralisation rates(Zhao *et al*., 1996) and the extrapolation of these results to field conditions is therefore difficult. Mineralised S may represent only 1-3% of total organic S (McGrath *et al*., 1996). The mineralisation process results in variable amounts of SO_4-S in soils during the growing season (Castellano & Dick, 1990). The amounts of SO_4-S mineralised in UK soils are generally considered to be low, especially in fields in continuous arable rotation with low organic matter levels, whilst SO_4-S is rapidly immobilised in soils which are accumulating organic matter (Syers *et al*., 1987). Little information is available for arable systems but Kirchmann *et al*. (1996) estimated that soil total S was decreasing at rates of 2-6 kg/ha$^{/}$year where there was nil input of S fertiliser in a long term continuous arable experiment, as a result of net mineralisation. In this experiment, the S added to the soil in various organic manures had a half-life of between 23 and 38 years.

Immobilisation of sulphate into organic forms in the soil, primarily by microbial activity which converts S into microbial biomass, can take place fairly rapidly (Zhao *et al*., 1996a). The rates of sulphate immobilisation are greatly influenced by substrate availability. Addition of organic carbon (C) sources, such as plant residues, greatly increases S immobilisation, which is positively correlated with the C:S ratio of the amended substrate. Incorporation of cereal straw, which has a wide C:S ratio, thus enhances S immobilisation and, in the short-term, decreases the availability of S to crops (Wu *et al.,* 1993). A potential benefit of immobilisation is that leaching losses may be decreased.

Soil type, crop rooting depth, land management practices and seasonal variation in soil microbial transformations are all important factors in the release, retention and supply of S in soil, as reported by Withers & Sinclair (1994).

Sulphur leaching

Leaching of S is a major pathway of S loss from agricultural land. Such losses are mainly in the form of sulphate, although a considerable amount of organic S is also soluble in water and prone to leaching (Arowolo *et al*., 1994; Zhao & McGrath, 1994). Factors such as climate, the S retention capacity and water holding capacity of the soil, crop growth and management practices all have an important influence on S leaching. Most UK soils have a limited capacity for sulphate adsorption. Water and 0.05M KH_2PO_4 extracted very similar amounts of sulphate for a range of UK soils with pHs above 6.0 (Curtin & Syers, 1990). This suggests that virtually all of the indigenous sulphate was in the soil solution and consequently, highly susceptible to leaching. Several studies here show that fertiliser S not used by crops is highly susceptible to leaching and therefore application of fertilisers containing sulphate in autumn should be avoided (*e.g.* Bristow & Garwood, 1984).

More detailed information on the sulphur cycle and turnover of soil organic sulphur is given in the review by Zhao *et al.* (1996).

4.3 Sulphur modelling

Syers *et al.* (1987) identified a need for a modelling approach which, in its simplest form, should be capable of predicting whether or not sulphur fertiliser is needed and should be further developed to provide information on amounts, form and timing of fertiliser sulphur application. A qualitative, risk assessment model was subsequently developed by McGrath & Zhao (1995). The model requires information on the atmospheric sulphur deposition and various soil characteristics as inputs. A sulphate leaching index is then constructed, according to rainfall, soil type, texture and pH. Potentially mineralisable sulphur in soil is calculated from the organic matter content. Sulphur depositions, the potentially mineralisable pool and sulphate leaching index are then combined and compared to the optimum sulphur requirement of a crop, to produce a deficiency risk assessment.

This model predicted that 11% of the UK land area is at high risk of S deficiency for cereals, and a further 22% at medium risk. The high risk areas are in south-east Scotland, the Scottish Borders, East Anglia, the Welsh Borders and south-west England. These areas are characterised by small inputs of S from the atmosphere, low content of soil organic matter and light soil texture. The model also predicted the medium and high risk areas will increase to 27 and 22% respectively by 2003, when the sulphur dioxide emissions in the UK are set to decrease to 40% of the 1980 level. As the high and medium risk areas coincide with the major arable areas in the UK, the extent of potential sulphur deficiency in cereals and other arable crops is actually much greater than these percentage figures. This modelling approach provides a large scale, national assessment but there is currently insufficient information available to enable the construction of a quantitative model for obtaining specific sulphur recommendations on an individual field basis. Such a model would require site-specific details of the sulphur immobilisation and mineralisation in soil, sulphate leaching and the pattern of crop sulphur uptake (McGrath *et al.,* 1996).

4.4 Changes in crop S status

The concentrations of S in UK wheat grain decreased considerably over the decade between the early 1980s and early 1990s and can largely be attributed to the decrease in S inputs from atmospheric deposition. The mean concentration of S in grain in a total of 793 samples collected in 1992 and 1993 was 1.35 mg/g (McGrath *et al*., 1995), which was much smaller than the mean of 1.72 mg g^{-1} for the samples obtained in an earlier survey during 1981 and 1982 (Byers *et al*., 1987a). None of the samples in the first survey was sulphur deficient, but the regional pattern of grain sulphur concentration corresponded closely with the estimated atmospheric sulphur inputs at that time. The mean N:S ratio increased from 12:1 in 1981-82 to 16:1 in 1992-93. Grain samples with low S concentrations in the later survey were located mainly in Scotland, Northern England, and the West and south-west of England, whereas samples from central England tended to have higher S concentrations. In 1992 and 1993, 7 and 26% of the samples had S concentrations below the critical value of 1.2 mg/g, respectively, whereas 10 and 7% of the samples had an N:S ratio greater than the critical value of 17:1. Breadmaking varieties had significantly higher grain N and S concentrations than other varieties, but little difference was found between varieties in grain N:S ratio. For the varieties Mercia in both 1992 and 1993 and Hereward in 1993, grain S concentration correlated better with loaf volume than grain N concentration (McGrath *et al*., 1995).

A separate survey, carried out by ADAS on cereal crops in England and Wales in both 1992 and 1993, gave similar results (Withers *et al*., 1997). In this survey, representative leaf and grain samples were collected from commercial winter wheat and winter barley crops at over 90 locations in England and Wales each year. The survey showed that the proportion of winter wheat and winter barley crops with low concentrations of S was related to the proportion of the crops grown on sandy soils each year. Both leaf and grain S concentrations were generally greater in wheat crops than in barley crops. Leaf S contents were significantly lower in malting varieties than in feed varieties of barley, but were not significantly different between breadmaking and feed varieties of wheat. Grain S and N:S ratio contents were generally lowest in malting barley varieties and greatest in breadmaking wheat varieties.

A small-scale ADAS Crop Centre survey of leaf sulphur levels in winter wheat crops on members' farms in 1996 indicated that 15% of the samples analysed were borderline for deficiency, according to total leaf sulphur concentration (Simpson, pers. comm.). None of the samples had N:S ratios above 16.0:1.

4.5 Deficiency

Susceptible soil types

Sulphur deficiency in cereal crops is likely to occur where crops are grown on sandy or shallow soils in long term arable rotations with little or no input of organic manure, in areas of the UK where atmospheric S deposition is now less than 20 kg/ha each year. Eastern Scotland, Scottish borders, East Anglia, South and South-west England, Shropshire and South Wales are the main areas where there is currently a risk of S deficiency on these specific soil types, especially where large amounts of N are applied. In future, medium and eventually some heavier textured soils are also expected to become S deficient.

Symptoms

Sulphur deficiency symptoms appear in cereals as a paling or slight yellowing of the youngest leaves during late stem elongation, when a continuing crop demand for S exceeds the supply from the soil and the atmosphere. The bottom leaves remain green, reflecting the low mobility of S once it is taken up by the plant. Symptoms typically occur in random patches across fields, which take on a freckled appearance from a distance. Sulphur deficiency also causes crop stunting, leaf narrowing and subsequently reduced grain yield. Yield losses may be due to reduced numbers of fertile ears (*e.g.* Taureau *et al*., 1987) and/or a reduction in the number of grains per ear (*e.g.* Scott *et al.,* 1984) rather than a reduction in grain size. Seasonal factors which may influence the occurrence and severity of deficiency in field crops were outlined by Withers & Sinclair (1994).

4.6 Yield response

Withers & Sinclair (1994) summarised work on grain yield responses, ranging from 10 to 100%, which had previously been obtained from S applications to cereals, mostly on sandy soils with low S status, in the USA, Australia, France and Germany. Findings from the numerous pot and/or field experiments which were carried out in the UK between the mid 1970s and early 1990s on the effects of S supply on cereals were also summarised by Withers & Sinclair (1994). The range of yield responses obtained across different sites between 1987 and 1995 are summarised in Table 7. Overall, yield increases in response to S application were obtained in 38 and 24% of the trials on barley and wheat respectively. There were also a number of experiments where S deficiency symptoms were observed but yield increases were not significant.

Table 7. Effects of S on yields of cereals in the UK and Ireland, 1987-95

Crop	Year of Trials	Responsive trials/No. of trials	% Yield increase at responsive sites	Locations of responsive sites	References
Barley	1987-1990	3/10	5-11	South Wales and Devon	Withers et al, 1995;
	1986-1990	3/6	9-32	Ireland	Conry, 1993
Wheat	1993	5/18	4-18	England and Scotland,	McGrath *et al*., 1995
	1994	3/19	5-9		
	1995	2/4	12-40		Zhao *et al*., in press

Sulphur deficiency symptoms were first reported in winter cereals in Scotland and Ireland during 1983 but were not observed in England and Wales until 1989. In Scotland, significant (P<0.05) yield increases, ranging from 0.26 to 1.05 t/ha, were obtained from S applications to winter cereals and spring barley at 6 sites, all located in north-east Scotland, out of a total of 33 sites between 1982 and 1988. In 1983, 'tramline comparisons' at four sites in north-east Scotland on sandy soils developed over fluvioglacial gravel had also shown yield responses in winter barley of between 5 and 28% (Scott *et al.,* 1984). In Ireland, yield responses ranging from 9 to 32% were obtained at 3 out of 6 barley sites between 1986 and 1990 (Conry, 1993). In England and Wales, only 3 out of 61 comparisons had given statistically significant positive responses to foliar sprays of elemental S up to 1985 (Syers *et al*., 1987). No further significant S responses were obtained in field experiments until 1990 when, averaged across all the S treatments tested, responses of 0.4 t/ha (6%) were recorded at 2 sites in Wales and one site in south-west England. No symptoms of S deficiency were recorded at these sites. However, a visual response to applied S was obtained in winter wheat (cv *Mercia*) on a loamy sand soil in Somerset in 1989 (Withers, 1993). This was the first occasion that S deficiency symptoms had been recorded in a field experiment in England and Wales and concentrations of S in leaf and grain were well below the critical thresholds for deficiency. A yield increase of 0.61 t/ha (10%) at this site was not, however, statistically significant.

In response to increasing concern over the effect of S deficiency on grain yield and quality in winter wheat, a number of HGCA-funded field experiments have been carried out since 1988. During 1988 to 1990, the impact of a foliar spray of elemental S (10 kg S/ha), applied in conjunction with foliar urea at milky ripe stage (GS 75) was tested on grain yield and baking quality in winter wheat. No statistically significant yield responses were obtained at any of the sites, although the lack of response may have been due to the method of S application rather than a lack of deficiency (Dampney *et al*., 1995).

The effects of S, applied as a spring dressing of potassium sulphate at a rate of 40 kg/ha S, were tested on the grain yield of winter cereals at 21 and 19 potentially S-deficient sites around the UK in the 1992/93 and 1993/94 seasons, respectively (Withers *et al.,* 1997). Yield responses were obtained at three sites at a significance level of $P<0.05$ in both 1992/93 and 1994/94 seasons, and at two further sites at $P<0.10$ in 1992/93. The yield increases from S application ranged from 4 to 18%. The responsive sites were located in Scotland, Scottish Borders, East Anglia and south-west England. The geographical distribution of the responsive sites agreed well with the model prediction produced by McGrath & Zhao (1995) and therefore validated the modelling approach. However, soil extractable S in spring was not a good indicator of S supply, nor was whole crop analysis. There was also no clear relationship between either grain S concentration or N:S ratio and yield response.

Distinct S deficiency symptoms were observed at one site in 1993 and seven sites in 1994. At sites showing deficiency symptoms, S application significantly reduced thousand grain weight but did not always increase grain yield. Soil extractable sulphate S in spring and uptake of S by full flag leaf emergence stage were significantly lower in 1994 than in 1993, relating to a 30% higher average winter rainfall over the 1993/94 winter compared to the previous winter. The average recovery of applied S was <10% in both years. Analysis of individual leaves undertaken in 1994 indicated that yield responsive sites could best be predicted by total S an N:S ratio analysis of second and third leaves at flag leaf emergence or at anthesis, but critical values could not be reliably estimated and were different for the two growth stages. The results indicated that further work was required, to develop a more reliable predictive or diagnostic indicator for S deficiency in cereals.

A series of ARC experiments tested the effects of S application on winter wheat over a total of six seasons. At each site, both soil and leaf tissue samples were taken at several stages during the growing season from untreated plots for S analysis and the results were compared against the subsequent yield response to applied S. The Louth site (cv. Hereward) in Lincolnshire, which had received an application of Gypsum the previous season, showed a high soil S status but some low leaf S contents during the autumn to spring sampling period (Table 8).

Table 8. Extractable soil S (ppm) and leaf S (%)in Untreated plots for sequential sampling dates, ARC Louth site

Sampling date	Extractable soil S			Leaf S
	0-30cm	30-60cm	60-90cm	
November 6	177	128	97	0.24

December 12	215	240	193	0.16
January 21	121	135	140	0.28
February 12	140	148	203	0.21
March 14	149	142	102	0.18
April 6	177	166	155	0.26
April 25	88	92	104	0.28
May 6	89	92	100	0.17

No significant yield responses were obtained at this site from S, which was applied as Red or White Gypsum in either autumn or spring at different rates (Table 9).

Table 9. Effect of gypsum application on winter wheat grain yields, ARC Louth site

Treatment - timing and product rate GS 13 (8/11/96)	GS 24 (14/2/97)	Yield (t/ha)	% Untreated
Untreated control		8.11	100
	30kg Red Gypsum	8.34	103
	45kg Red Gypsum	8.17	101
	45kg White Gypsum	8.16	101
	60kg Red Gypsum	8.14	100
45kg White Gypsum		8.13	100
45kg Red Gypsum		8.09	100
	30kg Red Gypsum	8.02	99

CV 1.90% LSD 0.27t/ha

The other ARC trial sites were located on soils with low S status (less than 4 ppm extractable S) in Dorset and tested a range of S-containing products at different application rates of S. In the first two seasons yield responses were +10% and +11% from the addition of S (Table 10). In 1996 and 1997, however, no yield responses were obtained from S applications despite low soil S and, when tested in May, low leaf S contents in untreated plots.

Table 10. Extractable soil S (ppm) and leaf S(%) in Untreated plots and yield response (%) to applied S, ARC Dorset sites 1994-97

Year	Sulphur rate (kg/ha)	Extr. soil S	Leaf S	Yield Response
1994	53	4	n/a	+10
1995	57	2	n/a	+11
1996	57	4	0.08	Nil
1997	57	3	0.15	-4

These results agree with the findings from other research work which have shown that soil analysis for extractable S, and leaf analysis prior to flag leaf emergence (GS39) for total S, do not reliably predict the risk of S deficiency in cereal crops. Leaf analysis between flag leaf emergence and mid-flowering (GS39-65) is, however, a good indicator of crop S status.

Cereals have produced yield responses to S fertilisers ranging from 4 to 40% across S deficient sites in the UK, but these have been confined so far to sandy or shallow soils in areas where the amounts of S deposited from the atmosphere are low (<20 kg/ha). As has been shown for winter oilseed rape (McGrath *et al*., 1996), the correct balance of N to S is an essential requirement for the satisfactory growth and development of cereals. Withers & Sinclair (1994) concluded that there was clear evidence for a strong interactive effect of crop N and S supply on either dry matter production or grain yield of cereals; when S is limiting, N application does not affect yield, whilst the yield response to applied S increases with increasing amounts of applied N. In areas of low S deposition, S deficiency has usually been detected first on oilseed rape and has then developed on cereal crops a few years later. Oilseed rape will act as an 'indicator' crop for the future spread of S deficiency in cereals to other soil types and a wider area of the UK.

Excess S may induce deficiency of other nutrients, such as copper, in crops. At a site in Cumbria with low Cu availability, grain yields of barley were decreased by applications of S in two consecutive years, even though S apparently improved vegetative growth (McGrath *et al*., 1995). Symptoms of Cu deficiency occurred on the plots treated with S. However, it is not known if this is a direct antagonism between S and Cu or a non-specific effect of increased biomass production and the resulting increased demand for Cu.

4.7 Grain quality for milling and malting

The S nutrition of a cereal crop can have a strong influence, on grain quality of the produce, because of its essential role in the syntheses of amino acids, proteins and some secondary metabolites.

