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COPPER DEFICIENCY IN UK CEREAL CROPS: OCCURRENCE, SIGNIFICANCE AND TREATMENT

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COPPER DEFICIENCY IN UK CEREAL CROPS: OCCURRENCE, SIGNIFICANCE AND TREATMENT

by

A. H. SINCLAIR

Mill of Craibstone, Bucksburn, Aberdeen AB2 9TS

P. J. A. WITHERS

ADAS-Bridgets, Martyr Worthy, Winchester, Hants. S021 1AP

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CONTENTS

Glossary

GLOSSARY

Chelate	-	**Organic chemical compound**
Cu O Cl	-	**Copper oxychloride**
$Cu (OH)_2$	-	**Copper hydroxide**
$Cu SO_45H_20$	-	**Copper sulphate**
EDTA	-	**Ethylene diamine tetraacetic acid**
FMA	-	**Fertiliser Manufacturer's Association**
FYM	-	**Farm yard manure**
Ligands	-	**In a complex ion, the ions surrounding the central ion**
MAFF	-	**Ministry of Agriculture, Fisheries and Food**
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 material**
Soil type	-	**The physical characteristics of a soil profile in terms of texture, depth, stoniness and drainage status.**
S	-	**Sulphur**

1 INTRODUCTION

Although the fungicidal property of copper (Cu) was known as early as 1761 it was not until 1931 that Cu was positively identified as an essential element for the healthy growth of plants. Deficiency of Cu was found in subsequent years to be the cause of crop failure or reduced yield on a restricted range of soils in most countries of the world. The first confirmation of Cu deficiency in the UK was made in 1947 in wheat grown on a deep fen peat in Norfolk (Pizer et al., 1966). Since then, Cu deficient soils have been identified in many areas. The most commonly and severely affected crops have been cereals.

Although Cu deficiency is known to reduce cereal grain yield and quality on certain soils in the UK, no recent attempt has been made to assess the significance of this nutrient to the UK cereals industry. Corrective applications of Cu are more widely used than in the past but yield loss often goes unnoticed because of confusion over or lack of distinct crop symptoms. There is also increased interest in the effect of grain Cu content on improving oxidation in the breadmaking process because of the ban on the use of the oxidant potassium bromate.

The purpose of this review is to assess the current importance of Cu to cereal production in the UK. The role of Cu in cereal nutrition and the effects of deficiency on yield and quality are reviewed. Unpublished data from field experiments carried out within the last 10 years are presented and future research priorities identified.

2 ROLE OF COPPER IN CEREAL PRODUCTION

2.1 Function of copper in cereals

Copper is required for many essential functions of plants, in particular the production of viable pollen for grain formation (Graham, 1975) and lignin for maintenance of cell wall structure (Graham, 1976; Brussler, 1981). It is a necessary component of many enzymes; its effects on ascorbic acid oxidase, cytochrome oxidase and phenolase have been studied in detail and reviewed by Walker and Webb (1981). It is found in quantities of 0.1 to 0.2 per cent in some plant enzymes and is an essential component of some proteins. The enzyme ascorbic acid oxidase, which controls the inter-relationship between ascorbic acid (vitamin C) and dehydroascorbic acid, is particularly important in breadmaking.

Copper enzymes and proteins are involved in many oxidation and reduction reactions within metabolic pathways in living cells. Copper is required for the energy producing reactions of respiration and photosynthesis and in the processes of assimilation influencing the production of carbohydrates, especially starch, by the green leaf. Copper is also associated with iron in the formation of chlorophyll of green leaves although not a component of this pigment. Copper also influences cell wall permeability and is involved in important processes related to the reduction of nitrate nitrogen to ammonium nitrogen in plants. Copper deficient plants can therefore have undesirable accumulations of carbohydrate, nitrate nitrogen and polyphenols in vegetative tissue (Anon, 1976). Copper deficient grain may not germinate because of a lack of the auxin hormone.

2.2 Uptake of copper

Unlike most other nutrients, relatively little Cu is transported to the root surface by normal mass-flow or diffusion processes. Uptake of Cu relies more on the activity of the roots themselves and involves an initial complexation of soil-adsorbed Cu^{2+} with organic acids either exudated from root cells or produced by micro-organisms (fulvic and humic acids) within the root environment (Shorrocks and Alloway, undated; Stephenson, 1986). Soluble Cu-amino-acid complexes have been shown to accumulate within the root free space and superficial water layer (Goodman and Linehan, 1979). The complexes are thought to dissociate at the cell surface before Cu^{2+} is transported across the plasmolemma into the cytoplasm.

Such a mechanism emphasises the importance of an adequately developing root system during crop growth and is probably necessary for plants growing in soil where roots may be intermittently exposed to soil-solution and to air. In the case, for example, of cereal roots the main axes and first order laterals are of such dimensions that the soil pores which they can enter are water filled only when the soil is at or above field capacity (Scott-Russell, 1977). Thus micronutrients might be adsorbed by the roots from soil solution and subsequently mobilised when the soil solution drains away allowing their uptake and translocation within the plant over an extended period (Linehan, 1984).

Copper is relatively immobile in the growing plant, being retranslocated from older tissue only with the onset of senescence and the mobilisation of nitrogen (Loneragan et al., 1980). Consequently, Cu must be taken up continually by the plant if a transient deficiency at the growing point is to be avoided.

Rye is notably more efficient at taking up Cu than other cereals. The offtake of Cu in cereal crops has been estimated at 4 g and 2.5 g per tonne (fresh material) grain and straw respectively (Archer, 1985).

2.3 Copper deficiency and cereal quality

Cereal quality is becoming of increasing importance in Europe as the supply of grain exceeds the demand. The most important quality markets are, for wheat, the baking and pasta industries and, for barley, the malting, brewing and distilling industries.

Although many attributes of quality depend strongly on genotype or environment, protein concentration and composition in and specific weight of the grain can all be influenced by the level and timing of nutrient fertilisation to a greater or lesser extent depending on the growing conditions. The effect of fertiliser use on the quality of wheat and barley has been reviewed by Russell (1986).

A shortage of Cu causes decreased grain size and results in shrivelled and blackened grains of low specific weight because insufficient starch is accumulated in the grain (eg. Reith, 1968; Nambiar, 1976). According to Brown and Clark (1977), Cu deficient grains also show increased amounts of non-protein nitrogen which may reduce breadmaking performance.

Genotype has the largest effect on the composition of protein in wheat grain but in certain circumstances levels of Cu in the soil are sufficiently low to affect the protein quality adversely, although there is very little information available (Russell, 1986). The effect of Cu deficiency on the baking quality and dough properties of wheat flour was investigated in Australia by Flynn et al. (1987). Wheat (Triticum aestivum L., cv Oxley) was sown at a site known to be deficient in soil Cu. Copper was applied as a foliar spray of copper pholate (15% w/w Cu in 100 litres/ha water) at late tillering and/or booting stages of plant growth (Table 1). Crop growth up to anthesis was significantly increased by the application of Cu at late tillering, the higher rate of application being more effective (Table 1), due mainly to an increase in the number of grains set per head. Applications of Cu at late booting stage had no significant effect on grain set as the treatment was applied too late to increase pollen viability and resulted in higher grain protein contents.

Table 1 **Timings and rates of foliar application of copper and effect on yield of grain and milling flour**

Timing	Cu rate (g/ha)	Yield (t/ha)	Milling Yield (%)	Loaf volume (ml)	Extensibility (cm)
Control	0	1.66	70.1	1500	18.9
Late tillering (GS 26)*	37.5	2.83	70.5	1500	18.2
Late tillering (GS 26)*	75	3.21	72.7	1490	16.9
Late tillering (GS 45-47)*	75	1.99	69.7	1510	18.8
Late booting (GS 45-47)*	150	2.04	68.2	1530	18.1
Late tillering and late booting	75 + 75	3.33	72.2	1560	16.7
Late tillering and late booting 75 + 150		3.22	71.8	1560	17.1
Significance		1%	1%	NS	1%
LSD ($P < 0.05$)		0.46	1.7	-	0.9

*GS = Zadoks growth stage (Zadoks et al., 1974)
Source: Flynn et al. (1987)

In this study by Flynn et al. (1987), doughs from copper-deficient wheats had weaker, stickier dough properties, which was evident from the loss in dough consistency during mixing. This occurred despite the higher grain protein levels in the Cu deficient samples. The application of foliar Cu at tillering or at tillering and booting resulted in a decrease in dough extensibility and tended to increase dough strength which was reflected in a better loaf shape and structure. Loaf volume was not an accurate indication of loaf quality in this experiment (Table 1). Adequate Cu supply after pollen production appears essential in order to ensure balanced dough rheological properties. The lower rate at late booting did not supply sufficient Cu to overcome this deficiency. For a balance of high yield and good baking quality, a continual supply of Cu was needed both before and after pollen formation (Flynn et al., 1987).

The brewing industry is an important quality market for barley in Europe. Distilling is a smaller market for barley as well as increasingly for wheat, but with less stringent quality standards. Beer making is a two stage process. Malting is a controlled germination process which produces the enzymes necessary to convert cereal starches to fermentable sugars. Brewing is the fermentation of these sugars by yeasts to produce alcohol. The condition of grain used in the industry has a considerable effect on the yield and quality of the end product. As with wheat, some of the attributes are affected by variety and environment and some can be affected by fertiliser treatment. Only certain varieties of barley are acceptable for malting. The most important character is the concentration of N in the grain which should be preferably below 1.6%. High N barley is normally unsuitable for malting, first because the amount of malt extracted is reduced, since there is less starch, and secondly because the malt produced contains soluble proteins which pass into the beer and impair its appearance and keeping qualities. Plumpness of the grain is also important although grain that is poorly filled is unlikely to pass the N test. There is no information on the effect of Cu deficiency on malting quality other than Cu deficient grains will have enhanced N content and reduced starch content compared to normal grain (Russell, 1986).

A satisfactory grain Cu concentration is clearly of significance to the milling and malting industries even though the benefits have yet to be quantified. Cereal grain of adequate Cu status is also desirable to the feeds industry to avoid the need for unnecessary livestock diet supplementation. The extent to which grain Cu concentrations can be improved by agronomic practice has not received a great deal of attention although this is a common parameter measured in field experiments.

Application of 22 kg/ha of copper sulphate, broadcast onto the soil, had no effect on the Cu concentration of the grain in experiments in Scotland (Reith, 1968). Grain Cu was increased by foliar application of 1 kg/ha copper sulphate to spring-sown oat and barley crops growing in soils containing less than 0.7 mg/kg Cu extracted by EDTA solution. Highest concentrations of Cu were found in grain grown in soils containing a higher content of extractable Cu (Table 2).

Table 2 **Effect of soil copper and copper addition to the soil on concentration of copper in oat and barley grain and straw (mg/kg).**

Soil copper range (mg/kg extracted by EDTA solution)	No. of experiments	Grain		Straw	
		No Cu	Cu* treated	No Cu	Cu * treated
0.31 - 0.66	15	1.9	2.0	1.5	1.6
0.83 - 1.00	4	2.7	2.5	1.4	1.6
1.03 - 3.42	4	3.2	3.0	2.3	2.2

* 22 kg/ha Cu SO_4 .5$H_2$0 broadcast on to soil
Source: Reith (1968)

In early experiments in England and Wales, increasing rates of copper sulphate applied to a sandy soil at Butley, Suffolk in 1952 had only a relatively small influence on the Cu content of barley grain, although it is interesting to note that larger increases were observed in the 3rd and subsequent years after treatment (Table 3).

Table 3 **Effect of soil-applied copper sulphate on grain yield and on grain copper concentration**

Copper sulphate applied to the soil in 1952	Grain yield in 1952	Grain Cu concentration ug/g				
kg/ha	t/ha	1952	1953	1954	1955	1956
0	0.7	1.6	1.6	1.1	1.2	1.8
11.2	1.18	1.9	1.3	1.0	1.2	2.5
22.4	1.58	1.5	1.4	2.0	2.6	2.4
33.6	1.55	2.0	1.8	2.0	3.2	3.4
44.8	1.49	2.7	2.0	1.3	2.0	3.0
67.2	1.85	1.8	2.6	2.8	3.8	3.7
134.4	1.76	2.5	3.3	2.4	3.6	4.4

Source: Caldwell (1971)

3 COPPER DEFICIENCY IN THE UK

3.1 Occurrence

The usual source of Cu in soils is from weathering of rocks containing trace amounts of Cu associated with some of the primary minerals, although Archer (1985) estimates that 100 g Cu/ha/year are deposited from the atmosphere in England (wet + dry). Copper is widely distributed in igneous rocks, but the abundance of Cu in basalt and granite is very different, the former having approximately 10 times the amount of the latter. Deficiency is much more common in acid soils derived from silica and alkaline soils derived from carbonate-rich sediments such as chalk and limestone.

Table 4 Rock type and typical concentration of total copper

	Igneous Rocks		**Sedimentary Rocks**		
	Granite	**Basalt**	**Limestone**	**Sandstone**	**Shale**
Cu (ug/g)	10	100	4	30	45

Source: Hodgson (1963)

Soils whose parent materials are rich in sulphides are rich in Cu because of the strong co-valent linkage between Cu and sulphur (Knezelc and Ellis, 1980). According to Archer and Hodgson (1987), lowest Cu was found in soils derived from sandstone, granite, sandy alluvium and glacial sands and gravels.

The total Cu content of mineral and organic agricultural soils of the UK ranges from one to about 100 mg Cu/kg though much larger amounts can be found near Cu mining areas or where there has been frequent use over many years of foliar sprays containing copper. However the most usual range in the very sandy soils is from one to 15 mg total Cu/kg soil and from 25 to 60 mg/kg in loams and clay soils.