Sulphur in the breadmaking process

The influence and importance of S, as a component of the amino acids methionine and cysteine, in the quality of milling wheat flour for breadmaking, were reviewed in detail by Withers & Sinclair

(1994), together with a summary of the characteristics of the four main forms of endosperm protein. Disulphide/thiol groups are essential for viscoelasticity of the dough during breadmaking. Studies in Australia in the early 1980s indicated that S nutrition plays an important role in breadmaking quality of wheat (Randall & Wrigley, 1986). These studies showed that S increased synthesis of S-rich storage proteins, such as the α-, β-, and γ-gliadins and decreased the proportion of S-poor proteins, such as the ω-gliadins. Also, the concentration of S in flour correlated positively with dough extensibility but negatively with resistance to stretching. In the UK, Byers *et al*. (1987b) also studied the effects of S on storage proteins and baking performance of wheat flour, using pot experiments. Loaf volume of bread was more than doubled when an adequate S supply was given, compared to the treatment receiving very little S during the entire growth period. Sulphur deficiency clearly reduces baking quality, as measured by loaf volume, due to poor dough elasticity. However, some experiments have also shown that application of S fertiliser to crops grown on soils with an adequate S supply for yield can benefit baking quality. The critical threshold values of <0.12% total S and >17:1 N:S ratio identified for yield may also be appropriate for breadmaking quality. McGrath *et al*. (1996) suggested that grain sulphur concentration may be an indicator of both protein quantity and, to some extent, quality, while grain nitrogen only reflects protein content. Rapid progress is also being made in manipulating the seed protein composition of wheat by transgenic techniques to improve quality (Shewry *et al*., 1994).

Until very recently, there was no information on the effects of S deficiency on breadmaking quality of wheat crops grown under UK conditions. In a series of field experiments testing mainly the effects of N in 1998-1991, a late application of elemental S had small or inconsistent effects on yield, and various breadmaking parameters (Dampney *et al*., 1995). Other experiments have also shown little or no effect of foliar applied elemental S on yield, grain S concentration and breadmaking quality (Griffiths *et al*., 1990; Schnug *et al*., 1993).

A more recent HGCA-funded project has investigated the yield and quality responses of breadmaking wheat to S (Zhao *et al*., in press). Yield responses, ranging from 12 to 40%, were obtained at 3 out of 11 sites testing a range of S rates, applied as spring dressings of ammonium sulphate, on milling wheat over harvest years 1995 to 1997. Quality responses, in terms of increased loaf volume, occurred at 6 of these sites. Yield and quality responses were similar in the three varieties (Hereward, Rialto and Spark) tested. An additional 50 kg/ha N, above N requirements for yield, increased grain protein, but generally did not increase loaf volume which seemed to be more closely related to grain S than to grain N. Although maximum yield response to sulphur occurred at 20 kg/ha S, higher application rates gave further increases in loaf volume at some sites. Late application of sulphur, after anthesis, was ineffective for yield and was inconsistent for quality, compared to a standard spring timing. Sulphur application tended to decrease thousand grain weight and specific weight, but had little effect on Hagberg Falling Number. Sulphur application increased gel protein weight, the proportion of polymeric proteins, and dough extensibility, while dough resistance was decreased. Plant analysis at early stem extension stage (GS32), for both total S and N:S ratio, was useful for diagnosing S deficiency. Grain S status related to quality in a rather linear fashion, so it was difficult to determine critical values. The relationship between grain S status and yield response was less consistent.

Sulphur and malting quality

Malting barley crops may possibly be less susceptible to S deficiency on low-S soils because they receive less N than feed barley crops or wheat. In reviewing this topic, Withers & Sinclair (1994) reported that similar changes to those in the amino acid balance and protein composition in wheat, have also been observed in barley when either high N rates have been applied or under conditions of S deficiency. These changes in the protein composition of barley grain which are caused by S deficiency, decrease the nutritional value to livestock (Shewry *et al*., 1993). However, it is not known to what extent such changes affect the quality of barley for malting and brewing processes, as there is very little information on the effect of grain S (and N:S) content. The results of the work on wheat breadmaking quality cannot be extrapolated to barley. High levels of storage protein, strengthened by di-sulphide bridges, which are essential to breadmaking quality, would have a deleterious effect on endosperm modification during malting. Shewry *et al*. (1993) briefly reviewed previous work indicating that the amount, distribution and properties of the S-poor and S-rich hordein storage proteins influence the malting quality of barley and Griffiths (1987) found that differences in the amounts of (S-rich) ‘B’ and (S-poor) ‘C’ hordein proteins appear particularly sensitive to environmental conditions during crop growth.

French workers suggested that C hordein could impair malting performance, by limiting water diffusion during the steeping phase (Benetrix *et al*., 1994), but did not present evidence to confirm this hypothesis. The observations on hordeins were also related to the malting grade of the cultivar rather than the malting performance of the samples used in the experiment. Work in Finland (Peltonen *et al*., 1994) suggested that, when environmental conditions favoured high nitrogen uptake, a larger proportion of D hordein disulphide bonds was synthesised and malting quality decreased. Molina-Cano *et al*. (1995) compared samples of 2 genotypes grown in both Spain and Scotland, over 2 seasons. In the first year, grain protein levels in Spain were exceptionally high and had adverse effects on quality characters. In the second year, however, extracts were higher in Spain than in Scotland, despite higher nitrogen levels, but storage proteins of Spanish grown samples had a considerably higher proportion of C hordein. Higher levels of water uptake during steeping were observed in the Spanish grown samples.

As well as yield loss, the potential reduction in grain quality associated with S deficiency is also a major concern, not only to the breadmaking industry but also to feed compounders. Smaller amounts of some essential amino acids in addition to lower methionine and cysteine contents in S-deficient cereal grain reduce the feeding value of wheat and barley to livestock. With the need to refine and manipulate livestock diets for optimum performance with minimal environmental pollution, cereal grain quality will become increasingly important, especially since cereals are now competitively priced with grass forage as a feed.

4.8 Diagnosis and treatment

Plant analysis

Plant analysis is now recognised as the most reliable means of diagnosing S deficiency, as it reflects the crop's response to variation in the supply of S from various sources. Withers & Sinclair (1994) reviewed published work on the use of total S and SO_4-S concentrations, also N:S and SO_4-S:S ratios in plant tissue as possible diagnostic indices for S deficiency in cereal crops. Research findings indicate that, currently, the best procedure is to sample only young, healthy tissue during the period of maximum S demand between full flag leaf emergence and mid flowering (GS39-65), when a total S concentration of 0.25% S or above *and* a N:S ratio of 17:1 or less would indicate a satisfactory S supply. Advisory experience in the UK suggests that visible symptoms are usually associated with N:S values well in excess of 20:1.

A pot experiment, testing the effects of sulphur supply on growth, nutrient content and biochemical responses of breadmaking and non-breadmaking varieties, showed that either total sulphur or sulphate-sulphur in whole shoots was a good indicator of deficiency for both varieties, while shoot N:S ratio was a less accurate predictor (Zhao *et al*., 1996a). There was also a well defined relationship between dry matter yield and the concentration of glutathione, a tripeptide, in the uppermost fully expanded leaves, which increased with increasing sulphur supply. Preliminary results from more recent HGCA-funded studies investigating the effects of sulphur deficiency on the distribution and size of different sulphur pools, (total S, sulphate-S, glutathione) outline the plant and their suitability as diagnostic indicators for crop sulphur status, also showed that the concentrations of sulphate and glutathione in winter wheat very closely reflected the sulphur nutritional status of the plants (Blake-Kalff *et al*., 1998). This project has also been investigating the possibility of developing a novel, immuno-based diagnostic technique as a simple and rapid field based method for determining glutathione in tissue sap. The initial results also suggested that the youngest and mature leaves respectively may be the best leaf ages to sample for sulphate and glutathione concentrations, if these determinations are to be used as possible diagnostic parameters in the future.

Soil analysis

The main method now used in the UK uses extraction with 0.05m potassium dihydrogen phosphate, to determine extractable total S or extractable sulphate -S by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) or ion chromatography respectively. Soil analysis can reliably predict the risk of sulphur deficiency in winter and spring oilseed rape (Withers *et al*., 1997; Chalmers *et al*., 1998). Although tentative guidelines for interpreting extractable total S levels in soil were reported by Withers & Sinclair (1994) for cereals, the HGCA-funded experiments in 1993 and 1994 showed, that soil analysis in the spring is not a good indicator of S supply (Withers *et al*., 1995).

Grain analysis

Although the range of N and S concentrations in cereal grain are much narrower than is found in plant tissue, grain analysis is considered to be a useful method for the diagnosis of crop S status. Grain analysis also overcomes the problem of variation in plant tissue concentrations due to differences in sampling methodology. A grain S concentration of <0.12% *and* a N:S ratio wider than 17:1 in the grain are now generally accepted as these critical values for breadmaking wheat (Withers & Sinclair, 1994). Both of these diagnostic indicators need to be considered because grain N:S ratio will vary, since the composition of grain metabolic, storage and functional proteins depend on the crop N and S supply.

Further work is needed on these diagnostic techniques, as the survey of S levels in cereal leaf and grain samples in 1992-93 showed no relationship between S or N:S ratio in leaves at anthesis and in grain at harvest, and crops which could be classified as S deficient by leaf analysis were not deficient according to grain analysis (Withers *et al*., 1997). Grain S analysis in isolation suggested an unrealistically large number of S - deficient sites and was considered unreliable for diagnosing a deficiency of S. Leaf analysis and grain N:S analysis indicated that only about 5% of sampled crops were short of S during vegetative growth.

4.9 Treatment

Form

Withers & Sinclair (1994) summarised the main range of sulphur containing fertilisers which are readily obtainable in the UK McGrath *et al*. (1996) classified the different fertiliser types into:

- Straight chemicals - those containing (a) sulphate, which is immediately available for crop uptake as it is water soluble, and (b) elemental sulphur or thiosulphate, which need oxidation in the soil before crop uptake can occur.
- Compound fertilisers - either solid or liquid; some are simple mixtures of chemicals, while others are granulated.

Both straight and compound sulphur-containing fertilisers may contain one or more other major nutrients, but elemental products supply only sulphur. The effectiveness of each main form of inorganic S was reviewed by Withers & Sinclair (1994) for cereal crops and by McGrath *et al*. (1996) for other susceptible crops as well. Elemental sulphur, if suitably formulated, can potentially be used as a slow release sulphur fertiliser, as it is insoluble in water and oxidation to sulphate occurs at temperatures which also favour crop growth. Factors affecting the oxidation process in soil: presence of suitable micro-organisms; particle size and effective surface area, also the distribution within soil of elemental sulphur: temperature; moisture and aeration status; pH are discussed in more detail by McGrath *et al*. (1996). Elemental S fertilisers with a spectrum of particle sizes have the potential advantage of releasing S over an extended period, thereby avoiding the risk of leaching associated with more soluble S fertilisers. The oxidation of elemental S is also an acidifying process, which may help to mobilise and improve crop uptake of trace elements in high pH soils (Schnug, 1987).

Sulphur can also be added to the soil-plant system in the form of livestock manures or sewage sludge biosolids, which have moderate but variable sulphur contents (Nicholson *et al*., 1997). About 10-15% of the winter cereal, and 25-30% of the spring barley crop areas receive some form of organic manure dressing in any one year (Source: British Survey of Fertiliser Practice), although most cereal crops do not receive regular manure applications since they are grown in continuous arable rotations. There is also increased recycling of biosolids to agricultural land as a result of the ban on dumping at sea and the EC Urban Wastewater Treatment Directive. However, although use of organic manures will make some contribution to the sulphur supply, application rates are often difficult to gauge in practice and there is currently only limited information on their S availabilities during the growing season. Where manures are applied, it tends to be in the autumn before the crop is sown and any SO_4-S released by mineralisation will be susceptible to leaching in free draining soils. The contribution of organic manures to the S nutrition of cereals is therefore probably small unless organic manures are regularly applied.

Rate and timing

The optimum rate of S application depends on the crop grown, its yield potential, the N supply and potentially also the chemical form of S fertiliser used. The results of field experiments in the UK indicate that an application of water-soluble S at a rate of 10-20 kg/ha (25-50 kg/ha SO_3), depending on severity of deficiency risk and potential yield, is required for cereal crops. Such application rates of S will only cause minor soil acidification and any subsequent sulphate leaching losses should not have any adverse effects on water quality.

Various studies have shown that soluble sulphate fertilisers should be applied in the spring at GS25-30, shortly before the start of stem extension, when crop demand for S increases markedly (Withers & Sinclair, 1994). There is a risk that soluble sulphate fertilisers applied too early in the spring can be readily leached before active crop growth has commenced, as for N applications to cereals. Similarly, applications of this form of S fertiliser during autumn are not recommended because of the leaching risk. More information is required on the extent to which yield can be recovered by application of S fertilisers once symptoms appear after stem extension, as few experiments in the UK have compared timing effects.

Residual effects of S fertiliser applications have not been widely investigated. In the UK, the recycling of straw may make a significant contribution to reducing the amount of fertiliser S required, although, in the short term, soil SO_4-S may be immobilised by straw incorporation (Wu *et al*., 1993). Cereal crops grown after oilseed rape may also be less susceptible to S deficiency because of the residual S remaining after S fertiliser applications to this break crop and the potential mineralisation of S from the straw residue.

5. COPPER

The incidence of Cu deficiency in cereal crops is greater in Scotland than in the rest of the UK. Foliar Cu sprays are typically applied to about 5% of the cereal area in England and Wales, and to 10% of cereals grown in Scotland (Source: British Survey of Fertiliser Practice).

5.1 Function and uptake

Function

Copper is required for many essential functions in plants, particularly the production of viable pollen for grain formation(Graham, 1975) and for maintenance of cell wall structure (Graham, 1976; Brussler, 1981). It is an essential component of many enzymes and some proteins (Bould *et al*., 1983), which are involved in oxidation and reductions within metabolic pathways in plant cells. Other roles of copper in plants, including respiration; photosynthesis; carbohydrate production; chlorophyll formulation; cell wall permeability, are summarised by Sinclair & Withers (1995). As copper is also involved in processes related to the reduction of nitrate nitrogen to ammonium nitrogen in plants, copper deficient plants can therefore have excessive accumulations of carbohydrate, nitrate nitrogen and polyphenols in vegetative tissue (MAFF, 1976). Copper deficient grain may not germinate, because of lack of the auxin hormone.

Uptake

In contrast to most other nutrients, relatively little copper is transported to the root surface by normal mass-flow or diffusion processes in the soil. Copper uptake is more reliant on root activity, involving initial complexation of soil-absorbed Cu^{2+} with organic acids either exuded from root cells or produced by micro-organisms (fulvic and humic acids) within the root environment (Stephenson, 1986). Soluble copper-amino acid complexes are also thought to contribute to copper uptake. This main mechanism of copper uptake emphasises the importance of adequate development of the root system during crop growth, and may thus enable copper uptake and translocation within the plant over an extended period (Lineham, 1984).

Bergmann (1992) suggested that copper uptake could sometimes be affected by ion antogonism from manganese, iron or zinc, depending on relative soil concentrations. Copper is relatively immobile in the growing point and is only translocated from older tissue with the onset of senescence of mobilisation of nitrogen (Longeragan *et al*., 1980). Copper must therefore be taken up continually by the plant, to avoid a transient deficiency at the growing point. Rye is notably more efficient than other cereals at taking up copper. The offtake of copper in cereals has been estimated at 4g and 2.5g per tonne (fresh material) in grain and straw respectively (Archer, 1985).

McGrath (1985) found that, in three high yielding (>10t/ha) winter wheat experiments on heavy textured soils, grain concentrations of copper, iron, zinc and sulphur, but not manganese, generally increased with increasing yield, rather than showing 'growth-dilution' effects. The increases in grain nutrient concentrations were most likely the result of increased uptake by the larger root systems produced by the crops given optimum nitrogen inputs (Barraclough & Leigh, 1984).

5.2 Deficiency

Susceptible soil types

Sinclair & Withers (1995) summarised information on concentrations of total copper in igneous (typically 10-100μg/g) and sedimentary (4-4.5μg/g) rocks, also concentrations of total and EDTA-extractable copper in England and Wales. The total copper content in mineral and organic agricultural soils in the United Kingdom/Britain ranges from 1 to about 100 mg/kg, although much larger concentrations can be found near copper mining areas or where there has been very long term, frequent use of copper-containing foliar sprays or of waste products with high copper content. However, normal ranges of total copper concentrations are 1-15 mg/kg soil in very sandy soils, and 25-60 mg/kg in loamy and clayey soils. Data for England and Wales indicate that EDTA - extractable copper, as a measure of 'available' copper to plants, is about 20% of the total copper concentration in soils (Archer & Hodgson, 1987).

Copper deficiency is much more likely in acid soils derived from silica and alkaline soils derived from carbonate-rich sediments. Organic and peaty soils, reclaimed heathland sands and shallow chalk soils with moderate to high (6-12%) organic matter contents are therefore most commonly deficient in copper in England and Wales (Archer, 1985). A general, regional classification of geological formations and examples of specific soil series, found to be susceptible to copper deficiency in England and Wales, is summarised by Sinclair & Withers (1995), The most extensive areas of copper deficient soils are in South-west and South-east England (shallow chalks) and in East Anglia (peats and heathland soils). in Scotland, copper deficiency occurs in soils derived from acid schists and granitic rocks, as well as peaty soils, and a comprehensive classification of Soil Association and Soil series, in relation to the probability of copper deficiency limiting the yield of cereals, has been produced (SAC/SARI, 1982). The classification used the total copper concentration in the subsoil in conjunction with the pedological drainage characteristics, to allocate soil series into three (low, moderate or high) categories of deficiency risk, as summarised by Sinclair & Withers (1995). No equivalent classification has been attempted for England and Wales.

Copper is readily absorbed by the clay and organic fractions in the soil, so only a part of the total copper present in soils is readily available for plant uptake. Some of the copper is also immobilised by micro-organisms. Copper does not leach easily through the soil, although mobility is slightly greater in sandy than in peaty or clayey soils, which leads to more severe deficiency in dry seasons. Mobility is, however, increased considerably in poorly drained soils. Most of the applied copper remains in the cultivated topsoil layer of well drained agricultural soils, often resulting in a sharp decrease in copper content at the subsoil boundary.

Analysis results indicate that 31% of soils tested in the North of Scotland and a similar percentage for the whole of Scotland , but less than 5% of soils in England and Wales, have extractable soil copper concentrations which may require a routine copper treatment for cereal cropping, because deficiency is possible or probable (Sinclair & Withers, 1995). A small - scale survey of copper levels in shallow chalk soils in West Berkshire in 1987 showed that 44% of the fifty fields tested were slightly deficient and should be treated when cropped with cereals (Wadsworth, unpublished).

Symptoms

Symptoms in the growing crop provide a valuable, but not infallible guide to copper deficiency. Deficiency symptoms are not often seen until the end of tillering even on very susceptible soil types. Yellowing and withering of the tips of the youngest leaf is often accompanied by spiralling of leaves. Crops remain stunted and struggle to achieve satisfactory growth. Ears have difficulty in emerging from the sheath and those that do emerge usually develop white tips which are devoid of grain. Awns of barley become white and brittle and are easily shed. Many weak tillers develop late in the season and the straw has a dirty green colour. Darkening (melanism) and blackening of the ears and straw occurs in copper deficient wheat grown on organic shallow chalk soils but is seldom seen in deficient wheat on sands and peat in England (Davies *et al*., 1971). The cause of the blackening associated with Cu deficiency in wheat has been attributed to the disease pathogen *Pseudomonas cichori* and is lessened but not eliminated when Cu fertiliser is applied (Piening *et al*., 1989).

Deficiency often results in an accumulation of carbohydrate and N with excessive tillering at the expense of ear formation, and causing greater susceptibility to lodging. Deficiency causes decreased grain size with shrivelled and blackened grains of low volume weight (*e.g.* Reith, 1968;

Nambiar, 1976), because insufficient starch is accumulated in the grain (Russell, 1986). Where the deficiency is particularly severe, anther abnormalities occur in some florets leading to pollen infertility and a consequent failure to set grain (Alloway & Tills, 1984). In less severe deficiency situations crops appear quite normal until ear emergence or even until harvest when the ears are not fully developed and are partially blind. Blind ears can also be a symptom of drought on sandy soils and does not necessarily indicate a Cu shortage. Wheat is more susceptible to Cu deficiency than barley or oats, but rye is much less susceptible (MAFF, 1976; McAndrew *et al*., 1984).

Sub-clinical deficiencies of copper, where there is no appearance of visual symptoms, can reduce cereal yields by 20% or more in the UK (Reith, 1968; Jordan, 1975; Alloway *et al*., 1983). ADAS experiments from 1983 to 1986 on shallow chalk soils (Andover series, <6% organic matter content in topsoil) also indicated yield responses but which were much smaller (4%), in the absence of visual symptoms (Sinclair & Withers, 1995). Sub-clinical deficiency is also a recognised problem in Australia (Graham & Narabiar, 1981). As a result of microscopic studies of pollen development in copper deficient and sufficient barley plants, Alloway *et al*. (1983) suggested a mechanism for causing male sterility, which could largely account for the yield depletion in sub-clinically deficient cereals; a marginally inadequate copper supply from the soil to the rapidly growing plant could cause a crucial deficiency at the relatively advanced growth stage when pollen formation occurs. Most of the copper already taken up will be contained in older leaves and not readily translocated so a late development of deficiency could disrupt the function of various copper-containing enzymes when vegetative growth appears normal. Male sterility at crop flowering will produce incompletely filled ears of grain and hence depleted yield. Alloway *et al*. (1983) also reported that reduced photosynthetic efficiency is another contributory factor to yield loss in copper-deficient cereals.

5.3 Yield response

Sinclair & Withers (1995) collated trials data on yield responses in cereals to foliar or soil applied copper at numerous sites in England and Scotland between 1948 and 1990, as summarised in Table 11.

Foliar treatments

The continuing trend for higher cereal yields means that more copper and other micronutrients are now required, and removed from, the soil in the harvested crop (McGrath, 1985). This raises the question of whether soils can provide an adequate supply of micronutrients to meet the greater demands of a higher yielding crop. Field trials in North-east Scotland in 1985-86 investigated whether increased levels of extractable soil copper were needed for high-yielding cereal crops

(Sinclair *et al*., 1990a; Table 11). yield responses of 14-15% were obtained at two sites, one with the lowest soil copper status (0.5 mg/kg) and the other as the lowest-yielding site, out of the five sites testing foliar applications of 0.5 kg/ha copper oxychloride, applied as equal splits at GS22/30 and GS31/32. Other forms (chelated and inorganic) of copper foliar sprays were tested at these sites, as well as copper oxychloride, with broadly similar results.

Another site tested a foliar applied ‘cocktail’ of 1 kg Maneb, 0.5 kg copper oxychloride and 0.5 kg Librel zinc per hectare, also applied as equal splits at G522/30 and G531/32, combined with three nitrogen rates (150, 200, 250 kg/ha N) to create different yield levels. A significant ($P<0.05$) yield response to the foliar applied Cu + Mn Zn (+10%) was obtained at 150 kg/ha N, but micronutrient application had no effect on yield at the higher nitrogen rates, which produced site yields of 9.2-9.4t/ha. Sinclair *et al*. (1990a) suggested that non-pH dependent mobilisation of copper increases as fertiliser nitrogen rate is increased, probably due to greater production of chelating agents by high-yielding, vigorous cereal crops.

Two sites also tested seedbed applications of 10kg/ha oxychloride, combined with three rates of nitrogen (nil, 150, 200 kg/ha N). Significant ($P<0.05$) yield responses of 22-25% were obtained at nil nitrogen input, despite moderate soil copper status (1.6-2.1 mg/kg), but there was no response to copper application at either 150 or 200 kg/ha N rates, despite doubling the plant offtake of copper in those treatments which had nil copper but received nitrogen fertiliser. Soil solution measurements at these two sites showed that mobilisation of copper into solution in the root-zone soil, which occurred through the season in nitrogen-fertilised plots gave similar concentrations of copper to those plots with nil nitrogen.

Table 11. Effects of copper application on yields of cereal crops in Britain, in experiments between 1948 and 1989.

Crop	Years	Soil Type	Responsive sites/ Total No. of sites	% yield increase at responsive sites	Site Locations	References
Foliar applied copper						
Spring cereals	1948-64	Peats and sandy soils	14/16	31->1000[d]	East Anglia	Caldwell, 1971
Spring cereals	1959-65	Organic shallow chalk (Icknield series)	19/52	20-250[d]	South and south-east England	Davies *et al*., 1971
Winter Wheat	1983-87	Brown shallow chalk (Andover series)	5/7	2-13 (mean 4)	Hampshire	Sinclair & Withers, 1995
Winter Barley	1984-86	Brown sands (Newport series)	5/7	10 (mean)	East Anglia	Sinclair & Withers, 1995
Winter Barley	1985-86	Sandy loam	2/5	12-13	North-east Scotland	Sinclair & Withers, 1995
Winter Barley	1986	Sandy loam	1[a]/1	10[a]	North-east Scotland	Sinclair *et al*., 1990a
Winter Barley	1985-86	Sandy loam	2/5	14-15	North-east Scotland	Sinclair *et al*., 1990a Sinclair and Withers 1995
Winter Wheat	1988-90	Organic shallow chalk (Icknield series)	3/6	11 (mean)	Southern England	Sinclair & Withers, 1995
Soil applied	**copper**					
Spring Barley & Spring Oats	1956-64	Freely drained sands and loams	20/30	7-20*c*	North-east Scotland	Reith, 1968 Pizer *et al*., 1966
Winter Barley	1985	Sandy loam	2*b*/2	22-25*b*	North-east Scotland	Sinclair *et al*., 1990*a*

a 10% yield response to Cu+Mn+Zn "cocktail" at 150 kg/ha N; No response at 200 or 250 kg/ha
b 22-25% yield response at nil N; No response to copper at 150 or 200 kg/ha N rates
c Mean responses at 22 kg/ha copper sulphate rate, for sites grouped by soil copper level.
[d] Very high % yield inceases at some sites because of very poor untreated yields.

The results from these Scottish trials were consistent with the idea that high-yielding crops may be more efficient in obtaining copper from the soil, given similar levels of extractable soil copper prior to seed sowing, as far greater mobilisation of copper occurs under a high yielding crop. Sinclair *et al*. (1990a) also concluded that it was unnecessary to routinely apply copper to every potentially high-yielding crop, unless the extractable soil copper level was low.

Caldwell (1971), Davies *et al*. (1971) and Sinclair & Withers (1995) reported results for different series of ADAS experiments which tested the yield responses of spring or winter cereals to foliar applications of copper oxychloride, across a range of soil types (Table 11). Details of treatment application rates and timing and extractable soil copper levels associated with yield-responsive sites in each experiment series, were all summarised by Sinclair & Withers (1995). The shallow chalk sites in 1983-86 and 1988-90, also the sand sites in 1984-86 tested applications of EDTA copper chelate, as well as inorganic copper oxychloride which supplied much higher amounts of copper. Mean yield responses to copper application were 4% and 11% at the responsive chalk sites in 1983-86 and 1988-90 respectively, and 10% at the responsive sand sites, with little or no difference in effectiveness between the two forms of copper. Copper hydroxide was also tested at the chalk sites in 1988-90 and, overall, all three forms of copper were equally effective at the responsive sites. The more recent studies have not examined effects of spray timing, but Davies *et al*. (1971) showed that copper sprays at late tillering gave consistently higher yields than when applied pre - tillering. Applications at both stages of tillering slightly increased yields.

Soil Treatment

Reith (1968) reported results for thirty field experiments, which tested the effects of seedbed dressings of copper sulphate, at rates from 5.5 to 110 kg/ha, on grain and straw yields of spring - sown barley and oats (Table 11). Extractable soil copper levels ranged from 0.3 to 4.7 mg/kg, but levels were less than 1 mg/kg at most sites. Only three out of twenty sites which gave significant ($P<0.05$) yield responses showed “white tips” symptoms of copper deficiency on the leaves, although second growth tillers were common in the nil - copper plots at these responsive sites. The difference in response between oats and barley was small, compared with the variations between years and sites, and the results for the two crops were combined when assessing copper effects. Copper application had a much smaller effect on straw, than grain yields. On deficient soils, the kernels of oat and barley grain were usually not properly filled, resulting in poor quality grain with low specific weight. Reith concluded that copper deficiency could easily be corrected by soil applications of copper sulphate at 11-22 kg/ha. In contrast, Pizer *et al*. (1966) recommended much higher rates, of 31-62 kg/ha, to prevent deficiency in East Anglia. These trials, both in England in and Scotland also showed that, on deficient soils, soil applied copper sulphate remained very effective for many years and that the residues were almost as efficient as the original dressings.

Comparison of soil and foliar treatments

Sinclair & Withers (1995) concluded, from limited trials work which had directly compared soil and foliar applications of copper, that foliar treatment may be reliable in increasing grain copper concentration, but that soil applied copper may give a more consistent response in grain yield, particularly in the second and subsequent five years or more after treatment. Soil applied copper was not , however, always effective at correcting deficiency in the first season after application, possibly because of insufficient mixing and distribution of copper in this top soil, which justifies an additional foliar spray in the first year.

5.4 Grain quality

Sinclair & Withers (1995) also reviewed information on the effect of copper on cereal grain quality, as well as yield. Copper deficient wheat grain, as well as being shrivelled, may also contain a larger amount of non - protein nitrogen, which may reduce breadmaking performance (Brown & Clark, 1977). Work by Flynn *et al*. (1987) in Australia showed that where copper deficiency in wheat was not correctly treated, the dough from copper - deficient grain had poorer baking characteristics.

Analysis of four hundred samples of wheat grain from the annual UK Cereal Quality Survey in 1992 gave minimum and maximum concentrations of 1.49-7.34, 7.48-55.38 and 9.93-40.88 mg/kg for copper, zinc and manganese respectively (McGrath *et al*., 1995a). Breadmaking varieties generally contained slightly larger concentrations of these elements. A bread making assessment, using wholemeal and white flours from six wheat varieties in this survey, showed only slight effects of adding copper on loaf quality. (McGrath *et al*., 1995a). The authors suggested that the major reason for this may be the masking effect of ascorbic acid, a powerful oxidising agent, which is added during the breadmaking process. Inter-site variations or other agronomic effects masking the influence of copper, such as interactions with other elements, may also be contributory factors.

The variations in the copper content of flour would seem to have only small effects on bread quality within the UK. Copper addition to flour can improve dough handling ability and, together with a low input of ascorbic acid, can improve baking quality through enhanced oxidation. There is no information on the effect of copper deficiency on the malting quality of barley grain except that copper - deficient grain will have a higher nitrogen, but lower starch contents compared to normal grain (Russell, 1986). A satisfactory grain copper concentration is thus important for both the milling and malting industries, although the benefits are unquantified. Cereal grain of adequate copper status is also desirable for the animal feed industry, to reduce the need for copper supplementation in livestock diets. A summary of early trials work showed that soil - applied copper had only relatively small effects on grain copper concentration (Sinclair & Withers, 1995).

5.5 Diagnosis and treatment

The methods used to diagnose copper deficiency are: characterisation of soil type, previous cropping history, soil and possibly plant analysis, together with any visual symptoms in the crop.

Soil and Plant Analysis

Soil analysis for extractable copper is universally used for identifying copper deficiency and the following interpretation guidelines are based on all the yield response trials work summarised in this review. The threshold levels for deficiency used by ADAS are: <2.5 mg/kg extractable Cu for soils with organic matter contents above10%, otherwise <1.0 mg/kg Cu. The SAC classification uses <1.0 mg/kg for probable deficiency and 1.0-1.6 mg/kg extractable soil Cu for possible deficiency, to interpret analysis results.

The difference in the copper concentration of healthy and deficient plants may often be only slight, so that plant analysis has only limited value compared with soil testing. Previous ADAS work suggests that copper concentrates <3 mg/kg (dry matter basis) in the leaf or whole ear, and <2 mg/kg in grain, could indicate deficiency, while SAC use <4 mg/kg in the plant prior to GS30 as a threshold guideline for deficiency. Older plant tissue contains more copper than younger tissues, related to copper mobility within the plant, also the copper concentration in above-ground plant material changes during the season. Sampling method and crop growth stage should therefore be taken account of when interpreting plant analysis results.

Treatment

Current treatment recommendations, as summarised by Sinclair & Withers (1995), outlined below.

Soil application, for seedbed incorporation

- ADAS recommend either 10kg/ha copper oxychloride or 20 kg/ha copper sulphate, although this treatment method is rarely advocated in practise.
- In Scotland SAC recommend a dressing of 5-10kg/ha copper oxychloride, depending on the extractable copper status of the soil.

These treatments should last for at least 5, perhaps as many as 10 years after application.

Foliar sprays:

- There are four main types: Simple inorganic; inorganic flowable suspensions; chelated products; "cocktails". There is a wide range of products on the market, as previously reported by Sinclair & Withers (1995).
- ADAS recommend either: copper oxychloride at 1 kg/ha, in 250 litres of water plus wetter, applied during late tillering; formulated copper oxychloride products at manufacturers recommended rates; or chelated products at full recommended rates.
- SAC recommend either: copper oxychloride at 0.5-1.0 kg/ha, depending on severity of deficiency, plus wetter in at least 150 litres once there is sufficient leaf canopy; or chelated copper products as an alternative.

"Cocktail" foliar feeds containing copper generally supply much smaller amounts of copper at recommended product rates than the specific inorganic or chelated copper products.

The recycling of sewage sludge bioproducts or other wastes, particularly pig slurry, FYM and distillery effluent, to agricultural land can supply substantial amounts of copper and could be of particular benefit on copper deficient soils. (Sinclair & Withers, 1995).

5.6 Deficiency and disease incidence

Evans *et al*. (1992) noted that soil-applied copper significantly reduced the incidence of ergot in wheat grown on copper deficient soil in Canada. The malformation of the ears of deficient plants with upper spikelets frequently failing to produce grain, is likely to reduce pollen production and to result in the glumes gaping for longer. Wood & Robson (1984) in Australia and Evans *et al*. (1992) in Canada found greater severity of take-all in copper deficient plants. No specific disease interactions with Cu deficiency have been identified in the UK, apart from the blackening effect associated with *Pseudomonas cichori* in Cu deficient wheat.

6. MANGANESE

Manganese deficiency is the most widespread trace element problem in arable crops in the UK and is most commonly seen in cereals, with an estimated 15 - 20% of the crop area being treated with manganese annually (Source: Annual Survey of Fertiliser Practice). In Scotland, 30% or more of the cereal area may receive a Mn spray each year. This deficiency has increased in importance over the years because of both the expansion of the cereal area, often onto land which may only be marginally suited for such cropping, and also the increased nutrient demand of higher yielding varieties. Finck (1987) reported an increased incidence of manganese deficiency in cereal crops in the Schleswig-Holstein area of Germany, which he associated with higher yielding (8-10t/ha) crops and their greater crop demand for manganese. In contrast, Sinclair *et al*. (1990a) reported that a number of spring and winter barley trials in the north east of Scotland showed that high-yielding crops are not necessarily more prone to manganese deficiency than are lower-yielding crops. Current UK guidelines for the diagnosis and treatment of manganese deficiency in cereals are largely based on experimental work carried out during the 1970s and 80s.