Organic soils, leached acid sandy soils, particularly reclaimed heathland, and shallow chalk soils containing moderate amounts of organic matter are most commonly deficient in Cu in England and Wales (Archer, 1985), although Caldwell (1971) found that Cu deficiency on chalk downland often did not manifest itself until 5 to 7 years after ploughing. The most extensive areas of Cu deficiency are in South-west and South-east England (organic chalky soils) and in East Anglia (peats and heathland sands). Less extensive areas of deficiency are also found in the midlands and in some northern counties. Breckland soils are particularly prone to Cu deficiency with levels of total Cu below 2 mg/kg (Thornton and Webb, 1980; Tills and Alloway, 1981a). Chalk parent materials are notably low (1-2.5 mg/kg) in total Cu (Davies et al., 1971).

There are two further main sources of information on Cu concentrations of soils in England and Wales. Soils were sampled from a depth of 0-15 cm from agricultural holdings as part of a Survey of Fertiliser Practice (Archer and Hodgson, 1986). The concentrations of total Cu and EDTA extractable Cu are given in Table 5.

Table 5 **Concentrations of total and EDTA soil copper. Adapted from Archer and Hodgson (1986)* and McGrath and Loveland (1992)[I]**

	No of samples	**Normal range**	**Overall range**	**Median**	**Log-derived mean**
Total Cu (mg/kg)*	1468	5.8-62	1.8-215	18.4	19.0
EDTA (Cu (mg/l)*	1477	1.2-19	0.5-75	4.8	4.9
Total Cu (mg/kg)[I]	5692	1.2-43	1.2-15	18.1	-
EDTA Cu (mg/l)[I]	5660	0.3-13	0.3-431	4.6	-

The data in Table 5 show that EDTA Cu is about 20% of total Cu. This value agrees with Jordan (1975) who studied 20 soil types and found that EDTA Cu ranged from 17 to 29% of total Cu. Data from the National Soil Inventory on EDTA and total Cu are presented by texture and soil group by McGrath and Loveland (1992).

A general classification of geological formations where Cu deficiency has been found by ADAS in crops is given in Table 6, along with examples of susceptible soil series where these have been named by the Soil Survey of England and Wales.

Table 6 Geological formations and soil series susceptible to copper deficiency in England and Wales

Region	Geological formation	Soil Series (examples)
Northern	Triassic Sandstone	Bowscar
	Fell Sandstone	-
	Lower Calcareous Grit	Firby
Yorks and Lancs	Fen-carr Peat and	Altcar association
	Raised Moss	-
	Postglacial Sands	-
West Midlands	Alluvium	Gilberdyke
	Triassic Sandstone	Grannymoor
East Midlands	Fen Peat	Adventurers
	Triassic Sandstone	Crannymoor
Wales	Acid Igneous	Ceriri
South West	Granite Head	Moretonhampstead
	Chalk	Icknield (organic phase)
	Upper Greensand	-
South East	Chalk	Idknield (organic phase)
	Lower Greensand	-
Eastern	Fen Peat	Adventurers, Fordham, Prickwillow
	Glacial Sands	Red Lodge, Freckenham

Source: Anon (1976)

As Cu is readily adsorbed by the clay and organic fractions in the soil and is correspondingly difficult to displace, only a part of the total Cu in soils is immediately available for uptake by plants. Some of the Cu is also immobilised by micro-organisms. Copper does not leach easily down the soil profile though mobility is slightly greater in sandy than in peaty and clayey soils. This lack of mobility leads to an increase in the severity of Cu deficiency in dry seasons. Mobility is increased considerably where soils are poorly drained. In contrast, in well drained agricultural soils most of the applied Cu remains in the cultivated topsoil, often resulting in a sharp gradient to the subsoil.

The total Cu contents of the B horizons (subsoils) of soil profiles have been used in Scotland (SAC/SARI, 1982) in conjuction with the pedological drainage conditions to make a provisional allocation of soil series to the three following categories of risk:

Low risk:	adequate soil Cu for optimum cereal production
Moderate risk:	on some soils (less than 50%) Cu may not be adequate for producing optimum yields of cereals
High risk:	soil Cu levels in most soils (more than 50%) not adequate for producing optimum cereal yields

The categories of total Cu contents in the B horizons (subsoils) <5, some < 5 and most < 15 (5-15) and <15 were used along with pedological drainage characteristics to allocate soil series (Table 7). Advisory data, where available, were used to modify the classification if necessary.

Table 7 Pedological drainage and total Cu concentration in B horizons in relation to risk categories of copper deficiency in Scotland

Pedological drainage	**Total Cu content in mg per kg soil <2 mm**		
	Low	**Moderate**	**High**
Freely-drained	>15	5-15	<5
Imperfectly-drained	>15	5-15	<5
Peaty podzols freely drained below iron pan	>15	5-15	<5
Poorly-drained (gleys)	5-15	<15	<5
Very poorly-drained	<5	5-15	>15

A comprehensive classification of Soil Association and Soil Series in relation to the probability of Cu deficiency limiting the yield of cereals has been produced (SAC/SARI, 1982). No similar classification has been attempted in England and Wales.

Very liberal or excessive use of nitrogenous fertilisers can accentuate Cu deficiency. This effect has been observed particularly in cereals grown on the susceptible organic chalky soils of the south and south-west of England which usually respond to high rates of N (Anon, 1976). Mitchell et al. (1957) and Davies et al. (1971) reported that Cu deficiency is more common in cereals following brassica crops.

Soil solution Cu

The supply of Cu 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 their Cu largely if not exclusively by uptake from solution. However, data relating to Cu 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 present in soil solutions are low and have, as a consequence, posed difficulties in analysis. McLaren and Crawford (1973) fractionated 24 contrasting soil types and found that only 0.1 to 0.2% of the total Cu was in the soluble plus exchangeable fractions (Table 8).

Table 8 Distribution of copper in different soil fractions

Soil fraction	% of total Cu
Soluble + exchangeable	0.1 - 0.2
Specifically adsorbed by clay	0.2 - 2.7
Organically bound	16.2 - 46.9
Oxide occluded	0 - 35.9
Mineral lattice	33.6 - 77.2

The high organically bound fractions are in contrast to the low soluble fractions.

Substantial increases in the concentrations of Cu 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, soil texture and pH from these sites are given in Table 9, which forms the basis of discussion in the following sections:-

Table 9 Site identification and soil characteristics

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

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

Soil parent material and extractable Cu

Soils derived from the same parent material may exhibit substantial differences in soil solution concentration. This is apparent from Fig 1 which represents data for spring barley at three sites on Stonehaven Association soils sampled in the 1984 season. Sites (C) and (D) showed substantial maxima in the concentration of Cu whilst another site (E) showed no increase in the concentration of Cu. (Fig 1; Table 9).

Although these soils were derived from the same parent material and appeared to be closely similar in all important physical characteristics, their previous history of cropping and management might have resulted in substantial differences in the forms and amounts of Cu present in their soil solutions. Indeed, if EDTA extraction of soil is an index of both Cu form and amount then substantial differences exist between these apparently similar soils (Table 9). Site E, which exhibits minimal mobilisation of Cu, has the lowest EDTA extractable Cu values of the three soils. However site D with an intermediate EDTA extractable Cu value shows the highest mobilisation and site C with a very high EDTA value has only intermediate mobilisation. Thus, EDTA extractable and root-zone soil solution values only correspond at one site. It is clear that no simple relationship exists between chemical extractability and the potential of the soil to release Cu into the soil solution. These three sites were not only on the same soil type but also very close to one another, sites C and D being less than 300 m apart whilst site E was some 20 km from sites C and D. Thus macroclimatic differences can be ruled out as factors controlling the extent of mobilisation at sites C and D. Site E might have experienced some differences in climatic influence.

Annual differences and soil temperatures

It seems likely that macro-climatic differences are important in influencing the extent and pattern of Cu mobilisation at some sites. Figure 2a shows data for Cu in the root-zone of spring-sown barley at a single site (site F) in three consecutive growing seasons 1983-1985. Figure 2b shows the soil temperature, at a depth of 100 mm, for each of the three seasons. The pattern of increasing soil temperature through the season to a maximum in July is broadly the pattern observed for soil solution Cu concentrations (Fig 2a). There are well established observations that Zn and Mn deficiency symptoms occur in field crops early in the growing season but frequently disappear by mid-season

Fig. 1 Copper concentrations (µM) in soil solutions in the root-zones of spring barley at three sites on Stonehaven Association soil. Source : Linehan et al. (1989)

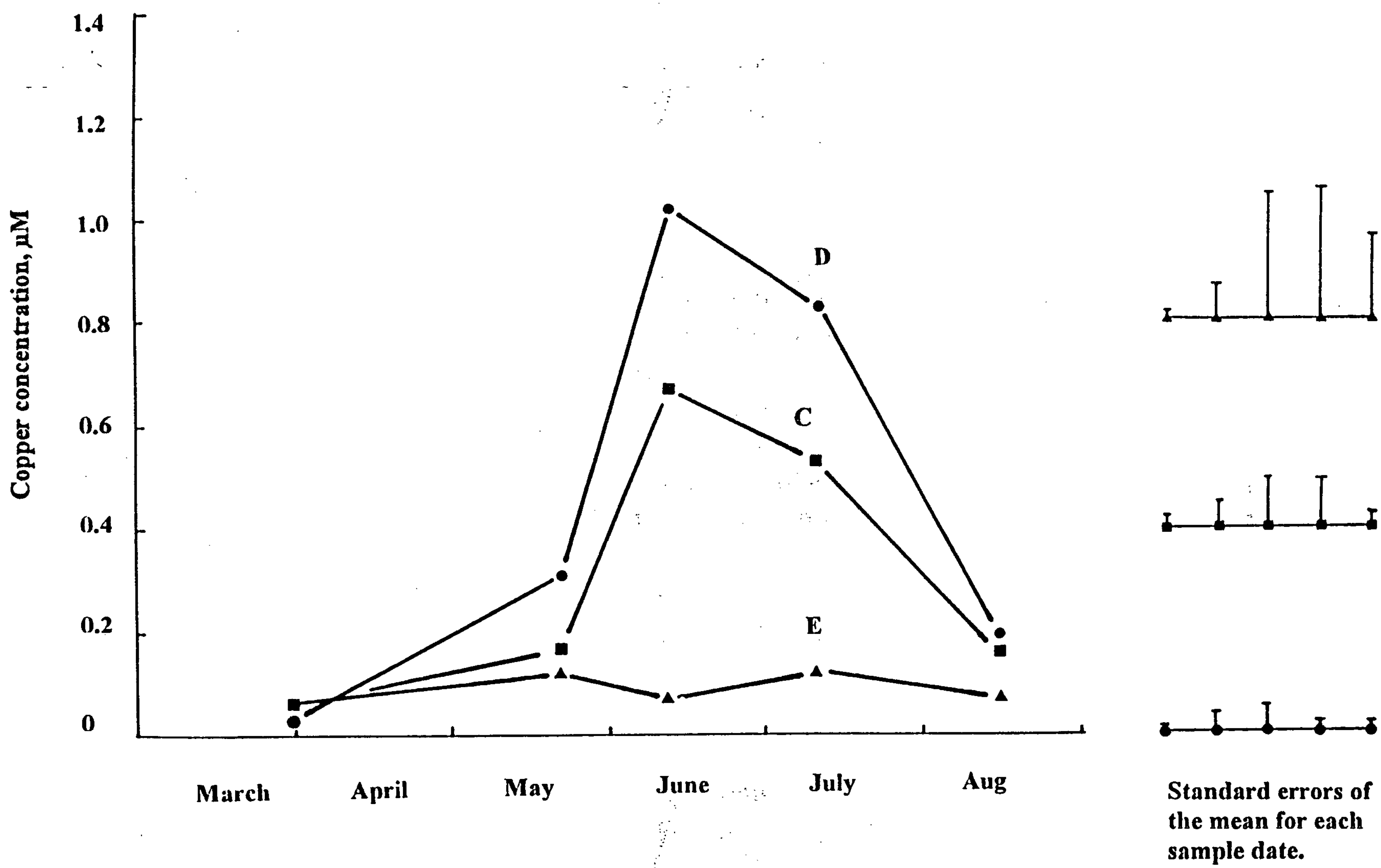


Fig. 2a Copper concentrations (µM) in soil solutions in the root-zones of spring barley at site F in three seasons.
Source : Linehan et al. (1989).