6.1 Function and uptake in plants

Function

Manganese has a role in many biochemical processes in plants and resembles magnesium in its biochemical function. It is required for photosynthesis and is both a constituent and activator of enzymes involved in protein synthesis and lipid metabolism. However, unlike some other essential trace elements which are usually integral components of enzymes, manganese can often be replaced by other metal ions in its role as an activator of enzymes (Burnell, 1988). A shortage of manganese often results in impaired activity of the nitrate-reductase-enzyme with consequent accumulation of nitrate in plant tissue.

Uptake

Manganese is probably absorbed by plant roots from the soil solution in divalent (Mn^{2+}) form. Microbial oxidation of manganese, to oxides of very low solubility, occurs relatively slowly at between pH 5 and 6 but increases markedly as the pH is raised to 7.5 (Wild, 1988). Manganese availability depends on the chemical reduction of these oxides by organic matter, also on some biological processes involving microbial or root products, and the rate of reduction increases at more acid pHs. Nutrient interactions can produce large differences in both crop growth and elemental uptake (Reisenauer, 1988). Competitive effects from macronutrient (potassium, magnesium, calcium) cations and zinc on manganese uptake are considered to be significant, while those from copper and boron are less important for plants. Applications of acidifying fertilisers such as ammonium sulphate have been shown to increase manganese uptake by crops, particularly in poorly buffered acidic and non-calcareous soils (Schung & Finck, 1982). Phosphate fertiliser applications may also increase manganese uptake through soil acidification, but the effect on the plant may depend on the relative uptake of phosphate and calcium (Wild, 1988).

Although manganese is more available in poor drainage conditions, shallow and restricted rooting in these conditions may reduce manganese uptake, especially if the topsoil becomes dry at some stage during the summer. Crops require a continuous supply of manganese since re-use/remobilisation within the plant is limited, particularly at low levels of supply. Transient deficiencies can thus occur, due to changing weather and soil conditions. The manganese content of plants varies greatly, usually from a trace up to 500 mg/kg in the dry weather, depending on soil manganese availability. Much larger, toxic concentrations can occur in plants growing on very acid soils. Data for UK crops shows plant manganese concentrations decreasing significantly with increasing pH (Sinclair, 1985). Maximum uptake of manganese in a winter wheat crop yielding 8t/ha is about 400-500 grams/ha, with 150-200 gramms/ha manganese removed in the grain at harvest.

6.2 Soil P status and the Mn nutrition of wheat

The incidence of Mn deficiency in cereal crops appears to have been substantial in Scotland for at least 15 years and were reported by Sinclair (1982) to have increased in the late 70s and early 80s. There are two possible explanations for the increasing problem. It might be that modern crop cultivars are more susceptible to Mn deficiency. Although possible it seems unlikely that such a change would occur across a range of crops. Another possibility is that there has occurred some change in soil chemistry which has adversely affected the availability of Mn to the plant or the plants ability to absorb it.

The capacity of soil surfaces to absorb and retain transition element ions at a given pH is known to be enhanced by the adsorption of phosphate onto oxide surfaces (Diaz-Barrientos *et al*., 1990). The increasing and continued use of phosphate fertilisers in arable agriculture has resulted in a build-up of phosphate in some Scottish soils (Sinclair *et al*., 1989). It is possible that this has resulted in increasing adsorption of Mn on to oxide surfaces in these soils, thus causing depressed soil solution concentrations and enhanced Mn deficiency in various crops.

A glasshouse experiment was designed to compare Mn concentrations in soil solutions and the Mn nutrition of wheat plants in soils which had received different amounts of both phosphate and lime some eighteen years previously. These treatments had significantly altered both phosphate status and soil pH with residual effects continuing into the early 90s when the site was abandoned. The use of these historically treated soils avoid problems of interpretation resulting from non-equilibrium conditions which occur in recently adjusted soils. Throughout the growing season the concentration of Mn in leaf tissue was lower in the limed treatments and in the phosphate treatments, while leaf P concentrations were higher in plants from high P status soils and in those from limed soils compared with unlimed (Table 12; Neilson *et al*., 1992).

Table 12. Mn and P concentration of wheat shoot dry matter after 116 days from sowing

Element	Soil treatment				
	P^0L^0	P^1L^0	P^0L^1	P^1L^1	S.E.
Mn (mg kg^{-1})	59.1	40.6	24.3	12.8	0.78
P (mg g^{-1})	1.93	2.20	2.00	2.49	0.004

P^0 = no added PO_4; P^1 = added PO_4; L^0 = no added lime; L^1 = added lime.
S.E. = Standard error of treatment means.

The depressed Mn values for limed treatments were explained in terms of depressed soil solution Mn concentrations resulting from elevated pH. However, the results for high P soils could not be related to soil solution composition. Neilsen *et al*. (1992) suggested that high soil P resulted in elevated plant P which interfered in the uptake and/or translocation of Mn, rather than by a direct effect of soil chemistry on manganese availability.

6.3 Deficiency

Susceptible soil types

The total manganese content of soils varies widely from a trace to over 7000 mg/kg soil, but is mostly within the range 200 - 3000 mg/kg, as compounds of manganese (II) and as oxide-manganese. A small proportion is present in the soil solution and thus immediately available to plants. as this soluble manganese is absorbed by plants, it is replaced in the soil solution by exchangeable manganese held by soil colloids. The amount available is strongly influenced by the pH and aeration status of the soil, organic matter content and soil microbial activity (Wild, 1988).

Batey (1971) summarised the main geological formations associated with manganese deficiency in England and Wales. Moderate to severe manganese deficiency in arable crops usually only occurs on

- Organic, peaty and marshland soils with a soil pH over 6.0, especially over 6.5
- Sandy soils (sand, loamy sand) with a soil pH over 6.5, especially over 7.0

Mild and transient deficiency is also commonly seen in cereal crops grown on poorly structured fine-textured soils (clay loam) with a soil pH over 7.0. Leached sand and podzolic soils are particularly low in manganese but in most other soils manganese is relatively abundant. Consequently, Mn deficiency is usually induced by low availability of soil manganese for crop uptake, rather than being due to an absolute shortage of soil manganese. The field conditions that can induce manganese deficiency in the UK are: high soil pH; high organic matter content; poor root development; poor root-soil contact, in under-consolidated (fluffy) seedbeds; low soil temperatures; and below average rainfall. The overall combination of these factors will dictate the severity of the deficiency in crops in any one season. The higher the organic matter content, the lower the soil pH needs to be to prevent deficiency occurring. A temporary shortage of manganese is also often induced under poor soil physical conditions, especially after periods of cold, dry weather which put a poorly rooted crop under stress. Bright sunny weather conditions can also accentuate Mn deficiency, compared with dull, humid conditions.

Symptoms

The relative susceptibility of cereal crops to manganese deficiency is in the order: oats > wheat > barley > rye. Marcer & Graham (1987), when comparing the growth and manganese absorption by seedlings of different cereal cultivars under both deficient and adequate manganese supply conditions, found that the amount of absorption was more closely related with the extent of lateral root growth than with efficiency of manganese uptake per unit of root. It may be that the more vigorous root system of barley, compared to wheat or oats, is better able to exploit the available manganese supply in soil. Spring varieties are more susceptible than winter varieties of cereals, presumably because of their quicker growth habit and different pattern of root development. Cereals also exhibit varietal tolerance to manganese deficiency.

The most characteristic symptom of manganese deficiency is leaf interveinal chlorosis which can quickly develop. The deficiency also shows as a general paling of leaves which can go unnoticed or be confused with other agronomic problems such as poor drainage conditions. In cereals, deficiency symptoms usually first appear in spring as patches of pale green, limp growth which if left untreated leads to general plant stunting and species specific leaf spotting. All leaves are affected, starting with the oldest leaves. Symptoms can appear at any time from about the third leaf stage until flag leaf emergence, depending on the season. Unconsolidated areas show the most pronounced symptoms, with wheelmarks standing out as green lines within the field. On more extreme soil types it is now common to find manganese deficiency in late autumn winter cereals. Initial symptoms are similar to a spring manganese deficiency except that if left untreated the crop suffers tiller death or even death of whole plants.

In oats, interveinal yellowing develops together with grey or buff coloured specks or streaks, in the basal halves of the leaves (MAFF, 1976). The streaks mainly may coalesce so that the leaf tissue above the affected area may remain green but hang limply. Severely affected leaves will eventually turn completely brown and wither. In wheat, the older leaves usually show faint chlorotic streaking, changing to interveinal white and eventually brown necrotic streaks in severely affected leaves. In barley, which is less susceptible to manganese deficiency than wheat, small brown or black spots and streaks develop along the interveinal tissue. In Scotland, manganese deficiency is more common in barley than in wheat, perhaps because barley is often grown on lighter, coarse-textured soil.

6.4 Yield response-foliar, soil and seed dressings

Trials work has shown that cereals can suffer up to 65% yield loss, if severe manganese deficiency is left untreated. The results reported here for UK experiment are mostly for foliar Mn treatments, as soil applied Mn is largely ineffective under UK conditions.

Spring application

Batey (1971) reported results from five ADAS trials in north Wales between 1959 and 1962, which gave average yield increases of 1.34t/ha (68%) in oats (4 sites) and barley from foliar applied manganese sulphate at 5.6 or 22 kg/ha. Manganese application to winter wheat on peaty loam soils at experiment sites in East Anglia during 1949 and 1952 increased yield by 1.22 t/ha (+60%) and 2.05t/ha (92%) respectively.

The mean yield response of 16 ADAS sites on wheat and barley between 1980 and 1982 according to severity of symptoms, are shown in Table 13. A significant yield response was obtained on only 5 sites (Royle 1985).

Table 13. Mean yield response to applied manganese in cereals, 1980-1982

Symptoms	Sites	Mean Control Yield (t/ha)	Yield response (t/ha) MnSO$_4$ (9 kg/ha)	EDTA-Mn (3 1/ha)
Widespread and Persistent	7	2.93	+0.93	+0.73 (a)
Patchy and Transient	6	4.29	+0.09	+0.11
No symptoms	3	5.49	-0.07	-0.14

(a) +0.85 excluding one site with no response to EDTA-Mn

The trials indicated that a yield response of between 10 and 65% (mean 30%) can be expected on crops suffering moderate to severe manganese deficiency. 9 out of 11 sites with leaf manganese <20 ppm (before treatment) showed yield increases >0.2t/ha (>7%). Chelated manganese products (supplying 0.2 kg/ha Mn) were only slightly less effective than manganese sulphate (supplying 2.88 kg/ha Mn). Application of half rate manganese sulphate (4.5 kg/ha MnSO$_4$, supplying 1.44 kg/ha Mn) was often, but not always, as good as full rate manganese sulphate. Application of half rate chelated product was less effective than full rate chelated product.

These trials also indicated that manganese spray applications to crops not showing deficiency symptoms may cause yield depression. This was also found in 1977 when 10 out of 14 cereal crops not showing deficiency symptoms but sprayed with 8 kg/ha MnSO$_4$ plus wetter showed yield depressions ranging from -0.10 to -0.41t/ha (3 sites were significant). Conversely, the trials in 1980 to 1982 showed that even where visual symptoms of manganese deficiency are seen in the crop, a response in yield to application of foliar manganese does not always occur. Linehan & Sinclair (1985) demonstrated that manganese deficiency may develop in early growth stages when demand is high but supply of manganese from soil solution is relatively low. As mobilisation of manganese in the soil solution progresses as the barley rhizosphere develops, supply can meet demand in some crops which then “grow away” from deficiency. No reliable soil test has so far been developed to allow predication of the situations where crops will “grow away” from a deficiency. Data in Table 14 also show that in two trials there was a statistically significant response to manganese sulphate but not to the lower addition of manganese from the EDTA chelate.

Six spring barley trials from 1981 to 1983 compared the yield response to 6 kg/ha manganese sulphate with 3 l/ha of EDTA-Mn. Both products were applied at GS15/16 to crops showing visual symptoms of manganese deficiency. Manganese ethylenebis (dithiocarbamate), Maneb, containing 18% Mn, was also applied at GS 15/16 to three of the trials (Table 14).

Table 14. Effect of different manganese foliar sprays to spring barley in Scotland, 1981-83

Year	Crop	Soil pH	Relative yield* Sulphate 6kg/ha	Chelate 3 l/ha	Maneb	S.E.	CV%
1981	SB	6.3	105a	103	-	0.053	2.8
1981	SB	6.4	105a	105a	-	0.064	3.1
1981	SB	6.3	110a	104a	-	0.112	3.3
1982	SB	6.4	99	100	98	0.128	5.0
1983	SB	6.4	106	99	101	0.250	10.4
1983	SB	6.6	110a	100	109a	0.106	6.1
		Mean:	106	102			

* = Control - 100
S.E. = Standard error of treatment means
CV = co-efficient of variation
a = significant at P<0.05

Autumn applications

Since 1982, 8 trials have investigated the need for autumn manganese sprays on winter barley (cv Igri) showing deficiency symptoms and with deficient or low leaf manganese levels before winter. Yield responses from these trials are shown in Table 15.

Table 15. Yield response of winter barley to autumn applied manganese

Site	Soil texture	pH	Control yield	Yield response (t/ha) to $MnSO_4$ Autumn only	Spring only	Autumn and Spring

			(t/ha)	(4.5 kg/ha)	(9 kg/ha)	(4.5+9 kg/ha)
1	Loamy sand	8.1	6.96	+1.34*	+1.34*	+1.63*
2	Loamy sand	8.0	6.67	-0.08	+0.16	+0.22
3	Organic sandy loam	6.8	2.82	+1.35(a)*	+0.24	+1.83*
4	Organic sandy loam	7.3	2.88	+0.54	+1.00 (b)	+0.65 (c)
5	Loamy sand	6.8	4.83	-	-0.18	+0.96*
6	Loamy sand	6.4	6.78	-	+0.11	-0.02
7	Organic SL	7.1	2.41	-	+1.30*	+2.73
8	Loamy sand	7.2	5.26	-	+0.38	+0.75
		Mean:	4.83	-	+0.54	+1.09
(a)	9 kg/ha $MnSO_4$		* P<0.05			
(b)	4.5 kg/ha $MnSO_4$					
(c)	4.5+4.5 kg/ha $MnSO_4$					

These trials indicated that autumn manganese sprays can be expected to give a distinct yield response (mean 10%) over and above that obtained from spring manganese sprays alone, on winter cereals showing deficiency symptoms in autumn (<20 ppm (100% DM) from 3 leaf stage). At site 3, autumn manganese treatment significantly reduced overwinter plant loss by 37 plants/m^2.

Manganese form

All ADAS trials since 1980 have enabled comparisons between chelated-Mn products and manganese sulphate. The efficacy of a number of different chelated products varied between sites and with application rates. Overall, chelated products were slightly less efficient than manganese sulphate for controlling spring manganese deficiency (see Table 11). At some sites in some seasons chelated products were just as effective when applied at or above full manufacturers' application rates. Repeated low rate chelate sprays gave good results in some trials but their efficiency could not be guaranteed in severely deficient situations.

The quantity of elemental manganese supplied by chelates at manufacturers' recommended rates was not sufficient to match the yield response to manganese sulphate at 5 out of 6 of the responsive winter barley sites investigating autumn manganese deficiency. Response at 4 sites comparing EDTA-Mn with manganese sulphate is shown in Table 16.

Table 16. Yield response of winter barley to EDTA-Mn compared to manganese sulphate

	Mn Application			% Increase over Control				Elemental
	Autumn	Spring 1	Spring 2	Site 1	Site 5	Site 7	Site 8	Mn kg/ha

Sulphate (kg/ha)	4.5	9	-	23	20	113	14	4.32
Chelate	1.5	3	-	22	-	-	-	0.279
(1/ha)	1	2	-	-	17	70	6	0.255
	1	1	1	-	12	68	4	0.255
	1	2	2	-	10	78	4	0.425
(Control yield t/ha)				(6.96)	(4.83)	(2.41)	(5.26)	

Two ADAS experiments in 1986 on spring barley (cv Atem) on loamy sand soils with pH 8.0-8.1 compared a single application of manganese sulphate with single or double applications of EDTA chelate (S Royle, unpublished) (Table 17). Both sites showed substantial yield increases to manganese application, but high standard errors at the Staffordshire site meant that the responses were only significant ($P<0.05$) at the second site. EDTA chelate applied as a single, 2l/ha spray was ineffective, but two sprays of 1l/ha gave yield responses comparable to the manganese sulphate treatment, while there was no additional benefit from two sprays at 2l/ha.

Table 17. Yield response (% increase) to manganese treatment on spring barley, 1986.

Product	Rate and Timing		Site location		Elemental Mn
	End May	Mid June	Staffs	Notts	
	kg/ha				kg/ha
Manganese Sulphate	9	-	23	12	2.88
	l/ha				
EDTA chelate	2	-	-11	5	0.17
	4	-	11	11	0.34
	1	1	20	14	0.17
	2	2	17	9	0.34
(Control yield (t/ha):			5.00	4.18)	

Glasshouse trials by Thow *et al*. (1989) compared the absorption, by spring barley, of foliar applied manganese in the form of either an EDTA chelate, inorganic liquid formula or manganese sulphate. The major factor determining foliar uptake of manganese was the concentration of elemental manganese supplied per unit area of ground by each product. The results did not show any influence of striation and composition of the counter ion, or presence of wetter and stickers, on manganese absorption.

An ADAS trial in 1997 on a severely manganese deficient, loamy peat soil in Cambridgeshire compared the effects of sulphate, nitrate, and chelated forms of manganese, each applied over four consecutive timings from GS22 to 31, on crop performance (Simpson, unpublished). Manganese sulphate was the most effective, and chelated sulphate was the least effective in increasing yield, compared to untreated. A manganese seed dressing treatment, which was also tested, was only partially effective in preventing deficiency wihout any supplementary foliar application of manganese . Use of a manganese seed treatment for crops grown on very deficient soils should eliminate the need for an autumn foliar application of manganese. A similar trial at this site in 1996 showed only very slight manganese deficiency symptoms in the untreated crop and no yield responses were obtained to any of the manganese treatments. Additional copper, sulphur and magnesium treatments, which were also tested, also gave no yield benefit.

Effects of soil consolidation, seed depth, form of nitrogen fertiliser and fertiliser placement

Manganese deficiency in barley occurs quite commonly in many areas of Scotland, mainly on coarse-textured soils developed from parent materials such as Old Red Sandstone. Deficiency symptoms are often not uniform throughout fields and better growth frequently occurs, for example, where soil has been compacted by tractor and implement wheels. Goldberg *et al*. (1983) and Holmes *et al*. (1983) reported the results of investigations in field experiments during 1977 to 1981 and, in addition, on 8 farms in different areas of south-east Scotland where Mn deficiency symptoms in spring barley crops had been reported by agricultural advisers. The variety Porthos, known to be susceptible to Mn deficiency, was used in most of the trials in south-east Scotland. The variety Golden Promise was used in north-east Scotland in similar field trials started in 1981 (Sinclair, 1982).

In three of the 1977 and 1978 experiments deep sowing at 8 - 12 cm on a loose seedbed reduced yield by a mean of 0.35 t ha^{-1} and showed more manganese deficiency compared to sowing at 5 - 8 cm. At Aberuthven and Coupar Angus, in 1981 also manganese deficient sites, when fertiliser was broadcast on the surface sowing at 4 - 6 cm reduced yield by 0.8 and 0.6 t ha^{-1} compared to sowing at 2 - 3 cm. However, at these two sites with exactly the same treatments except that the fertiliser was placed or combine-drilled the yields were similar for both sowing depths. Experiments with depth of sowing on sites not deficient in manganese and with broadcast fertiliser showed only a 2% loss in yield from deep sowing. All the effects point to the damaging effect of deep sowing on Mn deficient sites being caused by the displacement of the early root system from the acidifying effect of the fertiliser.

When seedbeds are consolidated prior to sowing, shallow drilling is enforced, while consolidation after sowing, ensures that surface soil and broadcast fertiliser are pressed down towards the seed. Consolidation of the uppermost few cm of soil is also likely to keep the fertiliser in contact with soil moisture. Although soil consolidation probably has other effects on plant growth, most of the 1.1 and 1.3 t ha^{-1} yield increases at the Mn deficient site at Aberuthven in 1980 and 1981 must have been caused by consolidation making the acidifying effect of fertiliser effective in the root zone (Holmes *et al*., 1983). When the fertiliser was combine drilled and the crop sprayed frequently with manganese, heavy seedbed consolidation had no effect on yield.

Combine-drilling an acidifying fertiliser (but not a non-acidifying fertiliser) with the seed rather than broadcasting it, was effective in controlling Mn deficiency and increasing yield substantially on Mn deficient sites (Holmes *et al*., 1983). Placement drills which place fertiliser between every second seed row and slightly deeper, gave similar yields to combine-drilling at two Mn deficient sites in 1981, but did not appear to control Mn deficiency so well early in the season (Holmes, 1982), who concluded that further comparisons between combine and placement drills were required.

Soil applications

Seedbed or banded soil applications of manganese sulphate or Mn-enriched fertilisers have been used in Australia for controlling Mn deficiency (Reuter *et al*., 1988), but this treatment method has been unreliable under UK conditions. Studies in the Netherlands have shown that soil applications of some forms of manganese chelate (Boxma & De Groot, 1971), also manganese silicate which could improve the residual Mn (Boxma & De Groot, 1985) can be effective sources of manganese for plants, but are not commercially practical. A granulated form of very finely ground manganese oxide is available commercially in the UK, for use as a soil treatment.

Seed treatments

Farley (1980) reported laboratory, glasshouse and field trials testing manganese oxide as a seed-pellet additive for controlling manganese deficiency in sugar-beet seedlings. Manganese deficiency was not completely cured by the pelleting treatment, but the treatment was useful as a starter in helping to control manganese deficiency early in the growing season, particularly when the seedlings were too small to be sprayed effectively. Manganese seed treatments were subsequently tested on cereal crops in Scotland.

A manganese-responsive site on a sandy loam soil derived from water sorted sand and gravel (Corby Association) in north-east Scotland, with a soil pH of 6.6 (Sinclair, 1982), was used in the 1982 growing season to test the efficacy of treating barley seed with manganese. Seed treatment of Golden Promise spring barley with manganese sulphate solution at a rate equivalent to 4.5 kg/ha increased manganese concentration in the above-ground crop at GS 14/15 from 25 to 47 μg/g and final grain yield was increased by 35% where NPK was broadcast, but by 45% where NPK was combine-drilled with the seed (Sinclair, 1983). Sinclair *et al*. (1984) reported a soil pH drop of 0.6 units in the root zone where ammonium nitrate-based NPK was combine-drilled with the manganese-treated seed. This acidification resulted in substantial mobilisation of manganese into the soil solution, enhancing the effectiveness of the manganese seed treatment by causing increased uptake of manganese and better early growth with increased tillering.

Glasshouse and laboratory experiments complementary to the 1982 field trials investigated the partition of manganese into barley plants following treatment of seed with radiochemical ^{54}Mn. At the 3-leaf stage of growth about 35% of the plant manganese was derived from the seed treatment. At ear emergence, both total manganese and radiochemical measurements indicated no difference between seed treatment and the control, which lead to the conclusion that seed treatment with manganese seemed to be effective only in early growth (Sinclair, 1984).

In 1983 two trials were sown with Kym spring barley treated with manganese sulphate solution at a rate equivalent to 4.5 kg/ha, one at the responsive site in the previous year and another in a sandy silt loam derived from Lower Old Red Sandstone sediments (Stonehaven Association) with soil pH 6.5. There were no statistically significant differences in yield due to treatments at the new site, while results from the responsive site are shown in Table 18.

Table 18. Effect of manganese seed treatment on grain yield (t/ha, 85% DM) of spring barley, 1983

	Untreated seed		Manganese treated seed		Mean
	No spray	Foliar spray	No spray	Foliar spray	
NPK broadcast	3.63	3.99	4.35	4.62	4.15
NPK combine drilled	3.51	5.48	5.06	5.22	4.82
Mean	3.57	4.74	4.70	4.92	
SE	0.222				

CV	12.2%

Source: Sinclair (unpublished)

There was a statistically significant (P<0.001) increase in yield to manganese seed treatment in the absence of foliar spray with 4.5 kg/ha manganese sulphate plus non-oinic wetter at GS 14/15. The response to seed treatment was greater where ammonium nitrate-based NPK fertiliser was combine-drilled with the seed, compared with broadcasting the NPK immediately prior to sowing. Foliar application of manganese sulphate gave a further yield increase in addition to the effect of the seed treatment at this severely deficient site.

Golden Promise and Golf spring barley seed, which had been manganese-treated by a commercial company, were sown at the responsive Corby site and at a shelly sand site of the Fraserburgh Association in 1984. There were no statistically significant differences in yield due to treatments at the new site, while results from the responsive site are shown in Table 19.

Table 19. Effect of manganese seed treatment on grain yield (t/ha, 85% DM) of two varieties of spring barley, 1984

	Untreated seed		Manganese treated seed		Mean
	Golden Promise	Golf	Golden Promise	Golf	
No foliar spray	5.02	5.34	4.76	3.98	4.78
Foliar spray	6.23	6.90	6.01	6.31	6.36
Mean	5.62	6.12	5.38	5.14	
SE	0.395				
CV	12.8%				

Source: Sinclair (unpublished)

There was a statistically significant (P<0.001) increase in yield to foliar application with 4.5 kg/ha of manganese sulphate plus non-ionic wetter at GS 14/15, whereas yield was on average 0.6 t/ha lower in treated compared with untreated plots. This commercial, manganese seed treatment did not appear to stick to the seed, accumulating in the bottom of the bags of seed.

A different company was used in 1986 to apply a film coating of manganese to Golf spring barley, which was sown at the responsive site. Statistically significant yield responses of 12%, 13% and 23% to seed treatment alone, foliar spray with 4.5 kg/ha manganese sulphate plus non-ionic wetter at GS 15, and seed treatment plus foliar spray respectively were obtained (Clayton *et al*., 1987). Two different manganese seed treatments of Golf were also tested at this site for another company. Only one of the products resulted in an increase in yield in the absence of foliar application with manganese sulphate. The highest response of 23% was obtained with a combination of manganese-treated seed and foliar spray (Sinclair, unpublished).

There is evidence that the concentration of manganese in the soil solution is lower through the autumn and early spring compared with late spring and summer (Linehan *et al*., 1989), which suggests that some crops may not obtain sufficient manganese in the autumn. The efficacies of 3 separate manganese seed treatments of Torrent winter barley were compared with spring foliar applications of manganese sulphate on a site in Aberdeenshire (grid reference NJ 982244). The soil was an imperfectly draining sandy silt loam of the Blackhouse series, derived from Old Red Sandstone sediments. Soil pH was 6.6. Each manganese seed treatment increased the manganese concentration in the above-ground plant material at GS 13, 21/2, although the increases were not significant at the 5% level (Sinclair, unpublished). There was no significant effect of manganese seed treatment on the plant survival over winter. Seed treatment and foliar application in spring did not increase grain yield. In fact one seed treatment significantly ($P<0.05$) lowered yield compared with the control, while another manganese seed treatment significantly ($P<0.05$) lowered yield compared with each of the other treatments. The lower yield appeared to be due to lower specific weight of the grain. This finding was contrary to earlier findings of an increase in specific weight of grain following greater uptake of manganese at the start of crop growth compared with the reliance on foliar application of manganese at GS 14/15 (Sinclair, 1982).

Currently, a manganese seed treatment is commercially available, can be applied to the seed alone or in conjunction with other named seed treatments.

6.5 Diagnosis and treatment

Diagnosis of the deficiency is usually made on recognition of visible symptoms and knowledge of the soil characteristics and field history, backed up by plant analysis.

Plant and soil analysis

A critical leaf manganese content of 20 ppm (100% DM) is used to diagnose deficiency in all crops, including cereals:

Plant Mn concentration (ppm)	Soil Status	Yield Response
<20	deficiency	yield response likely
20-30	low	yield response possible
30-40	satisfactory	yield response unlikely
>40	well supplied	no yield response

(a) Nitric - perchloric extract

Soil analysis of manganese (exchangeable and easily reducible extracted with N ammonium acetate and quinol) has not proved to be of any value in the diagnosis or prediction of the deficiency in this country. A study comparing four extraction methods (ammonium acetate, ammonium acetate + quinol, hydroquinone and DTPA) on either fresh or dried soil found no significant correlation between soil manganese level and plant manganese content over 108 paired cereal samples (Vaughan, 1985). Reisenauer (1988) classified the wide range of soil tests which have been developed for assessing manganese availability in soils into live main groups of extractants. He concluded from the results of many pot and field experiments, which compared soil analysis with plant uptake, that they have very limited ability for predicting the level of plant-available manganese in soil.

A simple microbial bioassay for determining plant-available manganese, developed in Canada by Germida *et al*. (1985), was able to identify manganese deficient soils.

6.6 Treatment

Soil Application

Soil application of manganese sulphate is never recommended for the control and treatment of manganese deficiency. Although high rates of manganese sulphate, either broadcast or combine drilled, have been shown to give some control of the symptoms, this treatment is much more expensive than foliar spraying and unreliable because the applied manganese may become unavailable to the crop. Combine drilling with ammonium-N compounds can reduce the severity of Mn deficiency in spring barley, but this technique and its associated slower drilling rate is only worthwhile if a deficiency is otherwise very likely to occur.

Foliar Application

Foliar spraying with manganese is the recommended method for effective control or treatment of manganese deficiency. Foliar Mn sprays should be applied when deficiency symptoms are first identified, provided there is sufficient leaf cover for Mn uptake at that stage, otherwise during late tillering to early stem extension (GS24-31) on fields with a known history of moderate to severe Mn deficiency problems in most years. A manganese spray application is not, however, normally considered worthwhile beyond about ear emergence, where a deficiency is identified late in the season. Where severe manganese deficiency occurs 2 or 3 sprays may be recommended. Autumn, as well as spring manganese sprays are, however, required on winter cereals is deficiency symptoms develop during the autumn, as deficient crops will be prone to frost damage and winter kill.

ADAS recommend that manganese sulphate, at 4.5-9.0 kg/ha plus wetter as the most effective and cheapest means of treating a deficiency although chelated products are also equally effective if supplied in sufficient quantity. Manganese sulphate can be difficult to dissolve, is not compatible with many other agrochemicals for tank mixing and can cause leaf scorch, especially on a stressed crop.

The two main alternative forms of manganese spray are:

- chelated products (mainly based on EDTA, but also phenolic acid or lignosulphate chelates); they have advantages of much greater compatibility with other agrochemicals, better solubility and no risk of crop scorch but supply less manganese and are more expensive.
- inorganic suspensions; these proprietary products are based on manganese sulphate as a flowable suspension, together with stickers and wetters in a tank mixable formulation. Some of these products also contain a proportion of chelated manganese.

ADAS advice is not to treat a crop until symptoms of manganese deficiency have been identified and/or confirmed by plant analysis except where moderate to severe deficiency has occurred regularly in the past, when a routine ‘insurance’ spray is advised. The increased incidence of manganese deficiency in recent years has meant the latter is more often the case in practice. Many farmers consider the small cost of manganese application justifies treatment even where symptoms would not have developed.

Where used in the autumn, manganese sulphate should be applied at 5 kg/ha in 250 litres water, plus wetter, when there is sufficient leaf cover, generally after the start of tillering (GS21). If frost is expected, a lower application rate, e.g. 2.5 kg/ha of manganese sulphate is advisable to reduce scorch risk to stressed crops. Applications of manganese as a foliar spray once symptoms have appeared will allow the crop to recover quickly and make normal growth. Foliar application beyond ear emergence is not considered worthwhile.

6.6 Deficiency and disease interactions

The effects of manganese deficiency on 'take all' root disease (*Gaeumannomyces graminis*) have been studied in detail in America and Australia (Hornby & Bateman, 1991). Australian experiments in the 1980s showed little effect of foliar manganese application on the disease, but application of manganese sulphate to the seed or, more particularly to the soil effectively reduced take-all. Subsequent work by Brennen (1992) in Western Australia suggested that, although 'take all' root disease (*Gaeumannomyces graminis*) in wheat was more severe in manganese deficient plants, soil applied manganese had no effect on 'take all' incidence. There were no beneficial effects of the applied manganese on 'take all' control at non-deficient sites. It appears that lignification of root tissue is closely implicated in take-all effects, and that manganese deficient plants are predisposed to infection by the fungus because of restricted lignification. Limited experimentation in the UK has, however, failed to find a close link between manganese and take-all (Hornby & Bateman, 1991). This may be because Western Australian soils, which are generally coarser textured with lower organic matter and fertility status than UK soils, support more take-all fungus and the fungus appears to be more infectious. nitrogen fertiliser, which can reduce take-all effects, is applied at much higher rates for cereals in the UK than in Australia or the USA.

As well as effects on 'take-all', Huber & Wilhelm (1988) summarised published work which had shown that manganese reduced the effects of mildew and several other diseases in cereal crops. Manganese may be involved in a plant mechanism which either conditions resistance, susceptibility or predisposition to particular diseases. In the UK, anecdotal evidence suggests that mildew incidence is often associated with manganese deficiency. Chamen *et al*. (1990) noted that manganese deficiency, induced by lack of soil consolidation, led to a high incidence of mildew in a winter wheat crop testing different soil management practices on a clay soil.

A fully integrated approach to preventing manganese deficiency in severe deficiency situations could involve:

- growing cultivars with greater tolerance to deficiency
- use of manganese seed treatments
- combine drilling of manganese-enriched or acidic fertilisers with seed

- adequate seedbed consolidation and avoidance of overliming
- foliar applications of manganese

7. ZINC

Worldwide, zinc deficiency is probably the most widespread trace element deficiency in cereals and is also very common in maize, leguminous crops and top fruit. This deficiency occurs across a wide range of soil types and climatic conditions. However, recorded cases of zinc deficiency in cereals within the UK are extremely rare. Increased nitrogen supply, from inorganic fertiliser dressings, has sometimes been associated with zinc deficiency in crops, possibly due to increased growth and 'dilution' of plant zinc concentrations. In America, zinc deficiency is more common in field crops following a crop with high zinc uptake, such as sugar beet.

7.1 Function and plant uptake

Function

The function of zinc in plant nutrition, also its chemistry in soil and the incidence of zinc deficiency in agricultural crops, have been extensively reviewed (*e.g.* Lindsay, 1972; Nriagu, 1980). Zinc is required by plants as an activator of enzyme-driven reactions involved in the synthesis of protein and growth promoting hormones (auxins) and in this respect is similar to the biochemical functions of manganese and magnesium.