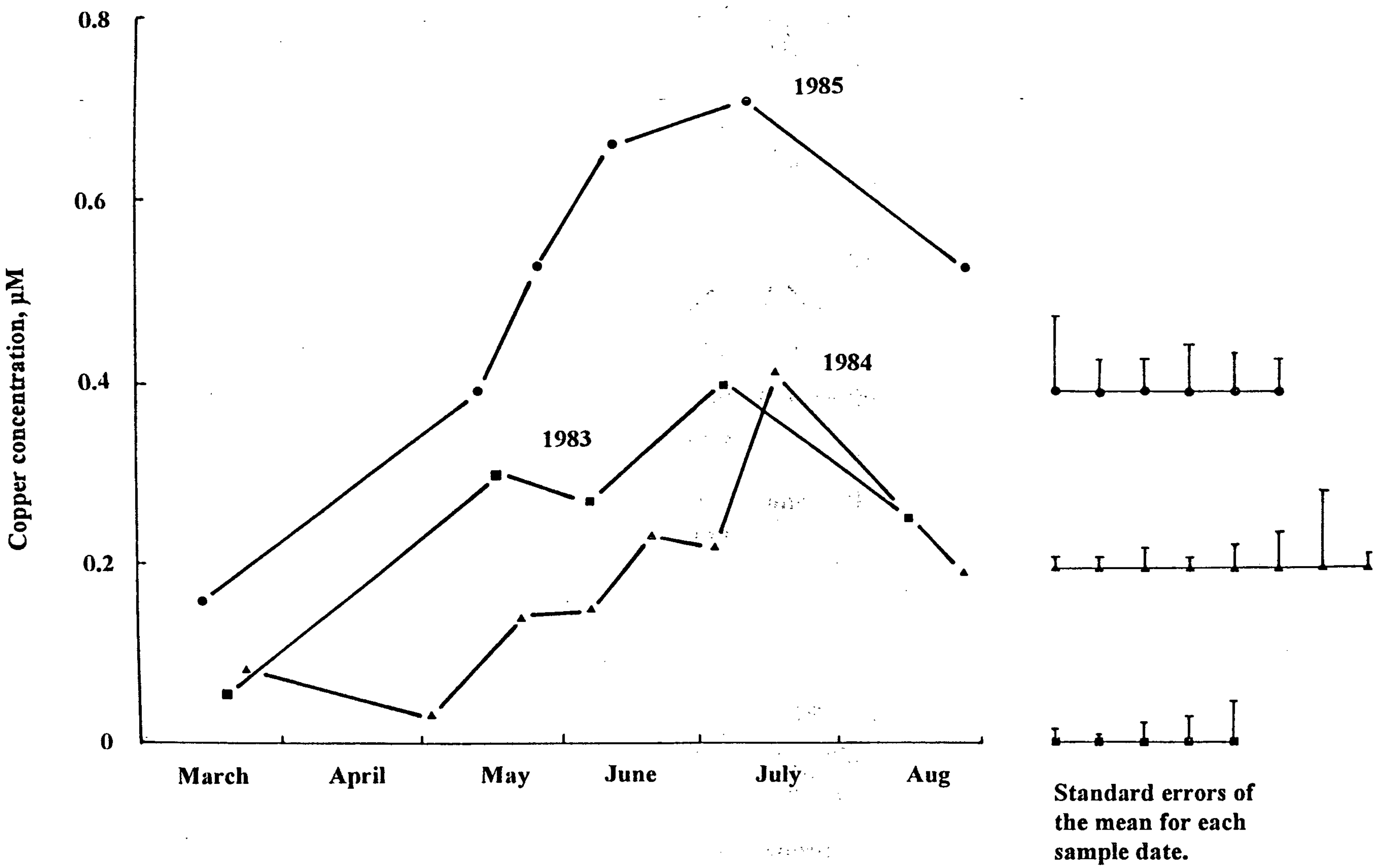
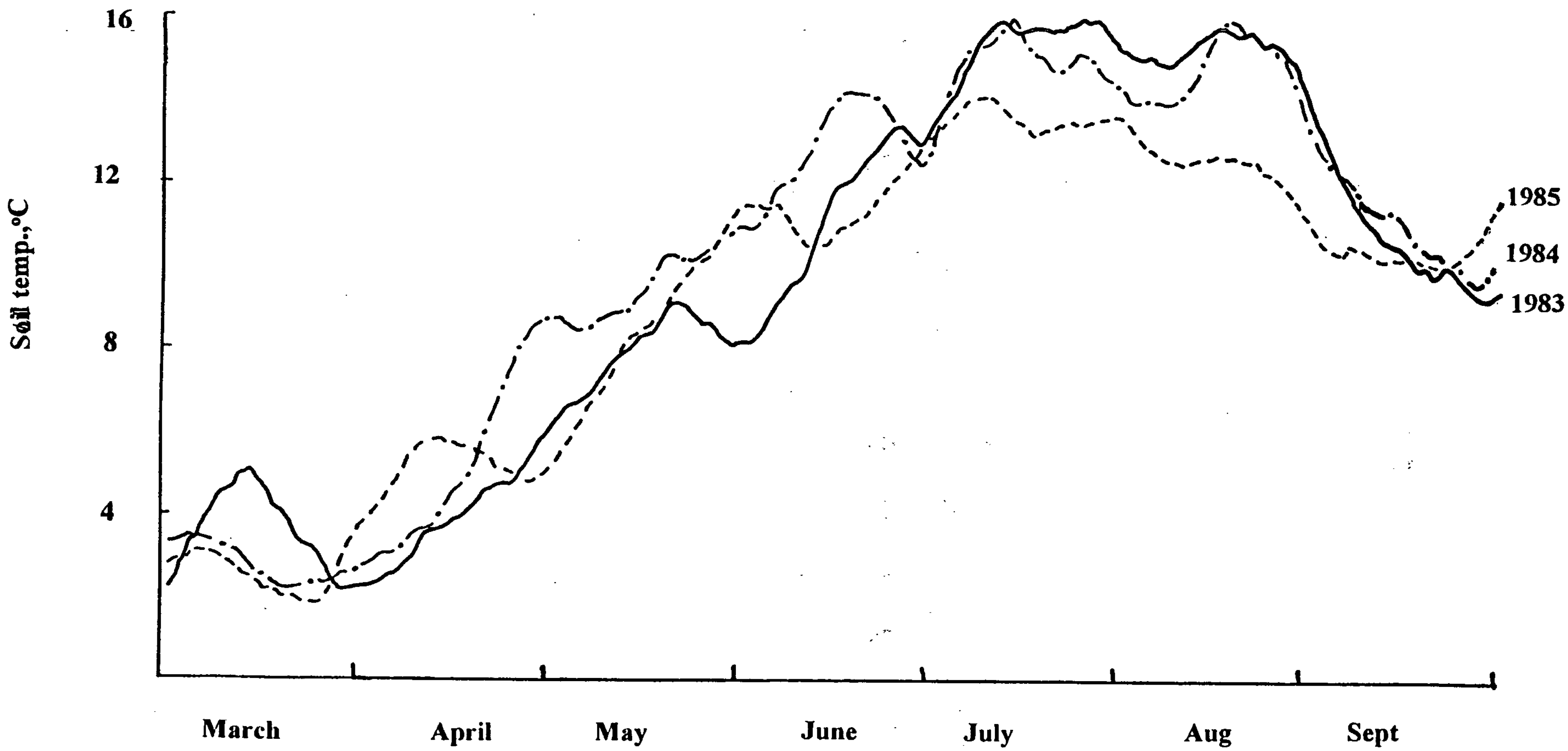


Fig. 2b Soil temperature at a depth of 100mm at site F in three seasons.
Source : Linehan et al. (1989).



(Pumphrey and Koehler, 1959; Linehan and Sinclair, 1985). It has been suggested that this phenomenon is related to increasing soil temperature (Bauer and Lindsay 1965; Schwartz et al., 1987).

The trend of increasing soil temperature through the growing season might explain the pattern of soil solution Cu concentrations, observed by Linehan et al. (1989). However, differences in temperature patterns between the seasons do not appear to provide an explanation for the differences in Cu concentrations which occur from one season to another.

Root-zone and fallow soil

Examination of the concentration of Cu in fallow as well as related root-zone soil show that the patterns of changing concentration are rather similar for fallow and root-zone soil (Linehan et al., 1989). The concentrations are however much higher in the root-zone than in the fallow soil (Fig 3). If these nutrients are not being translocated through the soil to the root-zone by mass flow of water Linehan et al. (1989), then they must be mobilised from otherwise immobile sources. Such mobilisation must be occurring in the root-zone at a relatively higher rate, compared with fallow soil, than appears from their concentrations because the period of rapid increase in concentration corresponds with the period of rapid plant growth and hence high demand for nutrients. Mobilisation must therefore occur at a rate in excess of that required to meet the demands of the plant. What is seen in the root-zone soil solution is the excess of supply over demand. It was clear that the quantities mobilised in the root-zone were very considerably greater than in fallow soil indicating an important role for the plant-root system and its associated micro-organisms.

Time of year of plant growth

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 Cu inevitably occurs much earlier in the season. This was demonstrated in adjacent fields of the same soil parent material by linchan et al (1989). Not only is the demand for Cu much higher in the autumn-sown crop but demand occurs much earlier in the year (Fig 4a). Maximum offtake of Cu by

Fig. 3 Copper concentrations (µM) in soil solutions from root-zones of spring barley and from fallow soils at site H.
Source : Linehan et al. (1989)

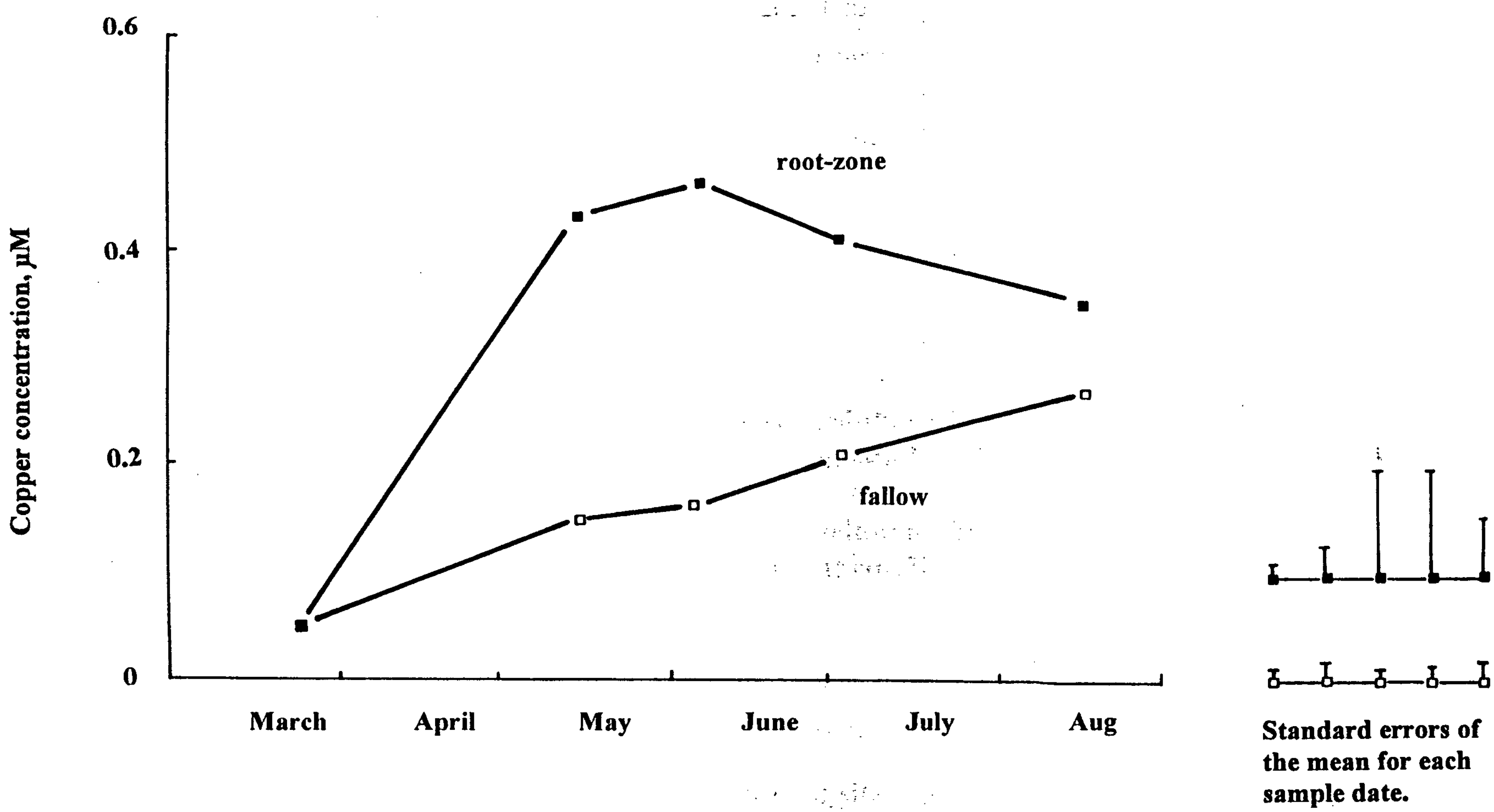


Fig. 4a **Copper offtake by spring-sown and autumn-sown barley.**
Source : Linehan et al. (1989).