Plant uptake

Zinc in soil is held on clays, hydrous oxides and organic matter, with most of the extractable zinc present in the clay fraction. Organic matter can form soluble complexes with zinc, enabling plant uptake, but it can also immobilise or 'fix' zinc due to other binding mechanisms. Much of the soil solution zinc is complexed with soluble organic matter from the breakdown of soil residues and from root exudates. These organic ligands keep zinc available at pH values where zinc would otherwise be 'fixed' into immobile forms. Despite this mechanism, crop uptake of zinc varies considerably, depending on soil pH. There is sparse, and often conflicting evidence on the antagonistic or stimulating effects of other nutrient ions on zinc availability and plant uptake (Lloyd, 1981). Zinc is largely immobilised in older leaves, once it has been taken up by the plant. Maximum uptake of zinc in wheat, which occurs around the soft dough stage, has been estimated at about xx g/ha of which *up to half* is removed in the grain. A pot experiment by Chahal & Randhawa (1977) showed that the maximum rate of zinc uptake by wheat occurred during tillering. Between tillering and ear emergence, only a quarter of the zinc requirement was obtained from the soil, with the remainder supplied by translocation of zinc already in the plant. These findings suggested that zinc availability during early growth is particularly important.

Wheat cultivars have been shown to vary in their response to zinc and associated plant tissue concentrations, this differential response appears to be closely related to their efficiency of utilising available zinc in soils (Brown *et al*., 1972; Shukla & Raj, 1974). Graham *et al*. (1992) also identified genetic variation for zinc efficiency in barley and oats, as well as wheat.

7.2 Deficiency

Susceptible soil types

Zinc deficiency has very occasionally been encountered in the UK in top fruit (Bould *et al*., 1983), forestry nursery stock (Anon., 1983) as well as in cereals, and is associated with sandy soils with high pH and phosphate status. The concentration of total zinc in soils is closely related to the soil parent material and is normally in the range 10-200 mg/kg. Typical total levels for agricultural soils are 5-70 mg/kg, with only a small proportion present as exchangeable zinc. Soils originating from basic igneous rocks have high zinc contents, while highly leached acid, sandy soils derived from more siliceous parent materials are particularly low in Zn. The ease with which zinc is fixed in the soil probably accounts for the poor movement or translocation of zinc through the soil. It is usually concentrated near the surface, as a result of plant uptake and recycling in crop residues.

In most soils, the total zinc content far exceeds crop requirement but the availability of zinc may be limited by several soil factors:

- **pH -** zinc availability is much lower at pHs above 6.0, because of reduced solubility, and is also lower in soils with high organic content. Liming may increase the zinc-fixing capacity of the soil, as a result of increasing the pH.
- **organic matter content -** zinc availability is lower in soils with high organic content.
- **phosphate status -** a high soil phosphorus level, due to regular and/or large fertiliser dressings, may reduce zinc uptake by crops and induce deficiency in susceptible crops (Olsen, 1972). This effect is generally considered to be caused by physiological inhibition of zinc movement from roots to shoots (*e.g.* Ragab, 1980), although phosphate additions can directly affect zinc sorption and fixation by the soil (Barrow, 1987).

Clay soils of high magnesium content may also fix zinc in unavailable form by strong adsorption on the clay minerals in place of magnesium, but this is not a significant mechanism in UK soils.

Symptoms

Plants suffering from zinc deficiency generally show interveinal chlorosis, with pale green, yellow or even white affected areas. A deficiency in cereals is most noticeable in the early stages of plant growth, with yellow streaks appearing at the second leaf stage (GS12), which may be more pronounced in barley than in wheat or oats . The entire leaf margin can become bleached. Growing points die and plants become stunted. In barley, well developed ears may be distorted with twisted, wavy awns; other ears may be blind. Work in other countries suggests that barley is more susceptible to zinc deficiency than wheat.

7.3 Yield response

The limited amount of trials work which has been carried out on cereals in the UK, has mostly tested the effects of foliar, rather than soil applied Zn.

Foliar applications

Zinc deficiency in cereal crops was first identified in north-east Ireland in 1985, when foliar-applied zinc significantly increased yield of spring barley by 70-288%, at three sites where deficiency symptoms were observed early in the growing season. MacNaeidhe & Fleming, 1988). Zinc concentrations in the foliage of deficient plants at GS30 were 14-15 mg/kg, associated with soil extractable zinc levels of 0.6-0.7 mg/kg (0.05M EDTA extractant). Zinc EDTA (7% Zn) at 3 l/ha gave a higher yield than zinc sulphate (22.8% Zn) at 10 kg/ha. Sites with only slight or moderate deficiency risk in Ireland have given yield responses of 5-10%.

Experiments at four sites in 1984 and one site in 1985, all in north-east Scotland, tested zinc applications on winter barley crops grown on soils with low extractable zinc status (Sinclair unpublished; Table 20). Sites A, B, C and D were chosen in 1983/84 because of a combination of similar low values of extractable Zn (Table 20), but widely differing yields of previous winter barley crops. All trials were of the randomised block design replicated five times. The foliar Zn treatments were applied as either 0.5kg EDTA (Librel) Zn per ha, split into equal applications at GS 22/30 and GS 31/32, or 0.5 kg EDTA (Librel) Zn per ha applied at GS 31/32, and included a non-ionic wetter.

Table 20. Site characteristics and yield response to foliar Zn, 1984-85

Site	Grid ref.	Soil Zn mg/kg	pH [1]	Control yield t/ha	Relative response to EDTA Zn 2 x 0.25 kg ha $^{-1}$	1 x 0.5 kg ha $^{-1}$	S.E.
A	NJ 692438	1.2	5.9	9.50	108 [2]	103	
B	NJ 945500	1.4	5.8	4.25	110	-	0.376
C	NO 758929	1.4	5.8	5.88	105	102	0.190
D	NJ 738451	1.5	5.9	8.50	104	104	0.172
E	NJ 701408	1.4	6.2	9.26	100	-	0.218

[1] pH of 1:1 suspension in water prior to each sowing
[2] significant at 5% level
S.E. = Standard error of treatment means.
Source : Sinclair (unpublished)

As the previous cropping and management may have resulted in substantial differences in the forms of soil micronutrients present at A to D, different yield levels were created by varying the N rates at site E in 1985 (Table). Yield results at site E are given in Table 21.

Table 21. Fertiliser N rate, yield of winter barley and response to foliar Zn at site E

Spring N kg ha $^{-1}$	Yield (t/ha) untreated	+Zn	Yield (as % untreated)
150	8.58	8.74	102
200	9.26	9.28	100
250	9.16	9.18	100
S.E. $\pm$ 0.218	CV% 4.8		

Source : Sinclair (unpublished)

Only site A, which gave a very high yield of 9.5 t/ha in the untreated control, showed a significant ($P<0.05$) response in barley yield to foliar applied Zn in this set of trials. However, a similarly high yielding trial at site E in the following year, 1985, did not respond significantly to foliar applied Zn. Extractable Zn was lowest at site A, at 1.2 mg kg $^{-1}$. A further series of trials were subsequently carried out, testing both foliar and soil applied zinc, on Scottish sites with extractable Zn values of less than 1.2 mg kg $^{-1}$ (Table).

Foliar and soil applications

The response of barley to soil and foliar applied Zn was studied at 5 sites with low soil Zn status in south-east Scotland during 1988 and 1989 (Paterson *et al*., 1991) and 2 sites in the Moray Firth area (Sinclair, unpublished). Site identification and details are given in Table 22 (A - E in south-east and F - G in Moray Firth area).

Table 22. Site characteristics for zinc trials on barley in south-east Scotland and Moray Firth, 1988-89

Site	Grid ref.	Texture	pH	EDTA Zn * mg/kg	Crop	Variety
A	NO 178078	sandy loam	6.2	1.0	winter	Magie
B	NO 346143	sandy loam	6.3	0.9	spring	Sherpa
C	NT 822504	sandy clay loam	6.8	1.0	spring	Blenheim
D	NT 803500	sandy clay loam	6.5	1.1	spring	Camargue
E	NO 025195	sandy clay loam	6.9	0.5	spring	Camargue
F	NH 735 480	sandy loam	6.0	1.1	spring	Camargue
G	NH 593640	sandy loam	5.9	0.6	spring	Camargue

* 0.05M ammonium EDTA
Source: Paterson *et al*. (1991) and Sinclair (unpublished)

Five treatments were tested at sites A - E (Table 22). Prior to broadcasting over the soil surface by hand, the granular Zn product (treatment 2) was thoroughly mixed with a suitable grade of coarse sand in the weight ratio 1:25 to improve the evenness of distribution. Foliar treatments were applied using a knapsack sprayer at growth stage 31 (Zadocks *et al*., 1974), and, in the case of treatment 5b, 14 days later. To aid wetting, two drops of a non-ionic surfactant was added to treatments 4 and 5. In 1988 (sites A, B, C), all five treatments were examined in a randomised block design of four replicates. In 1989 (sites D, E) only treatments 1, 4 and 5 were studied, these being part of a larger experiment set up to investigate various trace element products. At these sites three replicates of each treatment were used.

Table 23. Zinc treatments used in the south-east Scotland trials, 1988-89

Treatment no.	Treatment	Application rate	Zinc applied by treatment (kg ha^{-1})
1	Untreated control		
2	Granular zinc product (36% Zn as ZnSO4 + ZnO)	20 kg ha^{-1} broadcast to the soil	7.2

3	Zinc chelate (7% Zn w/w as zinc lignin polycarboxylate)	5 litres ha $^{-1}$ foliar	0.35
4	Zinc sulphate (23% Zn as $ZnSO_4.7H_2O$)	5 kg ha $^{-1}$ foliar	1.14
5	Zinc sulphate (23% Zn as $ZnSO_4.7H_2O$)	(a) 2.5 kg ha $^{-1}$ foliar	0.57
		(b) 2.5 kg ha $^{-1}$ foliar (14 days later)	0.57

Source: Paterson *et al*. (1991).

In general, no treatment had a significant effect on grain yield (Table 23). At site B, treatments 4 and 5 produced grain yields which were significantly (P<0.001) less than the untreated control. However, the SED value was very low at this site so, although the values are statistically significant, they are not necessarily biologically or economically important.

Table 24. Mean grain yields (t ha^{-1}) for the zinc trials in south-east Scotland, 1988-89

Treatment	Site				
no.	A	B	C	D	E
1	6.12	6.02	4.65	5.47	3.75
2	6.12	6.02	4.70	—	—
3	6.12	6.05	4.52	—	—
4	6.00	5.85	4.62	5.83	3.85
5	6.05	5.82	4.48	5.54	3.37
SED (DF)	0.12 (3)	0.05 (3)	0.08 (3)	0.24 (2)	0.42 (2)

Source: Paterson *et al*. (1991)

Paterson *et al*. (1991) reported that treatments 2 and 3 had virtually no effect on crop Zn concentrations. However, zinc sulphate (treatments 4 and 5) significantly increased crop Zn concentrations. As treatment 3 supplied only 30% of the amount of Zn present in the zinc sulphate application, it would suggest that foliar Zn adsorption may be governed more by the amount of Zn applied than by the form used. In both years, the split dressing of 2.5 + 2.5 kg ha $^{-1}$ zinc sulphate was more effective than the single 5 kg ha $^{-1}$ application in increasing Zn concentrations. As none of the five sites on sandy loam or sandy clay loam textured soils with low extractable zinc status (0.5-1.1 mg/litre) showed any yield response to foliar or soil applied zinc, Paterson *et al*. (1991) concluded that there was no evidence, at that time, of zinc limiting the yield potential of barley grown on such soils in south-east Scotland.

Each trial site (F and G) in the Moray Firth area in 1989 consisted of 5 randomised blocks of 7 foliar treatments as detailed in Table 25. Rates of zinc sulphate were reduced in order to supply the same rate of Zn as applied in typical, commercially recommended rates of zinc chelate.

Table 25. Treatments used in the Moray Firth area trials (1989)

Treatment no.	Treatment	Application rate	Zinc applied by treatment (kg ha $^{-1}$)
1	Untreated control		
2	Zn chelate (7.4% Zn as Zn EDTA)	1 litres ha^{-1}	0.074
3	Zinc chelate (7.4% Zn as Zn EDTA)	3 litres ha^{-1}	0.22
4	Zinc sulphate (22.8% Zn as $ZnSO_4.7H_2O$)	0.33 kg ha^{-1}	0.075
5	Zinc sulphate (22.8% Zn as $ZnSO_4.7H_2O$)	1.0 kg ha^{-1}	0.23
6	Zn chelate (6% Zn as Zn lignosulphonate)	1.25 litres ha^{-1}	0.075
7	Polygram (17% Zn as Zn dithiocarbamate)	1.0 kg ha^{-1}	0.17

Source: Sinclair (unpublished)

All the treatments at sites F and G were applied on the same day at early stem extension stage (GS 30/31) and a non-ionic wetter was included in each foliar spray. There was no effect of Zn treatment on the yield of spring barley at either site F or G. This lack of response was perhaps predictable from the Zn concentration in the plant material at GS 30/31, which average 23 and 21 mg kg^{-1} at F and G respectively. At site F, the higher rate of zinc sulphate and Polygram produced a similar, significantly higher Zn concentration 3 weeks after application at the 0.1% level than each of the other treatments. At site G, the Polygram produced a significantly higher Zn concentration at the 0.1% level than the lower rates of Zn EDTA and Zn sulphate, as well as the Zn lignosulphonate.

A further trial in Aberdeenshire (grid ref. NJ 823377) compared the response of Slejpner winter wheat to two foliar-applied Zn products at 2 rates with 5 replicates. Mean soil pH of the trial area was 6.1, EDTA extractable Zn was 1.6 mg kg $^{-1}$ and Zn plant concentration prior to treatment at growth stage 30/31 was 28 mg kg^{-1}. There were no statistically significant responses in grain yield from any of the Zn products (Sinclair, unpublished). The untreated yield was 7.4 t ha $^{-1}$.

The findings of all these trials gave no evidence for yield benefits to barley following soil or foliar application of Zn on soils which have between 0.5 and 1.5 mg kg $^{-1}$ EDTA extractable Zn, values currently classed as low by the Scottish Agricultural College. This is in contrast to the work of MacNaeidhe *et al*. (1986) who recorded increased grain yields following Zn treatment of barley grown on soils containing similar EDTA extractable Zn concentrations. Not only are soil types different between southern Ireland and Scotland but farm management practices vary. For example, Irish farmers have maintained very high soil pH levels (in excess of pH 7) for a large number of years. However, the Scottish trials showed that the prediction of response to Zn in cereals grown in Scottish soils was not straight forward.

7.4 Diagnosis and treatment

Zinc deficiency is very unlikely in UK cereal crops, even on very sandy soils.

Plant and soil analysis

Plant and soil analysis are both useful diagnostic techniques, in addition to visual symptoms. Lloyd (1981) grouped the range of chemical extractants which have been used to analyse soils for 'available' zinc into four categories: complexing agents, dilute acids, chelating agents and neutral salts. In the UK, 0.05m EDTA at pH 7.0, is used as the standard extractant by ADAS and SAC. A glasshouse experiment in Australia indicated that analysis of the youngest mature leaf blade was the best procedure for evaluating the zinc status of wheat plants, and that the critical zinc concentration for 90% relative yield was 16 mg/kg (DM basis) (Dang *et al*., 1993).

Current guideline thresholds for possible zinc deficiency, based largely on SAC data, are 0.5-1.0 mg/litre extractable Zn in soil and 15-20 mg/kg in plant leaves. In Ireland, soil analysis guidelines also take account of pH, while foliage concentrations less than 20-25mg/kg are associated with deficiency (Anon., 1989; 26).

Table 26. Interpretation of extractable zinc levels (mg/kg) in Irish soils

Deficiency Risk	Soil pH > 7.0	Soil pH < 7.0
Severe	<1.5	< 1.6
Moderate	1.0-1.5	0.6-1.0
Slight	1.5-2.0	1.0-1.7
Satisfactory	>2.0	>1.7

An ADAS survey in 1982 and 1983 of zinc levels in barley crops showed some low leaf levels (15-20 mg/kg) in some crops, mainly from the sandland (Breckland) areas of north-west Norfolk (Skinner, unpublished). Soil Zinc levels were moderately well correlated with leaf zinc levels, this correlation was improved when soil pH was also taken into account. A survey of arable farms in south-east Scotland indicated that only a small proportion (estimated at 13 per cent) are likely to have soils with extractable Zn concentrations less than 1 mg kg^{-1} (Berndt & Kershaw, 1989). The percentages of such potentially deficient soils are relatively high in Angus (27%) and Borders (20%). There were almost no low Zn soils in Lothian, which has quite a different distribution of Zn levels from those of the other regions within south-east Scotland. Soil pH, organic matter content and acetic acid-extractable phosphorus were poor predictors of low levels of extractable Zn.

Treatment

The two main options for preventing or treating zinc deficiency are:

- soil application- broadcast or banded dressings of zinc compounds or macronutrient fertilisers containing zinc, for seedbed incorporation
- foliar sprays with inorganic zinc compounds or zinc chelates.

In the rare instances where Zn deficiency is confirmed in a cereal crop grown in the UK, a corrective foliar spray treatment should be applied. The form of Zn used can be either:

- zinc sulphate at 5 kg/ha, preferably split as two equal applications of 2.5 kg/ha in 250 litres water, plus non-ionic wetter, towards the end of tillering (GS23-G30) and again 10-14 days later or
- a chelated form of zinc, at manufacturer's recommended rate and timing.

Foliar sprays are effective only for the current crop. If a soil is already known to be deficient, a soil application of zinc sulphate at 60 to 120 kg/ha, which should have an effective residual value for several years, is an alternative, if less convenient treatment method.

7.5 Zinc and disease incidence

Work in Australia has shown that wheat plants are more susceptible to take-all (*gaeumannomyces graminis* var. *tritici*) infection when deficient in zinc, but the severity of take-all was still high in zinc-treated plants, suggesting that high rates of soil applied zinc had no fungicistatic effect on take-all (Brennan, 1992a).

8. OTHER ESSENTIAL MAJOR AND TRACE ELEMENTS

This chapter briefly covers the other non-NPK elements (B, Ca, Cl, Fe, Mo) which are essential for plant growth but which do not cause deficiency problems in cereal crops under UK conditions.

8.1 Boron

Boron is an important structural component of cell walls and appears to have a general regulatory role in plant metabolic processes. A shortage of boron has been shown to interfere rapidly with cell division, cell membrane permeability and often results in phenolic compounds accumulating in plant tissue (Gupta, 1979; Shorrocks, 1991). Boron also has a secondary role in sugar translocation, protein synthesis and auxin metabolism.

Plant and soil boron concentrations can vary significantly, depending on time and method of sampling. The behaviour of boron in soil and plant is uniquely different to other trace elements and naturally high soil reserves or over-application of boron fertiliser can rapidly lead to toxicity in cereals and other sensitive crops(MAFF. 1976; Gupta, 1979). In Southern Australia, where boron toxicity from naturally high soil levels is a major factor limiting crop yields, studies have investigated the physiological and genetic control of wheat tolerance to high boron concentrations (Paull *et al*., 1992). Many dicotolydonous crops are susceptible to boron deficiency, which is most likely to occur on sandy soils with pHs above 6.5 (MAFF, 1976; Mengel & Kirkby, 1987). Deficiency symptoms typically show as dieback of the apical growing point on the main stem, with subsequent growth and dieback of side shoots (Bould *et al*., 1983). Other symptoms may include brittle leaves, stunting and poor setting of seeds.

Cereal crops, as monocotyledons, are not susceptible to boron deficiency and no cases of this deficiency have been recorded in the UK. Leaf boron concentrations in cereals are typically 5-10 ppm, whereas concenrations below 15-20 ppm in susceptible crops indicate a deficiency. Solution culture studies have, however, shown increased sensitivity of cereals to low boron supply during anthesis (Bould *et al*., 1983). The response of spring barley to boron was studied at 9 sites in north-east Scotland during 1972 and 1973 by Reith (unpublished). The sites covered a range of extractable soil boron values. Soils were derived from a range of parent materials including granite, slate, basic igneous till and Lower Old Red Sandstone sediments. Borax at a rate of 2.5 kg/ha B was broadcast immediately prior to sowing either

Golden Promise or Midas spring barley. The response in yield to boron application is shown in Table 27.

Table 27. Effect of boron application on the yield of spring barley, 1972-73

Site	1	2	3	4	5	6	7	8	9	Mean
Control (t/ha)	5.1	5.2	4.6	4.3	7.2	5.6	4.0	3.1	6.8	5.1
Relative yield with 2.5 kg/ha B	100	102	106	99	95	102	94	96	100	99

100 = control yield

There were no statistically significant effects of boron on the yield of spring barely at any of the sites (Reith, unpublished). ARC experiments in 1995 to 1997 also showed no benefit from boron application to winter wheat (Tables).

8.2 Calcium

Calcium has a major role in the structure, stability, or formation of cell membranes and in cell division (Bould *et al*., 1983). Calcium is taken up by plants in moderate amounts, similar to those for magnesium and sulphur. All soils supply sufficient calcium for cereal and other arable crop requirements, as soil pHs in arable rotations are usually maintained within the range 6.0 to 6.5. Calcium deficiency could only occur under conditions of extreme soil acidity, in which case aluminium and manganese toxicities would be the main cause of poor crop growth. Poor growing conditions can reduce calcium, as well as the other nutrient uptake, but calcium deficiency would not be manifested. There are no particular analysis methods for determining plant or soil concentrations of calcium and consequently no recognised critical levels for deficiency.

Where calcium deficiency has been induced in cereals in solution culture, the emerging young leaves remain trapped in subtending leaves, similar to some symptoms of copper deficiency (Bould *et al*., 1983). Leaves which have emerged remain rolled, chlorotic and may show some circular constrictions.

8.3 Chlorine

Chlorine is an essential plant nutrient and, as chloride, functions in both photosynthetic and protective activities within the plant (Bould *et al*., 1983). Chlorine deficiency is very rare throughout the world, as soils contain adequate amounts of chloride from deposition in rainfall. There are also appreciable inputs of chloride from some types of fertiliser dressings (Archer, 1985).

8.4 Iron

Iron has a number of important roles in plant respiration, chlorophyll synthesis and in photosynthesis. Of all the trace elements, iron is taken up in the greatest amounts but deficiency of iron in cereal crops is unknown. Whilst soils are normally well supplied with iron, plant uptake of this element is severely limited at high pH although, like zinc, iron has the ability to combine with soluble organic compound to facilitate plant uptake.

Iron deficiency has never been recorded in cereal crops grown in the UK. Heavy metal toxicity, as a result of excessive soil contamination, can however restrict iron uptake by plants and thereby cause chlorosis of younger leaves.

8.5 Molybdenum

Molybdenum is an essential constituent of the enzyme nitrate reductase, responsible for the utilisation of nitrate-nitrogen within the plant. This is the most important function of molybdenum and for this reason the molybdenum requirement of crops fertilised solely with nitrate is larger. Molybdenum is also important in other plant enzymatic processes, but is taken up by plants in much smaller quantities than other trace elements. Uptake of molybdenum is known to be limited by applications of sulphate to the soil.

Deficiency in susceptible crops is associated with acid sandy soils since, unlike other trace elements, molybdenum is strongly absorbed at soil pHs below 5.5 At higher pH values, molybdenum is released into the soil solution and more readily taken up by plants. Since molybdenum is so important in N metabolism, a shortage of molybdenum in vegetable brassicae and other susceptible crops produces symptoms of nitrate accumulation; leaves turn a grey/blue-green colour, curl upwards at the edges and often develop marginal necrosis.

Molybdenum deficiency has not been identified in cereal crops grown in the UK, where soils in arable rotations are usually maintained at pH 6.0 to 6.5. Molybdenum deficiency in wheat has been reported in New Zealand, as patches of poor, irregular growth and overall yellow paling, probably related to variation in soil acidity or soil texture. There is no evidence of molybdenum deficiency occurring in cereals as a result of the addition of sulphur fertiliser

9. A SUMMARY OF DIAGNOSTIC TECHNIQUES FOR IDENTIFYING NUTRIENT DEFICIENCIES AND TREATMENT NEED

The following factors should be considered when deciding whether to apply any minor or trace elements to cereals or other crops:

- soil type
- crop susceptibility
- visual symptoms
- history of symptoms in previous susceptible crops
- use of soil and/or plant analysis to predict or diagnose a suspected deficiency.

This chapter provides summary information on the diagnosis and treatment of non-NPK nutrient deficiences in cereals, as presented in earlier chapters of this review, also details of the analytical procedures used by ADAS and SAC for determining concentrations of these elements in plant and/or soil samples. The findings of a survey of Analytical Laboratories and Product Suppliers, carried out as part of this review, are also presented.

9.1 Deficiency Occurrence and Crop Symptoms

Cereals are not susceptible to deficiencies of the other essential minor (Cl) and trace elements (B, Fe, Mo) and no such deficiencies have, or are likely to occur in the UK. For Cu, Mg, Mn, S and Zn, soil type is the key factor affecting deficiency risk in cereals, as summarised in Table 28.

9.2 Diagnosis and Treatment

Some deficiency symptoms can be confused with other crop disorders e.g. severe frost or herbicide damage; waterlogging or drought and correct diagnosis is vital for effective treatment. Guidance on the appropriate use of plant and/or soil analysis for predicting or diagnosing minor and trace element deficiencies in cereals, and on treatment options, are shown in Table 29. Guidelines for interpreting the results of plant and soil analyses for these elements are given in Tables 30 and 31.

Table 28. Nutrient deficiencies - soil factors and crop symptoms

Element	Soil factors	Deficiency symptoms in cereals
Magnesium	Light textured soils. Waterlogging and compaction.	Interveinal chlorosis of older leaves. Symptoms can be transient.
Sulphur	Mostly sandy and shallow chalk soils	Paling of young leaves and patches of stunted growth.
Manganese	Mainly overlimed sandy and organic/ peaty soils. Some heavy textured soils.	Patche of pale floppy growth. Interveinal spotting or necrotic streaks, initially on older leaves.
Copper	Sandy and peaty soils with high pH. Some chalk soils.	yellowing/twisting/distortion of youngest leaves (after tillering stage), and ears. Sometimes excessive tillering and more lodging. Poor grain fill.
Zinc	Sandy soils with high pH and high phosphorus status.	Leaf chlorosis from an early growth stage, sometimes with leaf bleaching. Distorted or blind ears in barley.

9.3 Analysis methods and interpretation of results

Plant analysis

As well as helping to diagnose observed deficiency symptoms, plant analysis may identify subclinical deficiencies and enable nutrient inputs for the current and possibly future crops to be correctly modified (Bergmann, 1992). As an alternative approach to using nutrient ranges in plants, the diagnostic and recommendation integrated system (DRIS), originally developed by Beaufils (1971), uses nutrient ratios together with soil and environmental parameters to assess plant nutrient status. However, Kadar *et al*. (1981) concluded that this system was no better than standard plant or soil testing techniques for determining fertiliser requirements, unless there is an extreme deficiency or excess of one or more nutrients. Bergmann (1992) also suggested that the use of nutrient ratios, to assess the nutritional status of the plant, provides no real advantage over a system based on ranges of nutrient concentrations, unless the nutrient levels in plants are extreme. Shuman *et al*. (1992), for example, found that the sufficiency range method gave almost identical results to the DRIS approach in predicting manganese deficiency or sufficiency in soyabeans.

Table 29. Use of plant and soil analysis for predicting or diagnosing deficiencies and treatment options

Element	Appropriate test: Plant	Soil	Treatment options
Magnesium	Yes; sample affected leaves.	Yes	Foliar spray: 20-40 kg/ha Epsom salts + wetter (non-ionic). Seedbed application: Kieserite or calcined magnesite. Alternatively, use magnesium limestone, if soil pH also low.
Sulphur	Yes; sample young healthy leaves at flag leaf to ear emergence.	No	25-50 kg/ha SO_3 (i.e. 10-20 kg/ha S) Apply as water-soluble S fertiliser in early spring.
Manganese	Yes; sample middle leaves.	No	Foliar spray: 5-9 kg/ha Manganese sulphate + wetter (non-ionic) or a proprietary inorganic/chelated manganese product at recommended rate, applied in the spring. Additional autumn treatment, at 5 kg/ha Manganese sulphate, may be needed on severely deficient sites
Copper	Yes, but needs careful interpretation as only a guide	Yes	Foliar spray: 1.0 kg/ha Copper oxychloride + wetter (non-ionic) or a proprietary inorganic/chelated copper product at recommended rate, applied at mid-late tillering. Soil application: 10 kg/ha Copper oxychloride or 20 kg/ha Copper sulphate
Zinc	Yes; sample affected leaves.	Yes	Foliar spray: an equal, split application of 5 kg/ha zinc sulphate + wetter (non-ionic), or a proprietary inorganic/chelated zinc product at recommended rate, towards the end of tillering. Seedbed application: 60-120 kg/ha zinc sulphate.

Some general guidelines on the use of plant analysis, and interpretation of results, are :

- The interpretation of plant analysis is not an exact science. The concentration of any specific nutrient depends on the plant species, age of the plant, part of plant analysed, variety and even the level of the other nutrients present. Plant analysis will indicate those nutrients which are clearly adequate or deficient. In those cases where the values are borderline or a number of nutrients appear deficient, expert advice must be taken.

- For most nutrients values decline with maturity. Plant analysis ideally should be carried out early in the growing season when the plants are young. Interpretation of the results is easier and this also allows sufficient time for foliar nutrient sprays to be applied to overcome any deficiency.

- All samples submitted for analysis must be clean and free from dust or soil and ideally should not have been recently sprayed with any nutrient containing spray. The presence of soil can lead to falsely elevated values, making interpretation impossible. Analysis of both affected *i.e.* showing appaent deficiency symptoms and, for comparison, unaffected plant samples is often helpful for interpreting the results.

Many researchers have divided plant nutrient concentrations into five ranges: deficient, with visual symptoms; low, possibly latent (sub-clinical) deficiency; satisfactory; high; toxic. Threshold guidelines used by ADAS and SAC for deficiencies of non-NPK nutrients in cereal plants are given in Table 30.

Table 30. ADAS and SAC guidelines on threshold concentrations for nutrient deficiencies in cereal plants

Nutrient	Deficiency threshold
Magnesium	Less than 0.1%
Sulphur	Less than 0.2-0.25% S **and** N:S ratio above 17 to 1
Copper	Less than 3-4 mg/kg in leaf/ear
	Less than 2 mg/kg in grain
Manganese	Less than 20 mg/kg
Zinc	Less than 15 mg/kg

Boron concentrations would have to be below 2-5 mg/kg in cereals, compared with 15-20 mg/kg in susceptible crops, for deficiency.

The analysis methods for determining concentrations of these elements in plant material are al based on digestion of a dried and ground sample in aqua regia (nitric acid and hydrochloric acid), followed by atomic absorption spectrometry or by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) to determine the amount of element in the extract.

Soil analysis

The interpretative scales used by SAC for crops which are susceptible to a particular nutrient deficiency are given in Table 31. Cereals are not, however, particularly susceptible to magnesium deficiency and an absolute deficiency of this element would be unlikely at soil levels above 20 mg/litre Mg.

Table 31. SAC interpretative scales for extractable concentrations (mg kg $^{-1}$) of minor and trace elements in soil

Element	**Very low** Deficiency probable	**Low** Deficiency possible	**Moderate** No deficiency expected	**High** No deficiency	**Excessively high** Crop toxicity may occur
Mg	<20	20 - 60	61 - 200	201 - 1000	>1000[a]
S[b]	<3.0	2.0 - 6.0	6.1 - 10.0	>10.0	-
Cu[c]	<1.0	1.0 - 1.6	1.7 - 8.5	8.6 - 80	>80
Mn[b]	<1.5	1.5 - 2.5	2.6 - 20	21 - 40	>40
Zn	<0.5	0.5 - 1.5	1.6 - 10	11 - 80	>80

[a] EH is used for Mg only where Mg (mg/litre) is greater than Ca (mg/litre), which can occur on soils derived from ultrabasic rocks such as serpentine.
[b] Soil analysis alone is **not** sufficiently reliable for diagnosing or predicting S or Mn deficiency.
[c] On soils containing over 12 per cent organic matter, samples of both plant and soil should be analysed for Cu. If only extractable soil Cu is available, the results should be adjusted for the density of the soil. No adjustment is required for soil pH.
Source : Paterson (1996)

The corresponding deficiency thresholds used by ADAS for extractable concentrations in soil are: 15-20 mg/litre for Mg; <6 mg/kg for S, although soil analysis alone is not a reliable guide; <2.5 mg/kg Cu for soils with organic matter contents >10%, otherwise <1.0 mg/kg Cu. As no yield responses have been obtained so far from zinc applications to cereal crops in England or Wales, ADAS uses the SAC guideline of <0.5 mg/litre for Zn.

Soil analysis methods

Analysis procedures are briefly outlined below, full descriptions of the standard methods for Mg, Cu, Mn and Zn are given in Anon. (1986).

Sulphur. The soil is extracted with 0.016M potassium dihydrogen phosphate, using a soil:solution ratio of xx:yy (w/v) and shaking for xx hour. The total amount of S in the extract is measured by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

Magnesium. The soil is extracted with 1M ammonium nitrate, using a soil:solution ratio of xx:yy (w/v) and shaking for xx hour. After filtration, the Mg concentration in the filtrate is determined by atomic absorption spectrometry.

Copper. Cu is extracted from soil with 0.05M EDTA (adjusted to pH 7 with NH_4OH) at 20°C $\pm$ 1°C, using a soil:solution ratio of 1:5 (w/v), shaking for 1 hour and filtering immediately. The Cu concentration in the filtrate is determined by atomic absorption spectrometry.

Manganese. Extractable Mn is measured in 1M ammonium acetate at pH 7 (1:10 soil:solution ratio).

Zinc. Extractable Zn is measured in 0.05M EDTA (1:5 soil:solution ratio).

9.4 Survey of Analytical Laboratories and Product Suppliers

The grower relies heavily upon the advice of suppliers of products and on results from analytical laboratories of plant and/or soil tests to guide decision making on the need for, and the use of sulphur and other elements. The product range available from the industry both in straight elements and in multi element formulations is impressive The grower must have confidence that his decisions to use certain products on crops are based on correct diagnosis of deficiency and a satisfactory level of interpretation of likely response expected from specific element applications. However it is important to understand what consistencies of analytical field methods and interpretation of results exist across commercial analytical laboratories.