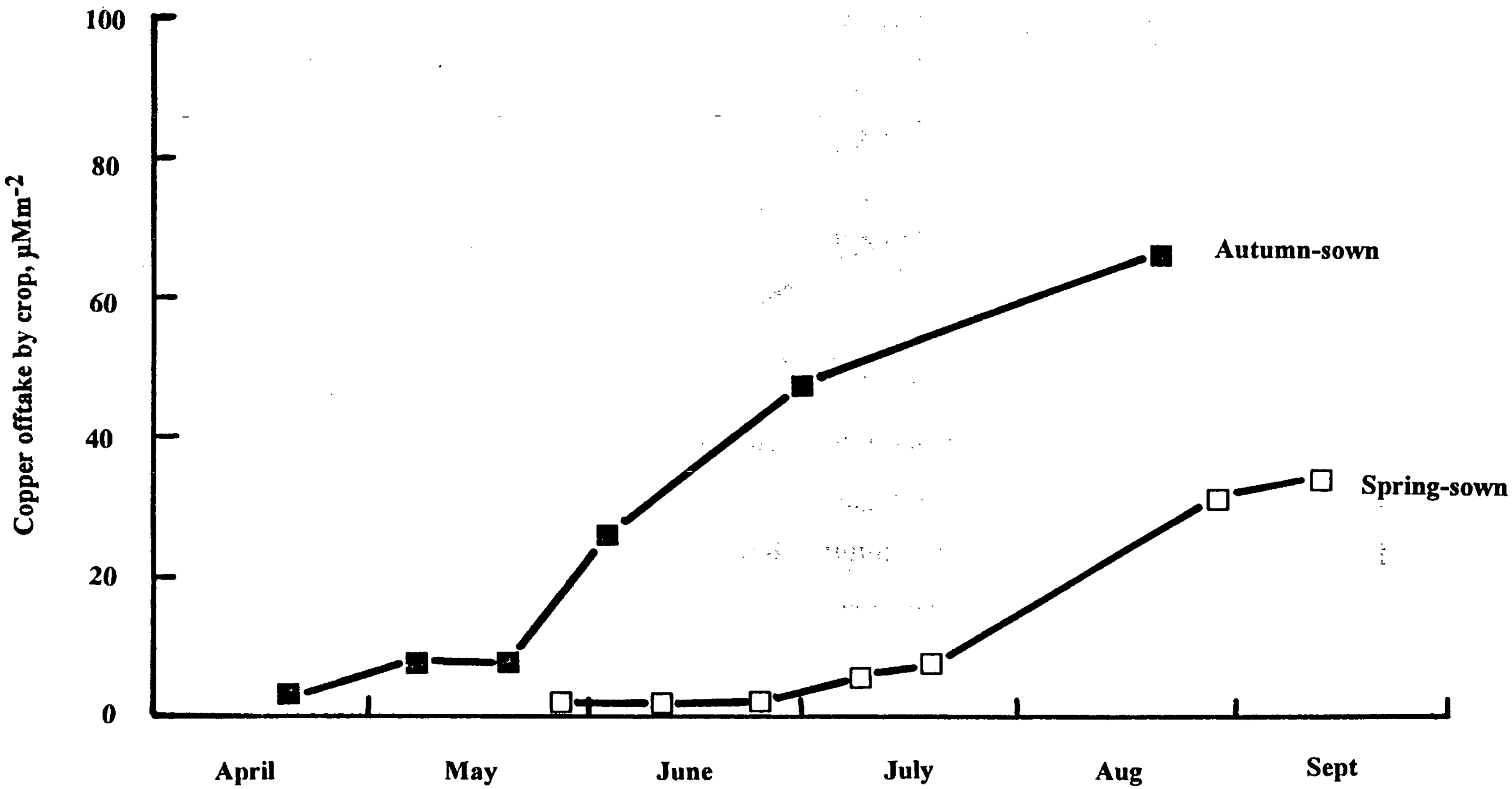
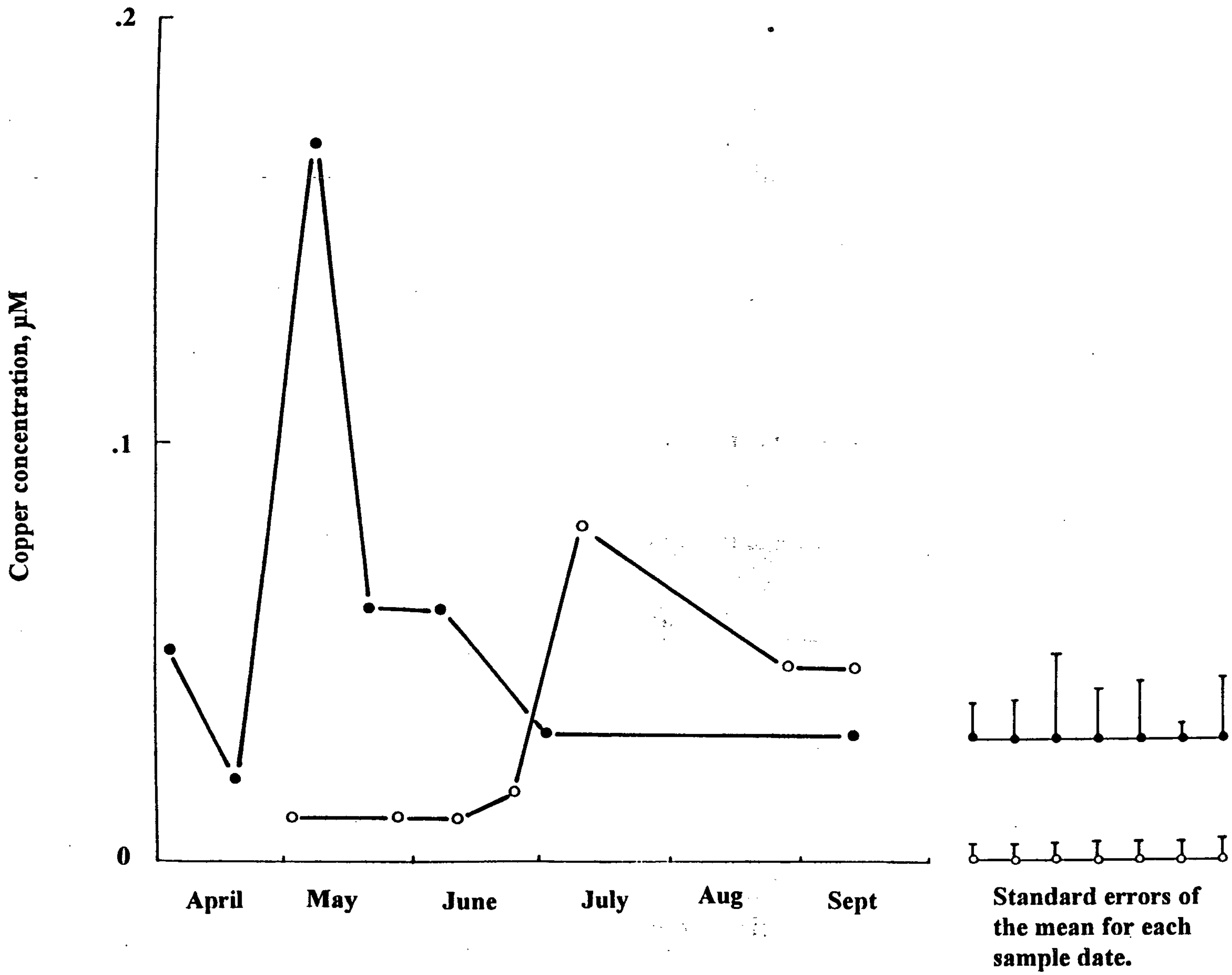


Fig. 4b Copper concentrations (µM) in soil solutions in the root-zones of spring-sown and autumn-sown barley.
Source : Linehan et al. (1989).



the autumn-sown crop occurred in mid-May, and early july for the spring-sown crop. For the autumn-sown crop the maximum Cu concentration in root-zone soil solution occurred in early May whilst that for the spring-sown crop occurred in early July (Fig 4b). Bearing in mind that the concentration of Cu 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. Demand for Cu is relatively low in the earlier part of the season. Thus, assuming that, for any particular crop, mobilisation of Cu starts early in the season, then there will be an excess of supply over demand for Cu early in the season when uptake is low, which helps to explain why symptoms of Cu deficiency are seldom seen until the end of tillering (section 3.2). 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.

Rate of replenishment of the soil solution with Cu 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 are much smaller. The release by micro-organisms of relatively small amounts of chelating ligands could thus mobilise nutritionally significant quantities of Cu. Differences in the extent and nature of exudation by plant roots might explain observations that cereal cultivars differ in their sensitivity to micronutrient deficiency (Nyborg, 1970). Varietal susceptibility to Cu deficiency has not been researched in the UK but breeding varieties less susceptible to Cu deficiency 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 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, and Cu concentration in soil solution were measured on 9 occasions from early May until harvest in early September.

The Cu 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 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 Cu in the soil solution was calculated from the concentration of Cu 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 Cu (T) as:

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

where C is the concentration of Cu 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, calculated for above-ground material only, was at a maximum in July at 0.43×10^{-9} mol Cu m root^{-1} day^{-1} (Sinclair et al., 1990b). This is lower than the value of 1.8×10^{-9} mol Cu m root^{-1} day^{-1} for 30 day old corn plants reported from the USA (Mengel and Barber, 1974). It is already clear that mobilisation within the root-zone provides a reservoir of soluble Cu available for uptake by the plant. 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 10).

Table 10 Length of time (days) required for crop uptake to deplete the soil solution of copper at 4 dates.

8 May	21 May	4 June	3 July
121.0	9.6	0.8	1.6

It is clear from the data shown in Table 10 that Cu in the soil solution is depleted more rapidly between 8th and 21st May in this experiment, than would be expected from Cu 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 the rate of depletion is driven by Cu uptake generated by crop growth it will be modified and limited by the balance between mobilisation and immobilisation within the root-zone which is dependent on microbial activity controlling the flux of organic ligands.

3.2 Symptoms

Symptoms in the growing crop provide a valuable but not infallible guide to copper deficiency. In Cu deficient cereals, symptoms can be confused with very similar symptoms caused by drought, frost or excessive herbicide use.

Visual symptoms

Symptoms of deficiency 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 acheive 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). The organism may enter a wound caused by the Cu deficiency but this symptom is not seen on oats or barley to any great extent.

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 (eg 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 and 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).

Subclinical symptoms

Alloway et al. (1983) have reported that subclinical (or hidden) deficiencies of copper can reduce the yield of many crops, including cereals, by 20% or more without the appearance of visual symptoms. Reith (1968) reported "white tips" symptoms of Cu deficiency on the leaves in only three out of 20 cereal experiments, where 18 out of the 20 gave significant responses ($P<0.05$) and the mean response was about 20%. However, on sites showing a response to Cu there were numerous second-growth tillers in the crops in the no-Cu plots and further second-growth tillers usually appeared from the cereal stubble after harvest. Jordan (1975) found an 18% increase in yield with no symptoms on sandy soils in Sussex. Unpublished ADAS data also indicated yield responses in the absence of visible symptoms (Table 20). Sub-clinical deficiency is also a recognised problem on Australian soils (Graham and Nambiar, 1981).

From microscopic studies of pollen development in Cu deficient and sufficient barley plants, Alloway et al. (1983) suggested a mechanism bringing about male sterility, which could account for much of the yield depletion in subclinically deficient cereals. They reported that a marginally inadequate supply of Cu from the soil to the rapidly growing plant could lead to a crucial deficiency of the element at the relatively advanced stage of growth when pollen formation is occurring. Most of the Cu already taken up by this time will have been bound in the older leaves and very little relocation occurs, so the late deficiency could result in the dysfunction of various copper containing enzymes when the vegetative growth appears relatively normal. The role of male sterility in yield depletion is to bring about incompletely filled ears of grain. Alloway et al. (1983) also reported that another contributing factor in the yield effects of Cu deficiency in cereals is the reduced efficiency of photosynthesis. Copper is a constituent of plastocyanin involved in photosythesis and therefore Cu deficiency could exert some effect on this most important of all plant physiological processes.

3.3 Diagnosis

The methods used in the diagnosis of Cu deficiency are:

1. characterisation of soil type
2. history of past cropping including use of Cu fungicides
3. analysis of soil samples for level of available Cu
4. visible symptoms in crops
5. analysis of plants for Cu content

History of past cropping

The history of growth of crops can give an indication whether an area is likely to be susceptible. For example, if cereals are not successful on a peaty soil yet most other crops grow and yield well, then copper deficiency might be the cause. In the past, frequent use of Cu fungicides prevented the development of Cu deficiency on otherwise deficient soils. An indication of a change from good to poor yields following a change in cropping which no longer requires fungicides or a change to a non-copper fungicide, can have diagnostic value.

Use of soil analysis

The extractable Cu in a soil as determined by analysis in the laboratory is universally used as a guide in the identification of Cu deficient areas. This is a reflection of the well known phenomenon that the total amount of Cu in the soil is not all plant available. However, Thornton and Webb (1980) reported that total Cu was a useful measure of Cu deficiency in sands and chalk soils.

In England and Wales Cu is extracted from a volume of soil with 0.05 M di-Na EDTA solution at pH 7.0 (Anon, 1986). The interpretation of results is shown in Table 11.

Table 11 Interpretation of extractable Cu in soils in England and Wales

Extractable Cu (mg/litre)	Index	Soil status	Interpretation
<1.0	0	deficiency	yield response likely.
1.0 - 2.5*	1	low	yield response possible on soils with >6% organic matter
2.6 - 4.0	2	satisfactory	yield response unlikely
>4.0	3	well supplied	no yield response

* Deficiency in cereal crops is unlikely where Cu concentrations on mineral soils exceed 1.6 mg/litre
Source: Withers and Grylls (1991)

In Scotland Cu is extracted from soil with 0.05 M EDTA (adjusted to pH 7 with NH_4OH) solution using a soil:solution ratio of 1:5 (w/v), shaking for 1 h and filtering immediately (MLURI/SAC, 1985).

The Scottish classification and interpretation of soil Cu levels are given in Table 12 for soils of all drainage classes containing up to 12 per cent organic matter.

Table 12 Classification and interpretation of soil Cu levels for cereal crops in Scotland

Extractable Cu mg/kg	Soil status	Interpretation
<1.0	VL (very low)	Deficiency probable
1.0-1.6	L (low)	Deficiency possible
1.7-8.5	M (moderate)	No deficiency expected
8.6-80	H (high)	No deficiency
>80	E (excessive)	Cu toxicity may occur

Source: MLURI/SAC (1985)

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 adjustments for soil pH are required.

Copper application for cereals is recommended by SAC where a yield response or deficiency is likely or possible ie. at Cu concentrations up to 1.6 mg/kg in Scotland and 1.6 mg/litre by ADAS in England and Wales. Sinclair et al. (1988) reported that 31% of soils analysed for the North of Scotland College of Agriculture during 1985-1987 contained less than or equal to 1.6 mg/kg of extractable Cu. ADAS surveys of the total and extractable trace element contents of soils between 1973 and 1980 indicate that less than 5% of soils in England and Wales have EDTA-extractable Cu levels at which routine treatment of susceptible crops might be advised, 1.6 mg/l (Archer and Hodgson, 1987).

Tills and Alloway (1983) compared eight soil test methods for estimating plant-available Cu on twenty English soils of a range of Cu status, pH values, textural classes, organic matter contents and calcium-carbonate equivalent values. Wheat (cv. Hobbit) was grown in each of the soils in pots in a greenhouse. At Zadoks growth stage 14 (Zadoks et al. 1974) the plant shoots were harvested, dry ashed and analysed for Cu concentration. Multiple regression analysis was performed with plant Cu concentration related to Cu extracted with various extractants and soil properties. The most significant equation accounting for 79.4% of the variation in plant Cu concentration was the one which included EDTA as the soil extractant. EDTA extractable Cu was by far the most significant factor in the regression equations, and it was therefore concluded by Tills and Alloway (1983) that EDTA solution at pH 7 appears to be the best of the extractants tested for predicting the Cu concentrations in wheat grown in pots. However, soil tests are normally adopted on the basis of their suitability for predicting yield-limiting crop deficiencies in the field rather than metal concentrations in plants. Tills and Alloway (1981b) found that DTPA was sometimes better than EDTA and DTPA is routinely used abroad (Lindsay and Norvell, 1978).

Effect of grain yield on level of critical extractable soil Cu values

The current higher cereal yields mean that more Cu is removed from the soil (McGrath, 1985). Field trials were carried out on commercial farms in the north-east of Scotland in order to investigate the need to raise the level of extractable soil Cu in Scotland for high-yielding cereal crops. Winter barley was grown in eight soils of a range of Cu status, different parent materials and organic matter content above 6%, at sites with a history of a range of previous yields. Information on the sites and soil Cu and Zn extracted in 0.5 m EDTA solution (MLURI/SAC, 1985) are given in Table 13. All soils were sandy loam in texture.

Table 13 Site identification and soil characteristics

Site	Soil Association[1]	Grid ref	pH	Extractable Cu mg kg^{-1}
A	Countesswells	NJ741062	6.2	0.5
B	Strichen	NJ945500	5.8	1.1
C	Countesswells	NO758929	5.8	1.4
D	Ordley	NJ738451	5.9	1.5
E	Countesswells	NJ750096	6.5	1.6
F	Foudland	NJ801308	6.5	2.1
G	Ordley	NJ701408	6.2	3.0
H	Countesswells	NJ741082	6.5	3.6

1 - Glentworth and Muir (1963)

All trials were of the randomised block design replicated three times at sites E and F, four times at G and five times at A. B, C, D and H. Foliar Cu was applied in 225 l/ha, including Agral wetter, by a motorised sprayer with a 3 m boom fitted with fan nozzles. 0.5 kg copper oxychloride per hectare was split into equal applications at GS 22/30 and GS 31/32 at A, B, C, D and H, and a cocktail of 1kg Maneb, 0.5 kg copper oxychloride and 0.5 kg Librel zinc per hectare was split into equal applications at GS 22/30 and GS 31/32 at G, and 10 kg/ha of copper oxychloride was applied to the ploughing and cultivated into the seedbed at E and F.

Dry matter accumulation and uptake of Cu by plant samples clipped at ground level were determined. Soil samples were obtained by carefully lifting root-penetrated soil from the top 150 mm horizon, retaining only soil obviously penetrated by roots, at sites E and F, and soil solutions were isolated by centrifugation (Linehan et al., 1989).

The data in Table 14 show that the greatest yield responses to foliar-applied Cu occurred at the site of lowest Cu status (A) and the lowest-yielding site (B). As the previous cropping and management may have resulted in substantial differences in the forms of micronutrients present at these sites, different yield levels were created by varying the N rates at sites E, F and G.

At E and F the interaction between extreme differences in yields and the response to soil-applied Cu were investigated by comparing the effect of no spring N top-dressing to winter barley with 150 and 200 kg/ha N, applied as either urea or ammonium nitrate (Table 15). Significant yield responses were found only in the absence of spring N, despite a doubling in plant offtake of Cu from plots which were untreated with Cu but given N (Fig 5). Mobilisation of Cu in solution in the root-zone soil occurred through the season, and concentrations of Cu, remaining even after a doubling in Cu offtake, were similar to those without N fertiliser (Fig 5). The form or rate of N fertiliser had no effect on the response to soil-applied Cu. The response to Cu in the absence of spring N top-dressing occurred despite the extractable Cu concentration at F being classified as "moderate" (MLURI/SAC, 1985).

Fig. 5 Copper offtake (–) and copper concentration (--) in soil solution from root-zones of winter barley
Source : Sinclair et al. (1990a).

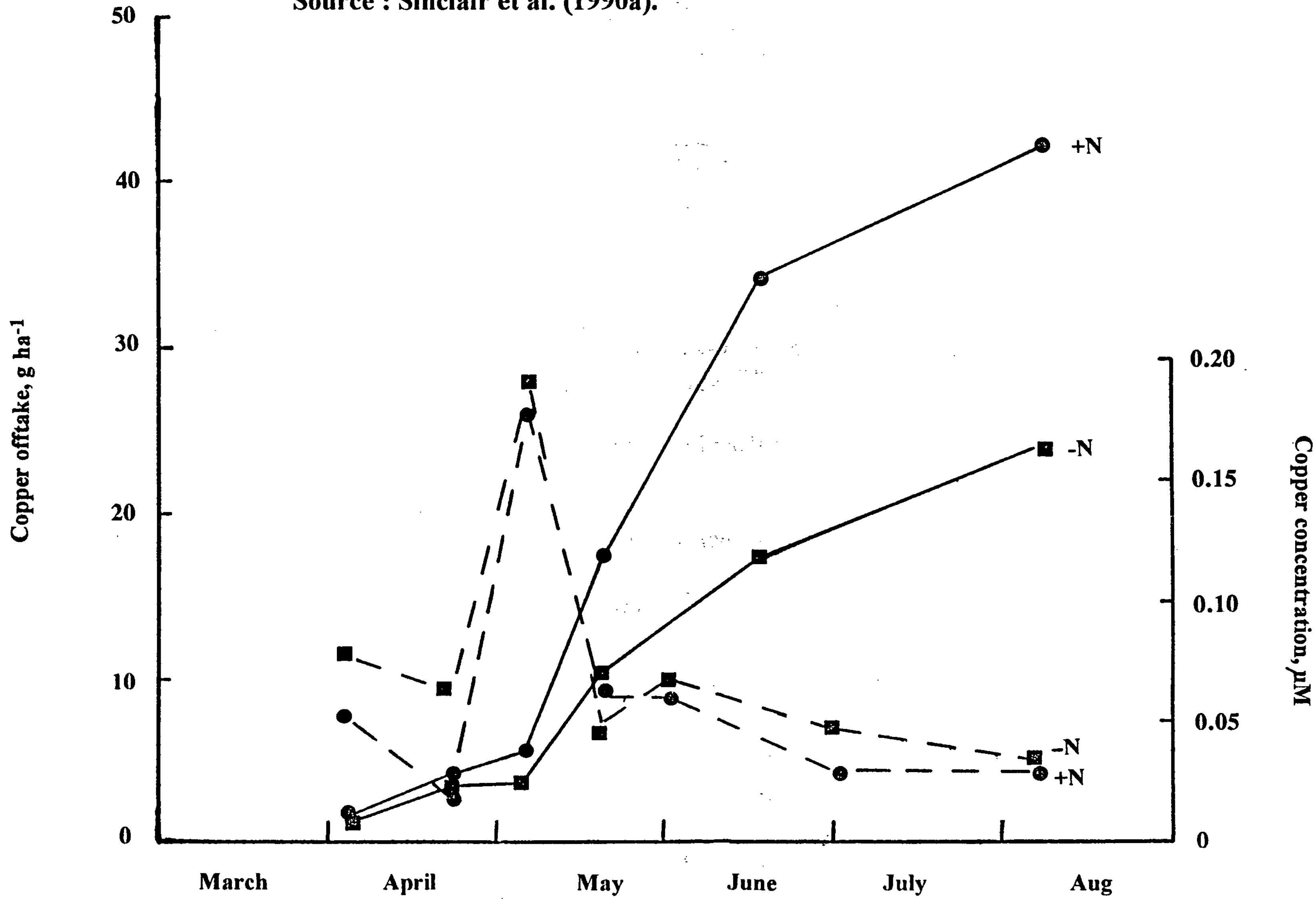


Table 14 **Yield of winter barley grain (t/ha) and response to foliar-applied copper xychloride**

Site	-Cu	+Cu	Relative yield + Cu	S.E.M.	CV%
A	8.06	9.22	114	0.296	8.8
B	4.25	4.90	115	0.376	17.9
C	5.88	5.93	101	0.190	7.0
D	8.47	8.68	103	0.172	4.4
H	7.74	7.85	101	0.117	4.0

Source: Sinclair et al (1990a)

Table 15 **Nitrogen fertiliser, yield of winter barley (t/ha) and response to soil-applied Cu**

Spring N form	Rate kg/ha	Site E Yield		Site F Yield	
		- Cu	+ Cu	- Cu	+ Cu
-	nil	3.02	3.69	2.67	3.34
urea	150	5.71	5.65	6.68	6.87
urea	200	5.60	5.68	7.40	7.52
NH_4NO_3	150	5.76	5.61	7.02	7.07
NH_4NO_3	200	5.51	5.89	7.88	7.74
S.E.M.			0.202		0.216
C.V.%			6.9		5.8

Source: Sinclair et al. (1990a)

At the high-yielding site G, the response of winter barley at 3 spring N rates to a foliar-applied cocktail of Cu, Mn and Zn showed that the optimum N rate, in the absence of foliar micronutrients, was 200 kg/ha but 150 kg/ha with micronutrients (Table 16). Sinclair et al. (1990a) suggested that non-pH dependent mobilisation of Cu increases as N fertiliser rate is increased, probably due to increased production of chelating agents by high-yielding, vigorous cereal crops. They concluded that it was not necessary to routinely apply Cu to every high-yielding cereal crop, whereas Tills and Alloway (1981b) showed that Cu uptake decreased on a Cu deficient soil when ammonium fertiliser was applied.

Table 16 **Fertiliser N rate, yield of winter barley grain (t/ha) and response to foliar Mn, Cu and Zn cocktail at site G**

Spring N kg/ha	Yield untreated	Cu+Mn+Zn	Yield (as % of untreated)
150	8.58	9.41	110
200	9.26	9.40	102
250	9.16	9.36	102
S.E.M.	0.218		
CV%	4.8		

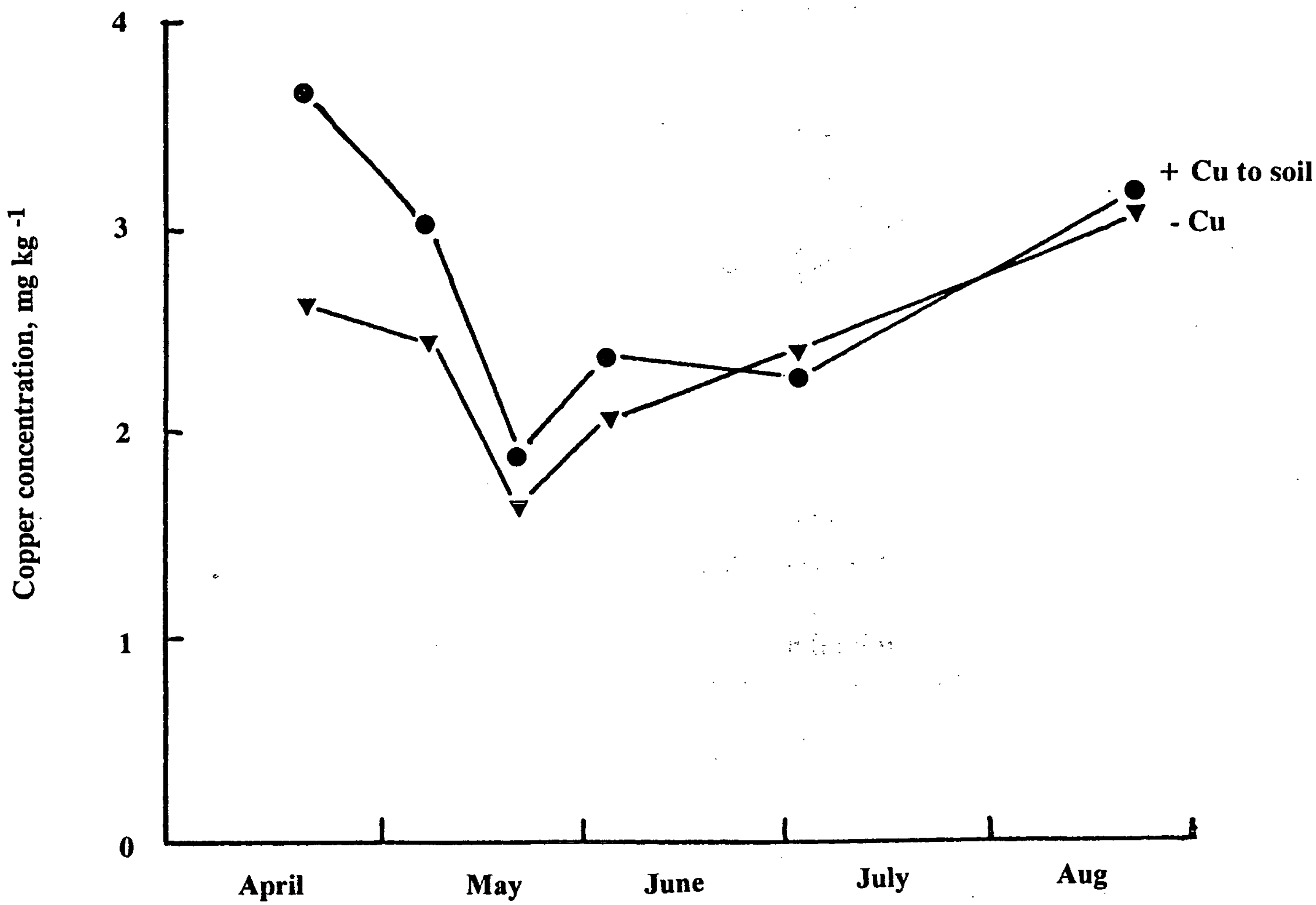
Source: Sinclair et al. (1990a)

The results of trials at sites A to H (Table 13) are consistent with the idea that high-yielding crops may be more efficient at obtaining Cu from the soil, given similar concentrations of extractable Cu prior to seed-sowing. Using E as an example, the concentrations of Cu in root-zone soil solutions of both the higher and lower-yielding crops were similar (Fig 5), but bearing in mind that the concentration of nutrients in the root-zone results from the balance between uptake and mobilisation, it is clear that far greater mobilisation of Cu occurred under the higher-yielding crop. In fact, mobilisation in the root-zone soil solution of the higher-yielding crop supplied sufficient Cu for optimum growth, whereas the lower-yielding crop, given no spring N top-dressing, was deficient of Cu.