A small survey was therefore undertaken as part of this review. Ten analytical laboratories and thirteen product supply companies were approached with questions concerning analysis methods, and guidelines on theshold levels for deficiency. The responses to this survey are briefly analysed.

Analytical Laboratories

Responses were obtained from six of the ten organisations that it was understood undertook commercial analysis of both soil and plant samples. The responses for soil and plant tissue analysis are summarised separately.

1. Soil analysis

As there are no universally recognised techniques for the analysis of some elements in soil it is inevitable that there are some differences in approaches used by different laboratories. Different analytical methods may be used to determine 'extractable' levels of a particular element, which may result in different amounts of element extraction of elements from a given soil sample. Consequently threshold levels for deficiency/acceptability may differ according to the proportion of the total element and content extraced by each method.

This has been a continuing problem within the industry when attempts have been made to cross compare results on 'absolute' values. Successful interpretation of laboratory results is dependent upon a full understanding of the analytical methods used, and the corresponding threshold levels for deficiency which apply to one particular method. This potential for misinterpretaion is clearly illustrated when the threshold values for satisfactory soil nutrient status are compared between different analytical laboratories.

Table 32. Threshold levels (ppm or 'extractable' soil nutrients considered to be satisfactory (range of responses from different laboratories)

Manganese	Copper	Magnesium	Boron	Sulphur
>2.5 to 9.0*	>1.7 to >4.1	>25 to >51	>0.5 to >1.2	>8 to 23

* most laboratories did indicate that manganese analysis from soil was very unreliable

There did not appear to be a good consensus of opinion as to the extractable soil level for each element that should be satisfactory for the growth of cereals For example, magnesium was considered satisfactory by one laboratory if above 25ppm in the soil sample, but only if above 51ppm by another laboratory. Equally the threshold for satisfactory sulphur level was 8ppm with two laboratories, but over 23ppm by one respondent.

2. Plant analysis

The same concerns, relating to the difficulty of intrepreting analytical results, apply to plant tissue, as well as to soil analysis. The respondent laboratories also indicated the minimum threshold levels for satisfactory crop growth that applied when interpreting their results for plant analysis (Table 33).

Table 33. Element concentration in plant tissue considered as satisfactory for cereal growth (range from different laboratories).

Magnesium	Sulphur	Boron	Copper	Manganese	Zinc
%		mg/kg			
>0.1 to >0.2	>0.25 to >0.28 >14:1 to >17:1 (N:S ratio)	>2 to >25	>3 to >7	>20 to >40	>15 to >25

Once again individual laboratories tended to use different threshold levels for element contents in plant tissues that were considered satisfactory for plant growth, Manganese, for example, was considered as satisfactory at 20ppm by one laboratory but needing to reach 40ppm by another laboratory to be satisfactory.The range for sulphur was narrower, only 0.25 to 0.28% content between the different laboratories. However two laboratories preferred to use N:S ration for interpreting plant sulphur analysis, but again the threshold level was inconsistent: one laboratory considered an N:S ratio greater than 14:1 to be unsatisfactory (sulphur deficient), whereas the other laboratory placed the unsatisfactory ratio at 17:1 or above.

It is very clear that the lack of standardisation in analytical techniques for these elements hence the disparity in guidelines and threshold level for deficiency in soil or plant tissue do create problems in interpreting results. Crossland *et al*. (1998) carried out a study, involving ten UK laboratories, to evaluate the variability of analysis for total concentrations of nitrogen and sulphur in four plant materials and extractable sulphur in two soil samples. Sub-samples of four plant and two soil samples were distributed to each participant. The laboratories agreed reasonably well in their analyses for total nitrogen in plant materials, but the variability for total S was considerably higher. Large inter-laboratory differences were also reported for extractable sulphur in soil. Although different analytical methods were used by laboratories for both soil and plant analyses, this did not explain the large variability in results. The authors concluded that diagnosis of sulphur deficiency, based on *sulphur* analysis, may have questionable validity if analysis results for plant and soil samples are not accurate. More method development and standardisation were advocated, to improve analytical reliability.

Product Supply Companies

A total of thirteen companies were approached who supply sulphur, magnesium and trace elements direct to the farmer. They covered the range of national distribution companies to specialised micronutrient suppliers. Responses were obtained from nine companies, covering:

- usage patterns of nutrients
- where they sent soil or plant tissue for analysis
- what threshold levels were used for the interpretation of results

A. Usage Patterns

Four companies indicated that usage of the nutrients covered in this review (always nominating individual nutrients) were on the increase. Four companies noted that magnesium usage had increased while three referred to Manganese and increased Copper and Sulphur usage were reported on one occasion. Two respondents noted specifically that the use of chelated products was declining, while inorganic based products were becoming more popular.

It was suggested by several respondents that more familiarity with deficiency symptoms, and the ability to recognise them, was probably the reason for the trend towards increased usage.

B. Analysis

Replies from all nine companies indicated that analysis of both soil and tissue samples were done through independent laboratories. There were no indications in the responses received, of detailed knowledge of the techniques used in these analyses.

C. Threshold Levels

In general the threshold levels used were those supplied by the analytical laboratory, with several references made to ADAS, SAC, Teagasc or NRM. Two companies suggested that the Mg threshold level may be too low. One supported this statement with the comment that Mg deficiencies were on the increase. The threshold level for sulphur was identified by one respondent as questionable, as data surrounding this threshold level produced inconsistent response. One respondent commented on zinc analysis and it suggested the frequency of zinc deficiency may currently be underestimated.

Implications of spatial and temporal variation in crop and soil nutrient status

Researchers have for many years been concerned about the large number of trials conducted on the nutrients considered in this review which, despite indicating leaf nutrient levels below deficiency thresholds, did not give yield responses following corrective treatment applications. The accuracy of laboratory determinations for elemental concentrations in either soils or plants is not being questioned. The concern relates to two factors:

- the possible transient nature of a deficiency that may be identified by a single sample test procedure.
- whether the correct layer of the soil profile or the correct component of the plant is being tested to assess nutrient status.
- the time and growth stage at which leaf tissue samples are taken for analysis

Two examples are given which underline the concern in these areas:

1. The HGCA funded project “Management Guidelines for Precision Farming” (Project No. 1743) has involved detailed analysis of several fields over a number of seasons, for their nutrient status. A series of reference points, on a 50m grid system within the fields, was tested on several occasions through each season for a number of elements. The frequency of testing on a spatial basis within each field was considerably in excess of that which is adopted for routine soil or tissue analysis of a defined area. Leaf Mn concentrations showed appreciable spatial and temporal variation.

2. For a number of seasons ARC have been conducting experiments which have monitored soil and tissue nutrient contents throughout the season. It is normal practice to sample a soil or crop only once during the season, and from those results decide if an application of a particular element is required. Based on a single result, and considering the values against recommended threshold levels, the decision can be taken as to whether to supply additional nutrients to a crop. The question is how accurate is that single test in relation to the total time that the crop is growing and has a nutrient requirement?

ARC have clearly shown that sampling at different times through the growing season can produce elemental concentrations in both plant tissue and, to a lesser extent soil that can vary enormously. The sample quoted below from an ARC (Caythorpe) trial on winter barley clearly illustrates the problem.

Table 34. Nutrient concentrations in soil (ppm) and leaf samples (% or ppm) from Untreated plots at sequential sampling dates, Caythorpe site

Sampling date	Sample type	Mg	Mn	S	Cu	B
	Soil (depth, cms)					
19/8/96		87	307	19	-	-
14/2/97		80	313	4	3.6	2
12/3/97	0-30	88	304	105	3.8	2.1
	30-60	70	190	236	3.9	1.2
11/4/97	0-30	116	294	4	3.6	2.1
	30-60	83	283	6	2.5	1.8
6/5/97	0-30	103	290	7	4.5	2.2
	30-60	83	237	8	3	2
	Leaf					
14/2/97	-	0.11	114	0.18	9.2	5.8
12/3/97	-	0.10	56	0.16	6.7	5.3
11/4/97	-	0.08	32	0.14	5.3	4.9
3/5/97	-	0.11	30	0.21	6.7	2.3

In soil analytical terms both the timing and depth of samples influenced the analysis result. The result of leaf tissue analysis can also be significantly influenced by the timing of the sampling, as also illustrated in data from ARC trials on foliar Mg, Mn or B sprays (Tables -) and on different forms and rates of S application (Tables -).

10. CONCLUSIONS

1. Deficiencies of Mg, Mn, S and, very rarely Zn, can occur in cereal crops and are usually associated with specific soil types. Each deficiency produces characteristic symptoms and different cereal types can vary in their susceptibility to some of these deficiencies. Cereals are not susceptible to deficiencies of the other non-NPK nutrients (B, Cl, Fe, Mo) which are also considered in this review.

2. **Magnesium**: cereals may show visual, and often transient deficiency symptoms but seldom give a yield response to magnesium applications, unless soil reserves of Mg are very low. This deficiency can be induced on a wide range of soils under conditions of crop stress caused by poor soil structure, restricted rooting and/or drought. Treatment is very rarely necessary, unless symptoms persist. The soil magnesium status should be maintained at Index 1 in arable rotations to avoid any risk of Mg deficiency limiting cereal yields. Magnesium application is very unlikely to improve grain quality on non-deficient soils.

3. **Sulphur**: the incidence of S deficiency in cereals has increased over the last decade because of the continuing decline in sulphur dioxide emissions from industry sources and lower atmospheric sulphur deposition. The occurrence of S deficiency in cereals is, however, variable and depends on the interaction between crop N and S supply during the growing season. Yield responses have ranged from 4 to 40% across deficient sites in the UK. Grain yield response does not always accompany the appearance of deficiency symptoms and may occur in the absence of any visual response to S fertilisation.

Currently, cereal crops grown on well drained sandy or shallow soils in parts of the North, South and South West of England, also Shropshire and South Wales, where atmospheric deposition is less than 20 kg S/ha/year, are likely to need sulphur. Heavier textured soils in these areas, and other parts of England and Wales, may also eventually become sulphur deficient. At present, about 15% of the total cereal area in the UK is treated with sulphur, while modelling predictions suggest that 30-40% of the UK land area may be at some risk of S deficiency for cereals. Sulphur deficiency is best prevented by spring application of soluble sulphate fertilisers, at 10 to 20 kg/ha S. S deficiency reduces breadmaking quality in wheat and increases in loaf volume have also been obtained at some sites in the absence of a response in grain yield.

Further development of plant diagnostic techniques, to identify S deficiency at a early stage, will enable more effective treatment in the growing crop. There is little information on whether low S (relative to N) in grain affects malting quality in barley; on effective treatment options for late foliar applications of S; or on S availability from livestock manures, biosolids and cumulative inorganic S applications for the rotation.

4. **Copper**: up to 5% of the cereal growing area in England and Wales, and 30% in Scotland may be deficient in copper. Deficiency may sometimes be sub-clinical, when yield is reduced in the absence of visual symptoms, for example on some shallow chalk soils; soil testing is particularly useful for identifying this potential problem. Copper treatments, where needed, are normally applied as a foliar spray of inorganic or chelated Cu in the spring. Alternatively, where a deficiency has previously been identified, Cu can be applied as a soil dressing of copper oxychloride or copper sulphate prior to sowing. This method is less convenient than using annual foliar sprays, and an additional foliar Cu spray is probably needed in the following first season, but a single soil application has a residual value for at least five years. Further information is needed on the extent of sub-clinical deficiencies, and varietal tolerance to Cu deficiency.

5. **Manganese**: Mn deficiency is the most common trace element deficiency in cereals and other arable crops and typically 15-20% of the total cereal area may be treated with Mn annually. Soil applications of manganese are generally ineffective and deficiencies are best prevented or corrected by foliar spraying with manganese sulphate or a proprietary chelated or inorganic Mn product. Autumn, as well as spring treatment may be necessary on very deficient soils. Manganese seed dressings, combined with subsequent foliar sprays, may be useful for very deficient sites where deficiency may develop while there is still very little plant cover for foliar uptake. Take-all disease in cereals does not appear to be exacerbated by Mn deficiency under UK conditions, but increased mildew incidence is often associated with deficient plants.

Treatment strategies which integrate seed and/or foliar treatments with good soil management practices, need to be developed further, especially for more deficient soils.

6. **Zinc**: Zn deficiency has occasionally been identified on sandy soils with high pH and P status in Ireland and Scotland, but has not so far been encountered in England and Wales. The average annual rate of Zn deposition from the atmosphere exceeds crop removal of Zn, even in high yielding crops, although there is little information on the actual availability of this deposited source of Zn to crops. The Zn status of crops grown on sandy soils in areas with relatively low Zn deposition should, however, be re-examined. Foliar spraying with zinc sulphate, or a proprietary chelated or inorganic Zn product, is recommended for the treatment of Zn deficiency.

7. High yielding crops do not necessarily need trace element (Cu, Mn, Zn) applications because of their greater nutrient demand, as such crops are more efficient at obtaining these nutrients from soil reserves and greater mobilisation of these trace elements occurs in the rooting zone of high yielding crops. Existing soil threshold levels for deficiency are appropriate for both high and low yielding crops.

8. The potential deficiency risk associated with each nutrient can be initially assessed from a knowledge of soil types within each field, combined with any history of observed symptoms or confirmed deficiencies in previous susceptible crops. Soil analysis should be used to more accurately predict the likelihood of Cu or Zn deficiency on candidate soil types. Where a nutrient deficiency is suspected as a result of visual symptoms in the crop, leaf analysis for Mg, Mn S and Zn will diagnose or confirm whether the symptoms are caused by a deficiency of any of those nutrients. Where a particular deficiency problem is clearly identified, an appropriate amount and form of the specific element should be applied as a preventative or corrective treatment.

9. Published guidelines on nutrient deficiency thresholds in plants and soils are based on standard methods of analysis and may not be appropriate for interpreting results which are obtained by other analytical procedures. A survey of the main commercial analytical laboratories and product supply companies in the UK showed that a wide range of deficiency threshold levels are used for some nutrients to interpret soil and plant analyses. Knowledge of the analysis method used is therefore important for the correct diagnosis of a suspected deficiency by plant or soil analysis.

11. RECOMMENDATIONS

11.1 Technology Transfer

1. A Growers' Guide is needed on the Mg, S, Cu, Mn and Zn nutrition of cereals, to assist farmers, consultants and other members of the agricultural industry in the correct diagnosis and treatment of specific deficiencies and to avoid unnecessary use of these nutient inputs.

2. Greater standardisation of:
 - crop and soil sampling procedures
 - analytical methods and associated interpretative guidelines on deficiency thresholds
would improve the accuracy of diagnosing nutrient deficiencies in cereal crops.

11.2 Research topics for further study

Recommendations are given for further research work on aspects of Cu, Mn, S and Zn deficiencies.

1. Current research work is developing plant diagnostic techniques which can reliably predict S deficiency at an early stage in the growing crop. This topic should continue to receive a high piority, as it will enable early diagnosis of S deficiency and allow effective treatment of the crop, instead of resorting to the existing, retrospective assessment of crop S status by leaf analysis after flag leaf emergence.

2. Malting quality assessments are required to establish the effect of grain S and N:S content on malting quality of barley grown under different environmental and NS fertiliser conditions throughout the UK. Further information is also required on the yield response of barley to fertiliser S since most research to date has focused on winter wheat. The possible interaction between S and Cu deficiencies, and related treatment requirements, should also be investigated further.

3. The S availability of livestock manures and biosolids, both in the season of application and subsequent residual effects, require further evaluation for arable rotations. Residual effects from regular annual applications of inorganic S fertilisers through the crop rotation also merit investigation.

4. The use of Mn seed treatments may be particularly beneficial for very deficient soils but has not been widely tested. Few, if any, experiments have examined a sufficient range of application rates

for chelated and inorganic forms of Mn, to determine the most economic dose rates. Field crop studies are needed to improve treatment strategies for the prevention or correction of Mn deficiency. Such studies would include the use of seed treatments, in combination with a range of foliar application rates, timings and forms of Mn, to determine more precisely the optimum Mn input requirements according to the severity of deficiency.

5. There is little or no information on the relative susceptibility of current cereal varieties to either Cu or Mn deficiency. Work in other countries has identified genetic variation in the trace element utilisation by cereals and their tolerance to deficiencies of these two nutrients. Existing variety trials could be used to provide leaf and grain samples for Cu, Mn and also Zn analysis, to determine whether there are any varietal differences in trace element utilisation. In the longer term, consideration should be given to the breeding of varieties which are more tolerant to particular deficiencies.

6. More data are needed on S mineralisation and immobilisation rates in arable soils, to enable site-specific modelling of S deficiency risk.

7. More information is needed on the possible use of late foliar sprays of S to mitigate the effects of deficiencies which may be identified during the latter part of the growing season, as S deficiency becomes more widespread and severe.

8. Although average total rates of atmospheric deposition for Cu and Zn are similar to, or greater than, crop removal of these two nutrients, the rates vary with location and the crop availability of these nutrient sources is not well quantified. Crop surveys, based both on national grain quality surveys and on ‘targeted’ soil and crop sampling on marginal soil types for deficiency, are needed to investigate the extent of sub-clinical deficiencies of Cu and Zn in areas more remote from industrial activity.

9. The potential use of remote sensing techniques, for early detection of nutrient deficiencies and targeted corrective treatments, should be investigated.

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