Plant analysis

In reviewing previous ADAS work, (Withers and Grylls (1991) suggested that plant analysis was of limited value because there was only a slight difference in the Cu concentration of healthy and deficient plants, but that Cu concentrations <3 mg/kg in the leaf/grain/whole ear (100% DM) can indicate that a deficiency may be present. SAC use plant analysis to predict the need for Cu addition and consider a Cu concentration <4 mg/kg in the DM prior to GS 30 to be low (Anon, 1992). The same threshold is reported by Stephenson (1986). The data in Fig 6 of Cu concentration in winter barley plants from site E (Table 15) confirm however, the view of Withers and Grylls (1991) that the difference in the Cu concentration of healthy and deficient plants may be small. The concentration of Cu in above-ground plant material changes during the season (Fig 6). Thus, it is essential that the stage of crop growth is known before the result of plant analysis can be interpreted. When sampled at ear emergence, McAndrew et al. (1984) considered plant Cu concentrations to be low when they ranged from 3.0 - 4.9, 2.3 - 3.7 and 1.7 - 2.5 mg/kg (in the DM) for wheat, barley and oats respectively. Data from early ADAS experiments indicate that older tissue contains more Cu than younger tissue, which is consistent with the reduced mobility of Cu once in the plant. Copper concentrations in spring wheat, for example, were 4.0, 3.0, 2.1 and 2.4 mg/kg in first, second, third and top internodes, respectively (Caldwell, 1971). According to Archer (1985), <2 mg/kg Cu in the grain is considered deficient and this may be used as an indication of sub-clinical deficiency.

Fig 6 Copper concentration in winter barley
Source : Sinclair (unpublished)



4 TREATMENT OF COPPER DEFICIENCY

4.1 Soil treatment

The effect of Cu treatment on yield of grain and straw of barley and oats in thirty field experiments in north-east Scotland were reported by Reith (1968). All the soils were freely drained and had clay contents between 6 and 21% and loss on ignition values between 3 and 15%. All the soils were derived from glacial drifts of fluvio-glacial sands and gravels and had pH values between 5.2 and 6.7. The extractable Cu (MLURI/SAC, 1985) varied from 0.31 to 4.7 mg/kg Cu, most of the soils containing less than 1 mg/kg.

Copper was applied to the soil just before sowing the crops at rates ranging from 5.5 to 110 kg Cu sulphate ($CuSO_4$. $5H_20$)/ha, most measurements of the response to Cu being made with a 22 kg/ha dressing.

All the oat and barley crops were sown in spring. The 'white tip' symptoms of Cu deficiency were observed during the growing season on the leaves in only three experiments. In the others vegetative growth was normal in the no-Cu plots, but in a number of cases these plots produced grain and straw which did not ripen properly, remaining bluish-green in colour. On sites showing a response to Cu there were numerous second-growth tillers in the crops in the no-Cu plots and further second-growth tillers usually appeared from the cereal stubble after harvest.

The difference in response between oats and barley was small compared with the variations between years and between sites, and the results for these two crops were combined. The yields in Table 17 show the average effect of 22 kg Cu sulphate/ha applied broadcast on the production of grain and straw at three ranges of EDTA-extractable soil Cu contents. At levels below 0.7 mg/kg grain yields usually showed a clear increase following Cu treatment, eighteen out of the twenty experiments giving significant responses ($P < 0.05$). The mean response was about 20% but there were large variations between experiments, the individual responses ranging from one to over 100%. The response to Cu was generally greater with low rainfall (less than a total of 150 mm during May, June and July) than with high (over 175 mm during these months), and it was largest with late sown crops following swedes and turnips (Reith, 1968).

At soil levels between 0.8 and 1.0 mg/kg extractable Cu, grain yields usually showed a small response, two out of the five experiments giving significant increases and the mean response being just 7%. In the 5 experiments with soil Cu between 1.03 and 3.42 mg/kg, Cu dressings did not increase grain yields (Table 17). The linear correlation coefficient for the thirty no-Cu grain yields with the soil EDTA Cu values was 0.36, which was significant ($P < 0.05$). The linear correlation coefficient for the thirty grain responses with the soil EDTA Cu values was - 0.48, which was significant ($P < 0.01$).

Copper application had a much smaller effect on the yield of straw than on the yield of grain, and the means for the three ranges of EDTA - Cu values are given in Table 17. At levels below 0.7 mg/kg Cu only six of the seventeen experiments gave significant responses, and the Cu-treated mean was only 8% higher than the no-Cu yield of straw. At higher levels Cu treatment had no positive effect on straw yields.

On deficient soils the kernels of oat and barley grain were usually not properly filled, resulting in grain of inferior quality and of low volume weight. The mean Cu contents in grain and straw (Table 17) show that the values for the crops receiving 22 kg Cu sulphate/ha were practically the same as those for the no-Cu treatments but there was a trend for the content to increase with high levels of EDTA-extractable Cu in the soil.

Table 17 **Average effect of copper applications on spring-sown oats and barley in field experiments (yields in t/ha and Cu contents in mg/kg dry matter)**

		Grain			Straw		
Soil Cu mg/kg extracted by EDTA		**No of expts**	**No Cu**	**Cu* treated**	**No of expts**	**No Cu**	**Cu* treated**
Mean 0.50	Yield	20	2.56	3.07	17	2.82	3.05
(Range 0.31-0.66)	Cu content	15	1.9	2.0	15	1.5	1.6
Mean 0.91	Yield	5	2.35	2.53	4	3.3	3.3
(Range 0.83-1.00)	Cu content	4	2.7	2.5	4	1.4	1.6
Mean 1.86	Yield	5	3.42	3.32	4	2.45	2.31
(Range 1.03-3.42)	Cu content	4	3.2	3.0	4	2.3	2.2

* 22 kg $CuSO_4 . 5H_2O$ per hectare applied broadcast to soil

Source: Reith (1968)

In a few experiments rates of 5.5, 11 and 110 kg/ha copper sulphate were compared with the 22 kg/ha dressing. The 110 kg/ha treatment always gave practically the same yield as the latter and produced grain and straw with similar Cu contents. The yields of grain produced by the 5.5 and 11 kg/ha treatments were occasionally slightly lower than those produced by the 22 kg/ha treatment, but the differences were never statistically significant (Reith, 1968).

In four experiments, Cu sulphate mixed with ordinary superphosphate, was combined-drilled at rates up to 22 kg/ha with either oat or barley seed. In all cases the yields were practically the same as those obtained with the corresponding rates broadcast. There was no evidence of either beneficial or harmful effects of combine drilling Cu sulphate.

Reith (1968) concluded that Cu deficiency can easily be corrected by applying 11-22 kg Cu sulphate/ha. This is considerably less than the dressing of 31-62 kg/ha commended by Pizer et al.

(1966) to overcome the deficiency in East Anglia. Historic experiments testing soil-applied Cu fertiliser in England and Wales generally show that soil treatment is effective but practical advisory indicates that Cu availability from soil treatments may not be sufficiently rapid in the first year after application..

This difference between the effects of soil reserves and of Cu applications on the content in cereals may be associated with distribution within the soil, potential availability and with intensity and capacity factors in the supply of Cu in solution to roots. Applications give pockets of Cu-treated soil in which the intensity is raised, while reserves, which are much more uniformly distributed within the soil, supply Cu throughout the growing season at varying intensities depending on the magnitude of these reserves.

The linear correlation coefficients between soil contents and the responses in grain yield to Cu applications, although significant, are rather low. There was nearly always a response to Cu at EDTA soil contents below 0.7 ppm, but there was no suggestion of a response at values above 1.0 mg/kg. Thus the limiting value reported by Reith (1968) for mineral soils in northern Scotland was appreciably lower than the value of 2.5 mg/kg suggested by Pizer et al. (1966) for East Anglia.

4.2 Foliar treatment

Table 18 summarises ADAS data on yield response to foliar applications of Cu oxychloride on different soil types:

Table 18 **Yield response of cereals to foliar applications of copper oxychloride**

Soil Types	Year	No of sites	Cereal Spring/Winter	Yield response t/ha Mean	Range	Notes
Peat/Peaty	1948-64	14	Spring	1.59	0.65-3.19	(a)
Organic chalk (Icknield Series)	1959-65	19	Spring	0.85	0.24-1.45	(b)
Brown Chalk (Andover Series)	1983-86	5	Winter	0.29	0.13-1.46	(c)
Brown Sands (Newport Series)	1984-86	5	Winter	0.68	0.43-1.25	(d)
Organic Chalk (Icknield Series)	1988-89	3	Winter	0.68	0.26-1.49	(e)

a) Control yields were often extremely poor and Cu treatment often doubled yields. Available soil Cu levels on these responsive sites were <1.6 mg/l (Caldwell, 1971).

b) Sites showed 'blackening' symptoms. Unreplicated yield comparisons on spring cereals showed significant yield responses of >0.38 t/ha on a further 19 out of 52 sites. Yield responses generally were associated with Cu levels up to 2.5 mg/l Cu but especially below 1.0 mg/l. Organic matter levels were greater than 7% (Davies et al., 1971).

c) These soils contained up to 1.1 mg/1 available Cu but rarely showed visual symptoms. One further site (1.1 mg/l Cu) gave no yield response.

d) All these sites had soil Cu levels <1.0 mg/l. Copper treatment did not control symptoms of 'blind grain' which was probably caused by drought. A further 2 sites with soil Cu levels of 1.2 and 1.4 mg/l gave no yield response in winter barley.

e) No visible symptoms. Soil Cu levels of 0.7, 0.7 and 1.0 mg/l.

Five sites (1963-65) on shallow organic chalk soils were used to evaluate different Cu treatments in the control of Cu deficiency in spring barley (Table 19).

Table 19 Yield response to various copper fertilisers at five sites on shallow organic chalk soils during 1963-65.

Treatment	**Mean yield (t/ha)**
Control	2.42
2.2 kg/ha Cu oxychloride spray	3.24
0.8 kg/ha Cu sulphate (1 spray)	3.28
0.8 kg/ha Cu sulphate (2 spray)	3.33
34 kg/ha Cu sulphate (soil applied)	3.09
222 kg/ha Cu sulphate (soil applied)	3.34

Davies et al. (1971)

Application of Cu increased yield by about 35% with no significant differences between treatments.

Unpublished ADAS experiments carried out between 1983 and 1986 evaluated two different rates of Cu oxychloride and EDTA foliar Cu sprays in the control of Cu deficiency in winter cereals (Table 20).

Table 20 **Yield response to various copper fertilisers at 4 sites on shallow chalk soils (1983-1986).**

Treatment	Mean yield (t/ha)
Control	6.96
Copper oxychloride 300 g/ha Cu	7.31
Copper oxychloride 700 g/ha Cu	7.22
Copper EDTA 65 g/ha Cu	7.15
Copper EDTA 130 g/ha Cu	7.25

Application of Cu increased yield by 4% with little difference between the treatments. 100 g/ha Cu as EDTA and 300 g/ha Cu as Cu oxychloride would seem adequate to control the deficiency at these sites.

In further ADAS experiments at 5 sites on sand soils (1984-86), 93 g/ha Cu as EDTA gave the same yield response (10%) in winter barley as 1100 g/ha Cu as Cu oxychloride. Lower rates of Cu oxychloride were not tested.

Six sites (1988-90) evaluated increasing rates of Cu, as either Cu oxychloride, Cu hydroxide or EDTA-Cu, applied to winter cereals on shallow organic chalk soils. Three sites showed consistent positive yield response (+11%) but yields were too variable to accurately predict amounts of each form of Cu for optimum yield response. The data suggested that up to 600 g/ha Cu may be required when applied as Cu oxychloride or hydroxide although 150 g/ha Cu was quite adequate at the most responsive site. Up to 150 g/ha Cu was required when applied as a chelate. Overall, the three forms of Cu were equally effective (ADAS, unpublished).

Sinclair (unpublished) carried out 5 trials on commercial farms during 1985 and 1986, which compared the effect of a range of spray products on the response in yield of winter barley. Each product was applied as a split dressing at growth stages 15/22 and 23/31 in 225 l/ha of water. A total of 0.25 kg/ha of Cu was supplied by each product. Results are given in Table 21.

Table 21 **Comparison of foliar sprays on yield of winter barley (t/ha)**

Treatment	**Site***				
	A	**B**	**C**	**D**	**H**
Control	8.06	4.32	5.99	8.54	7.67
Vytel Copper	8.68	4.90	6.30	8.86	7.71
Cuprokylt L	9.34				7.65
Phenolic Copper	9.18				7.58
Copper oxychloride	9.22	4.99	6.03	8.76	7.79
Cu + Zn + Mn cocktail	8.96				7.66
Cutonic Copper		4.65	6.30	8.65	
Copper sulphate		4.93	6.07	8.53	
S.E.M.	0.296	0.321	0.162	0.172	0.117
CV%	8.8	17.9	7.0	4.4	4.0

* sites as described in Table 13.

ADAS experiments at three sites (1964-65) on shallow organic chalk soils evaluated different timings of Cu treatment to control Cu deficiency in spring barley (Table 22).

Table 22 **Yield response to timings of copper foliar sprays**

Treatment		**Mean yield (t/ha)**
Control		3.10
2.2 kg/ha Cu oxychloride:	pre-tillering	3.24
	late tillering	4.15
	pre + late tillering	4.32
0.8 kg/ha Cu sulphate:	pre-tillering	3.90
	late tillering	3.95
	pre+ late tillering	4.18

Source: Davies et al. (1971)

Copper sprays at late tillering gave consistently higher yields than when applied pre-tillering. Spraying twice slightly increased yields.

4.3 Comparison of soil and foliar treatments

The results in Table 23 for six experiments with sprayed Cu indicate that foliar treatment was not as effective in raising yield as soil dressings (Reith, 1968). Extractable soil Cu was less than 0.7 mg/kg in these experiments. There was variation in results between experiments but foliar treatment was never better than soil applications, the response to the soil treatment being significantly better than to the foliar in three experiments. However, foliar treatment was more effective in raising the Cu concentration of the mature crop, and this was consistent in all six experiments. This higher concentration appeared to be due to the absorption of Cu through the leaves (Reith, 1968).

Table 23 Comparison of soil and foliar copper treatments on mean yield and copper content of 6 spring-sown oats and barley trials

	No Cu	22 kg $CuS0_45H_20$ broadcast on soil	1 kg $CuSO_45H_20$ sprayed on crop
	Grain		
Yield (t/ha)	1.75	2.38	2.20
Cu content (mg/kg)	1.9	2.0	2.8
	Straw		
Yield (t/ha)	2.45	2.80	2.31
Cu content (mg/kg)	1.6	1.6	2.7

Source: Reith (1968)

Sinclair (unpublished) compared the effect of soil and foliar application of Cu on the yield of winter barley in 1985 at sites E and F (Table 13). Copper oxychloride (10 kg/ha) was applied to the ploughing and cultivated into the seedbed. Foliar application was 0.5 l/ha of Cutonic Copper in 225 litres water at growth stage 24/30 and repeated at growth stage 31. The results are given in Table 24.

Table 24 **Comparison of soil and foliar copper treatments on yield of winter barley (t/ha)**

N form	N rate kg/ha	untreated	Site E soil Cu	foliar Cu	untreated	Site F soil Cu	foliar Cu
-	nil	3.02	3.69	2.79	2.67	3.34	2.77
urea	200	5.60	5.68	5.54	7.40	7.52	7.78
NH_4NO_3	200	5.51	5.89	5.67	7.88	7.74	7.83
S.E.M.		0.202			0.216		
C.V.%		6.9			5.8		

Source: Sinclair (unpublished)

There was a significant response to soil-applied Cu in the absence of spring top-dressed N at each site, but no response was obtained from the foliar treatment. In early ADAS experiments comparing different forms of applied Cu, soil applications were not always effective in correcting deficiency in the first year and an additional foliar spray was often required. This led to the current ADAS recommendations of a foliar spray (Withers and Gryllis, 1991).

4.4 Residual effects of copper treatment

The results from field experiments measuring the residual effects of Cu dressings on cereal yields are given in Tables 25 and 26 (Reith, 1968). Comparing the three no-Cu yields in Table 25, the 2.48 t/ha grain yield at the highest rate of N is significantly lower than the 3.20 t/ha ($P< 0.01$) and is just significantly less than 2.90 t/ha ($P< 0.05$). Thus, the deficiency of Cu was greatly aggravated by using N to increase herbage growth in the preceding 3 years, and Reith concluded that the higher rate of N presumably depleted the readily available Cu in the soil. There were no significant differences between the yields produced by the residual effects of either the 22 or 110 kg/ha copper sulphate treatments at any of the three N levels.

Table 25 **Effect of nitrogen applications on the response to copper treatment on yield of oats (t/ha)**

	kg/ha $CuSO_45H_20$ applied in 1957									
	0	**22**	**110**	**0**	**22**	**110**	**0**	**22**	**110**	SE*
	kg/ha N per annum 1957-1959									
		0			**99**			**198**		
1957-59 mixed herbage 9 cuts (t/ha dm)	13.9	14.7	15.4	21.0	22.2	22.9	27.6	28.8	26.9	0.79
	kg/ha N for 1960 oat crop									
		16.5			**27.5**			**38.5**		
1960 oats, grain	3.20	3.52	3.59	2.90	3.38	3.50	2.48	3.61	3.46	0.151

* The S.E., based on 45 DF., can only be used for testing differences between Cu rates and apply to the means for the 110 kg Cu SO_4 $5H_20$ treatments.

These values have to be multiplied by $1/\sqrt{2}$ and $1/\sqrt{3}$ to produce the S.E. for the 0 and 22 kg $CuSO_4$ $5H_20$ treatments respectively.

Source: Reith (1968)

The grain yield in Table 26 shows significant residual effects of Cu in all three experiments. There were remarkably small differences between the residues from the 5.5, 11, 22 and 110 kg/ha treatments. The Cu dressings were still effective in the ninth season after application in the 1956 and 1958 trials.

Table 26 Residual effects of copper applications on yield of spring cereal grain (t/ha)

			kg/ha $CuSO_4$ $5H_20$					
Copper applied	**Crop**	**Year**	**0**	**5.5**	**11**	**22**	**110**	**S.E.**
1956	Oats	1959	1.30	1.94	2.21	2.10	2.25	0.146
	Oats	1964	1.36	2.75	2.91	2.90	3.10	0.129
1958	Barley	1964	3.99	-	4.18	4.21	-	0.114
	Oats	1966	1.86	-	2.11	2.12	-	0.046
1964	Oats	1965	3.21	-	3.44	3.55	3.54	0.078
	Oats	1966	2.19	-	2.35	2.38	2.34	0.086

Source: Reith (1968)

In another experiment commenced in 1956, rates of 0, 1.4, 2.8, 5.7 and 28.5 kg/ha Cu were applied to a newly established ley on a Cu deficient fluvioglacial sandy soil. After three years in grass, which was cut and removed three times per year, an oat crop was grown in 1959 to measure the residual value of the Cu dressings, and the yields are given in Table 27. There were significant residual effects but very little difference between Cu rates, except that the 1.4 kg/ha treatment gave the smallest increase. Since 1958 the grain yields for the cereal crops in 1968, 1973 and 1974 showed significant residual effects. In 1974, eighteen years after the Cu dressings were applied, the residue from 1.4 kg/ha Cu increased the yield of grain by 0.5 t/ha which was nearly the same as the increase of 0.6 t/ha from the higher rates of 2.8 to 28.5 kg/ha. The rate of the original dressing had very little effect on yield but it had a considerable effect on the Cu concentration in both grain and straw, the concentration being higher the higher the rate applied. In 1974 the original dressings of 0, 4, 2.8, 5.7 and 28.5 kg/ha Cu produced barley grain containing 1.1, 1.6, 2.1, 2.4 and 3.2 mg/kg Cu, respectively. The corresponding contents in the straw were 0.8, 1.1, 1.3 and 1.7 mg/kg (Reith, unpublished).

In a further experiment on a deficient soil of the Ordley series where 0, 2.8, 5.7, 8.6 and 11.4 kg/ha Cu were applied in 1957 or 1958, the barley plants, sampled in 1973 at the start of stem elongation, contained 2.2, 3.2, 4.0, 4.7 and 5.5 mg/kg Cu, respectively. In another experiment on a deficient soil of the Ordley series where 0, 2.8, 5.7 and 28.5 kg/ha Cu were applied in 1964, the yields of oat grain in 1974 were 2.96, 3.49, 3.60 and 3.74 t/ha, respectively, showing very significant residual effects but very little response to rate of application (Reith, unpublished). These results clearly demonstrate that copper sulphate applied to these deficient soils continues to be very effective for many years and that the residues are practically as efficient as the original dressings. A considerable proportion of the applied Cu must be retained by the soil in a form available to plants but not sufficiently mobile to be leached. The average annual rainfall in the area varies between 640 and 800 mm, while the loss by transpiration and evaporation is about 450 mm.

Table 27 Long-term residual effects of copper dressings on yield of grain (t/ha)

		Copper treatment - kg/ha applied in 1956					
Year	**Crop**	**0**	**1.4**	**2.8**	**5.7**	**28.5**	**S.E.**
1959	Oats	1.31	1.95	2.22	2.11	2.26	0.147
1968	Barley	4.19	4.95	5.29	5.13	5.20	0.123
1973	Oats	2.44	2.82	2.95	2.56	3.00	0.115
1974	Barley	3.53	4.02	4.10	4.13	4.16	0.090

Source: Reith (unpublished)

In a long-term ADAS experiment on a shallow chalk soil Cu sulphate (90 kg/ha) applied to the soil in spring 1961 gave the same residual response in spring wheat as a spray treatment in 1965 (Table 28).

Table 28 Residual effect of soil-applied copper on yield of spring wheat (t/ha)

Treatment	Yield t/ha		
	1963	1964	1965
No copper	2.48	1.06	1.26
90 kg/ha Cu sulphate 1961	3.25	2.51	1.98
2.2 kg/ha Cu oxychloride spray 1965	-	-	1.88

5 SIGNIFICANCE OF COPPER DEFICIENCY IN UK CEREAL CROPS

5.1 Current use of copper

Information on the use of minor elements on agricultural crops is collected as part of the annual surveys of fertiliser practice in England, Scotland and Wales. The data in Table 29 for England and Wales of the mean application of Cu sprays to a range of crops over the 5 years from 1987 to 1991 clearly show that cereals receive by far the most Cu. (Chalmers et al., 1991).

Table 29 Percentage of crop area and actual crop area (hectares) receiving copper sprays (mean of 1987-91)

Crop	Percentage %	Area ha
Spring cereals	4.6	22,910
Winter cereals	4.5	122,490
Potatoes	1.5	1,690
Sugar beet	1.3	2,570
Oilseed rape	1.9	6,480
Other tillage	1.5	8,020
All grass	0.2	8,560
Total area		112,720

In Scotland the percentage of cereal area receiving Cu sprays is about 11%, equivalent to about 50,000 ha. Copper sprays are applied to a lower cereal area than are manganese sprays (Table 30).

Table 30 Percentage of cereal area receiving copper and manganese sprays (1991)

Crop	England and Wales		Scotland	
	Cu	Mn	Cu	Mn
	%		%	
Spring cereals	3.4	18.7	10.5	31.9
Winter cereals	5.8	21.4	11.6	36.0

Source: Survey of fertiliser practice (unpublished)

5.2 Management options

Copper may be applied to cereal crops either as fungicides, soil applied fertilisers, foliar nutrient sprays, or in pig slurry/dung (Klessa et al., 1985), sewage sludge (DOE, 1993) and bio-plant effluent from distilleries (Reith et al., 1979). The main UK suppliers of Cu-containing products for agriculture are listed in Appendix 1.

The inorganic compounds copper oxychloride, cuprous oxide and copper sulphate may be applied to the soil, as the simple salt (Table 31). These salts are normally dissolved or suspended in water and sprayed onto the soil. Copper salts are also included in some blended fertilisers and applied to the soil.

Table 31 Copper-containing powders for soil treatment

Product	Company	Type	% Cu
Copper oxychloride	various	Cu OCl	50
Copper sulphate	various	$Cu\ SO_4\ 5H_2O$	25
Cuprous oxide	various	Cu O	50

The current ADAS recommendation for soil application is either 10 kg/ha copper oxychloride or 20 kg/ha copper sulphate to the seedbed, although soil applications are rarely recommended in practice (Withers and Grylls, 1991). In Scotland, SAC recommend that 5-10 kg/ha of copper oxychloride, depending on soil Cu status, is applied before sowing and worked into the soil (Paterson, 1992). These treatments should last for at least 5 years, and perhaps even 10 years based on the results of the trials on Cu residues (Section 4.4).

The sources of Cu foliar sprays may be divided into 4 main categories: simple inorganic, inorganic flowable suspensions, chelated products and cocktails. There is a wide range of products on the market (Table 32). The range is confusing because there is no standardisation over the method of expressing the concentration of Cu. Copper may be expressed as a percentage of the compounds atomic weight eg. Key Feeds Chelated Cu, but in the vast majority of products, the Cu content is expressed either as Cu % w/w (weight Cu expressed as a percentage of the weight of a product), or Cu % w/v (weight Cu expressed as a percentage of the volume of a product). The use of the w/w notation for liquid products leads to confusion during calculation of application rates of Cu as the specific weight of the liquid needs to be taken account of in order to compare with concentrations expressed as w/v.

The ability of a Cu-containing foliar spray to tank-mix with a pesticide often influences the choice of product. It is difficult to find information on tank mixability of the simple, non-formulated inorganic salts. This is probably partly due to the absence of these salts from the product ranges sold or manufactured by the main agrochemical companies. In Scotland, unformulated copper oxychloride is mixed with a wide range of fungicides, but in England such mixes have produced unacceptable scorch.

Table 32 **Copper-containing foliar sprays**

Product	Supplier	% Cu	Formulation	Recommendation l/ha
Powders		w/w		
Copper oxychloride	various	50	inorganic	
Copper sulphate	various	25	inorganic	
Cuprokylt	Universal	50	inorganic	
Librel Copper	Atlas Interlates	14	EDTA	
Rexolin Copper	Grace	14	EDTA	
Flowable suspensions and liquids:				
Cuprokylt L	Universal	27	inorganic	1.5 - 4.0
Cutonic Copper	Lambsons	25	inorganic	0.8
Headland	WBC Technology	25	inorganic	
Librel Liquid Copper	Atlas Interlates	9.2	EDTA	0.8
Librel MX-8	Atlas Interlates	1.0	EDTA	3.5
Libreleaf Copper	Atlas Interlates	4.0	lignosulphonate	1.0
Rexolin Liquid Copper	Grace	9.4	EDTA	
Vytel Liquid Copper	Rhone-Poulenc	9.3	EDTA	
Vytel Cereal Mix	Rhone-Poulenc	3.6	EDTA	6.0
Coptrel 500	Phosyn	50	inorganic	0.25 - 0.5
Coptrel 250	Phosyn	25	inorganic	0.5
Mn/Cu 321	Phosyn	12.5	inorganic	1.0
Key Feed Copper	Stoller	6.2	phenolic	1.3 - 2.5
Key Feeds Mn + Cu	Stoller	1.6	phenolic	2.5 - 10.0
Liquid Copper	Clifton	9.5	EDTA	
Copper 25	Clifton	25	inorganic	0.5
Plant Feed Copper	Hortag	6.3	lignosulphonate	2.5
Plant Feed Mn + Cu	Hortag	1.2	lignosulphonate	2.5 - 5.0
Proleaf Cu	AgrEvo	9.4	EDTA	0.8 - 1.1

The chelated products are most commonly based on EDTA, although phenolic acid and lignosulphonate chelates are also available. Their major advantage is that they are often bought as liquids and are compatible with a wide range of pesticides. Proprietary formulated inorganic products are mostly based on copper oxychloride or copper hydroxide, bought as a flowable suspension along with stickers and wetters in a tank mixable formulation.

The current ADAS recommendations for foliar applications are copper oxychloride at 1 kg/ha in 250 litres of water plus wetter applied during late tillering; formulated copper oxychloride products eg. Cuprokylt at manufacturers recommended rate of 1 kg/ha of the powder of 1.5 - 4 litres per hectare of the liquid; or chelated products at full recommended rates (Withers and Grylls, 1991). SAC recommend application of 0.5 - 1.0 kg/ha copper oxychloride, depending on severity of copper deficiency, plus wetting agent in at least 150 litres of water when there is sufficient leaf canopy, while chelated compounds are recommended as an alternative (Paterson, 1992). Withers and Grylls (1991) have reviewed the manufacturer's recommended application rates of proprietary foliar sprays (Table 32). Copper may also be applied to cereals in multi-nutrient "cocktail" foliar feeds. Examples of these foliar feeds are given in Table 33.

Table 33 Examples of multi-nutrient "cocktail" foliar feeds

Product	Supplier	% Cu W/V	Recommended rate l/ha
Vytel Nitro-Plus	Rhone-Poulenc	0.27	9-24
Vytel Microplex	Rhone-Poulenc	1.5	
Headland Vertex	WBC Technology	0.016	
Key Feeds Harvest Plus	Stoller	2.0	
Proleaf N-trace	Schering	0.05	5
Libspray 211	Atlas Interlates	0.016	6
Foliar Nitrophoska	BASF	0.012	1.5 - 8
Maxicrop	Maxicrop	0.00012	8-12
Phosamco	Phosyn	0.1	3

These products supply between only 0.0096 g Cu at the lowest rate of Maxicrop and 64.8 g at the highest rate of Vytel Nitro-Plus.

A number of Cu-containing fungicides are listed in The UK Pesticide Guide (1993). These products are used to control blight in potatoes, downy mildew in brassicas, mildew, leaf spot and glume blotch in wheat, and mildew and leaf blotch in barley (Table 34).

These fungicides are not widely used, although Bordeaux mixtures are used in organic farming (Lampkin, 1990). However, the overall contribution of Cu to the soil-crop cycle from these fungicides must be very small.

Substantial quantities of Cu are applied to land in the UK during recycling of waste products. For example, the mean concentrations of Cu in sewage sludge applied to agricultural land in 1991 were 552 and 393 mg/kg of dry solids in England/Wales and Scotland respectively (DOE, 1993). The current quantity of sludge applied to agricultural land supplies about 237 and 4 tonnes of Cu per annum in England/Wales and Scotland respectively.

Table 34 Copper-containing fungicides

Product	Supplier	Type
A Blight in potatoes		
Comac Bordeaux Plus	MKC Products	$Cu SO_4.5 H_20$+ lime
FS Bordeaux Powder	Ford Smith	$Cu SO_4 .5H_20$ + lime
Wetcol 3	Ford Smith	$Cu SO_4 .5H_20$ + lime
Top-Cop	Stoller	$Cu SO_4.5H_20$ + S
Comac Macuprax	MKC Products	$Cu SO_4.5H_20$ + cufraneb
Cuprokylt	Unicrop	Cu O Cl
Cuprokylt L	Unicrop	Cu O Cl
Cuprosana H	Unicrop	Cu O Cl
FS Dricol 50	Ford Smith	Cu O Cl
Headland Inorganic Liquid Copper	WBC Technology	Cu O Cl
Comac Parasol	MKC Products	$Cu (OH)_2$
B Mildew, leaf spot, glume blotch in wheat; mildew, leaf blotch in barley		
Ashlade SMC Flowable	Ashlade	Cu O Cl + maneb + S
Rearguard	Unicrop	Cu O Cl + maneb + S
Tripart Senator Flowable	Tripart	Cu O Cl + maneb + S
C Downy mildew in brassicas		
Ridomil Plus 50 WP	Ciba-Geigy	Cu O Cl + metalaxyl

These amounts are expected to rise to about 470 and 10 tonnes of Cu per annum, respectively by the year 2006 as dumping at sea will be prohibited after 1998. The addition of 480 tonnes of Cu in 880,000 tonnes of sewage sludge dry solids is equivalent in terms of total Cu to applying 5 kg/ha of copper oxychloride to 192,000 ha per annum. This represents a substantial return of Cu to agricultural land, equivalent to a value of £1.15 million at £1.20 per kg of copper oxychloride. The addition of Cu in sewage sludge is limited to 7.5 kg/ha/annum over 10 consecutive years (Statutory Instruments, 1989). New treatment processes for wastewater sludge will produce thermally dried granules. There are no trials information on the availability of Cu in these new products to cereal crops.

Substantial quantities of Cu are also returned to the land in other waste materials, particularly pig slurry and FYM, and distillery effluent.

The decision on whether or not to apply Cu is often based on an individual field test for EDTA extractable soil Cu, and this approach is considered here in relation to the Scottish cereal industry.

The Soils Inventory of Scotland will contain an extractable soil Cu value for topsoil at each 10 km grid intersection point (Paterson, personal communication, MLURI). The number of soils in this Inventory is about 750, which includes samples from hill land and permanent pasture, as well as cereal-growing areas. However, Cu data are available from the Scottish Soil Fertility Information System (SSFIS). SSFIS is based on data from soils that are analysed for advisory purposes by SAC (Sinclair et al., 1988). Samples are analysed as a result of requests from individual farmers and not as a result of systematic sampling. Copper analysis has been requested as part of a regular soil testing programme more frequently than any other micronutrient. Results of Cu analysis during 1985, 1986 and early 1987 of 1391 soil samples from the northern half of Scotland are reported in Table 35.

Table 35 Distribution of extractable soil Cu values into soil Cu status

Extractable Cu mg/kg	**Cu status**	**Percentage of samples within each status**
<1.0	VL	10
1.0 - 1.6	L	21
1.7 - 8.5	M	64
>8.5	H	6

Source: Sinclair et al. (1988)

For the whole of Scotland around 2,500 samples have been analysed annually by SAC. Although some of these soils were sampled either to identify the cause of a crop or animal problem, the distribution of the Cu values over the last 8 years has remained similar to those in Table 35 with 10% very low, 20-25% low, 60-70% moderate and 5% high (Paterson, personal communication, SAC).

The total area of cereals recorded in the Scottish Office Department of Agriculture and Fisheries June 1991 census was 467,471 hectares, producing a forecasted total of 2.09 million tonnes of cereals (SOAFD, 1992).

If the following assumptions are made for Scotland:

1) no preference for wheat, barley, triticale or oats with soil Cu status;
2) 10% of cereal-growing area in very low Cu status with yield reduction of between 15 and 25%;
3) 20% of cereal-growing area in low Cu status with yield reduction of between 2 and 8%;

then taking the two extreme positions of yield reduction for each Cu status the increase in yield due to Cu treatment is between 40,000 and 86,000 tonnes per annum (Table 36). These figures correspond to 1.9 and 4.1% respectively of current cereal production in Scotland, and at £100/tonne represents a loss to the cereal industry of between £4 million and £8.6 million.

Table 36 Estimation of increase in cereal production in Scotland following Cu treatment

Soil Cu status	% cereal area	1991 cereal production (tonnes)	Low response (tonnes)	High response (tonnes)
VL	10	209,000	31,350	52,250
L	20	418,000	8,360	33,440
			39,710	85,690

6 CONCLUSIONS

1. Copper deficiency most commonly occurs in cereals when EDTA - extractable Cu in the soil is $\leq$ 1.6 ppm. Based on this criteria up to 5% of the cereal-growing area of England and Wales and 30% in Scotland may be sufficiently low to impair grain yield or quality.

2. A reduction in yield of cereal grain due to a shortage of Cu can occur without visual symptoms of deficiency in the crop. Where symptoms appear they are rarely seen until the end of tillering when yellowing and withering of the tops of the youngest leaf is often accompanied by spiralling of leaves. Grain yield reductions of up to 20% are not uncommon in field trials in the UK.

3. Copper deficient grain contain increased concentrations of non-protein nitrogen which may reduce breadmaking performance, although there is very little information available on the satisfactory grain Cu concentration for the milling and malting industries.

4. Foliar application of Cu may be more reliable in producing an increase in grain Cu concentration, whereas soil applied Cu may give more consistent response in yield of grain, particularly in the second and subsequent 5 or more years after soil treatment. The lack of response in some circumstances to soil-applied Cu in the year of application may be due to insufficient mixing of Cu with the soil. Thus, a foliar application of Cu for the first crop after soil application appears to be justified.

5. Trials have shown that it is not necessary to apply Cu to every high-yielding cereal crop, because high-yielding crops may be more efficient at obtaining Cu from the soil and greater mobilisation of Cu into soil solution occurs in the root-zone of these crops.

6. A substantial quantity of Cu is returned to the land in waste materials. However, the benefit to the UK cereal industry is not obvious as there is no information on the availability of Cu to cereal crops from some of these waste materials.

7 RECOMMENDATIONS FOR FURTHER STUDY

There are a number of specific aspects of the Cu nutrition of cereals where knowledge is lacking.

1. Yield responses in cereal grain to Cu have been reported without the visual appearance of symptoms of Cu deficiency in the crop. A survey of Cu concentrations in wheat and grain to establish the extent of sub-clinical deficiency is required.

2. A satisfactory grain Cu concentration is clearly of significance to the milling and malting industries, although the benefits have yet to be quantified under UK growing conditions. The relationship between grain Cu and quality requires to be established.

3. The influence of N, S and Cu interaction on grain quality in view of the strong S-Cu linkage probable in grain protein requires to be investigated.

4. There is a dearth of information on varietal susceptibility to Cu deficiency. Existing variety testing trials could be used to provide grain for Cu, N and S analysis and for tests on breadmaking and malting quality. This work should be linked to the study of the effect of grain S (and N:S) content on malting quality in barley, as recommended in the HGCA-funded Research Review No. 30 on 'Sulphur nutrition in the UK: Effects on yield and grain quality'.

5. The quantity of Cu applied to land in urban wastewater sludge is expected to rise as dumping to sea becomes prohibited. New treatment processes will result in production of thermally dried granules. There are no trials evidence on the availability of Cu to cereal crops in these new products. Work is urgently required to establish any benefits from Cu in these new products to the UK cereal industry.

6. A survey of farmer awareness to Cu deficiency is recommended.

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Appendix I Some UK Suppliers of Agricultural Copper Products

Universal Crop Protection Ltd
Park House
Maidenhead Road
COOKHAM
Berkshire
SL6 9DS
06285-26083

Cutonic Ltd
Aire and Calder Works
CASTLEFORD
West Yorkshire
WF10 1LU
0977-510511

Phosyn Chemicals Ltd
Manor Place
The Airfield
Pocklington
YORK
YO4 2NR
0759-302545

Atlas Interlates Ltd
Gladden Place
SKELMERSDALE
Lancs
WN8 8SX
0695-33535

Clifton Agriculture
119 Grenville Street
Edgeley
STOCKPORT
Cheshire
SK3 9EU
061-476-1128

Hortag Chemicals
Salisbury Road
Downton
SALISBURY
Wiltshire
SP5 3JJ
0725-22822

Stoller Chemicals Ltd
23 Marathon Place
Moss Side
LEYLAND
Lancs
PR5 3QN
0772-454443

Rhone-Poulenc
Poleacre Lane
Woodley
STOCKPORT
Cheshire
SK6 1PQ
0614-946363

AgrEvo
East Winch Hall
East Winch
KING'S LYNN
Norfolk
PE32 1HN
0553 841 581

BASF plc
PO Box 4
Earl Road
CHEADLE HULME
Cheadle
Cheshire
SK8 6QG
0161 485 6222