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SULPHUR NUTRITION OF CEREALS IN THE UK: EFFECTS ON YIELD AND GRAIN QUALITY

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SULPHUR NUTRITION OF CEREALS IN THE UK: EFFECTS ON YIELD AND GRAIN QUALITY

by

P. J. A. WITHERS

ADAS-Bridgets, Martyr Worthy, Winchester, Hampshire S021 1AP

A. H. SINCLAIR

SAC-Aberdeen, 581 King Street, Aberdeen AB9 1UD

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CONTENTS

1. ABSTRACT

The incidence of sulphur (S) deficiency in agricultural crops in the UK has increased in recent years due to a reduction in the amount of S falling onto agricultural land from industrial emissions of sulphur dioxide and the almost complete absence of S in modern fertilizers. Whilst multi-cut systems of grassland production and oilseed rape are the most S demanding, there has been increasing concern over the incidence of S deficiency in cereal crops in the UK and the implications for crop yield and quality. Whilst HGCA-funded research projects are currently evaluating the development of S deficiency in cereals and identifying appropriate plant and soil analysis procedures for its diagnosis and prediction, there is an interim need to provide guidelines to farmers and the agricultural industry on the most appropiate methods of correction of S deficiency. Drawing on previously unpublished experimental data and advisory experience of ADAS and SAC, this review summarises the role of S in the nutrition of cereals, draws together information on the the most appropriate methods of S fertilization and discusses the future significance of S deficiency to the UK cereals industry.

Sulphur is an essential nutrient required for protein formation and a number of enzyme reactions within plant cells which are required for satisfactory crop growth. The S-containing amino acids cysteine and methionine are particularly important in forming disulphide bonds during breadmaking. Although the S requirement of cereals is comparatively small (10-30 kg S/ha), grain yield responses of up to 30% have been obtained in UK field experiments on sandy and/or shallow soils in areas receiving < 20 kg/ha/year from the atmosphere. Deficiency symptoms of leaf paling and crop stunting occur during stem extension and have been recorded in cereal crops in southwest, northern and eastern England, Wales, Scotland and Ireland. They are often transient in nature and their occurrence varies considerably from season to season depending on the supply of both nitrogen (N) and S. Deficiency is more pronounced at high rates of N application and is characterised by wide N:S ratios (> 17:1) in both young leaf tissue and grain. A knowledge of soil type and location together with retrospective crop analysis is currently the most reliable guide for S fertilizer need. It is recommended that potentially susceptible crops are sampled between full flag leaf emergence and anthesis to assess the future need for S fertilizer on individual fields.

Although there has been limited opportunity to evaluate alternative methods of S fertilization for cereals in the UK, experimental evidence to date indicates that applications of 10-20 kg S/ha applied as soluble sulphate fertilizer just prior to stem extension is the most appropriate means of preventing S deficiency. Elemental S fertilizers have been

shown to be less effective than soluble sulphate fertilizers when applied at the same rate and time. Elemental S fertilizers have potential residual value but further work is required to optimise their performance. It is not known to what extent any yield loss associated with S deficiency can be controlled by application of S once symptoms appear.

Numerous experiments have shown that a shortage of S relative to N supply alters the balance of amino acids and the protein composition of the grain. These changes are considered to reduce the nutritional value of feed varieties and flour quality in breadmaking wheat, although quantitative evidence for UK varieties is lacking. It is not known to what extent grain S content affects the malting process.

Crop surveys in recent years indicate that up to 10% of the UK cereal crop may be sufficiently low in S to impair either crop yield or grain quality. With the increasingly rigorous controls over the industrial emissions of sulphur dioxide to the atmosphere, the incidence and severity of S deficiency in cereals in the UK is forecast to increase. There is little doubt that S has become as important a nutrient as phosphorus or potassium and a continued research effort is required to ensure that cereal grain production and quality are not impaired. Future research priorities are identified.

1. INTRODUCTION

Cereals currently occupy approximately 16% of the total agricultural area in the UK and about 20 million tonnes of cereal grain are produced each year (Anon. 1994). The cereal market is dominated by wheat and barley of which only a relatively small proportion (25%) is utilized by the breadmaking and malting industries (Fig. 1). Following on from the dramatic improvements in plant breeding and crop agronomy during the 1970's, high yielding varieties of winter wheat and winter barley, which respond to high rates of nitrogen (N), now dominate the UK cereal market. Consequent with these changes, there has been a large increase in the use of straight N fertilizers since 1969 (Chalmers *et al.* 1990). Such concentrated fertilizers (eg ammonium nitrate) contain little or no sulphur (S) and the lack of fertilizer S inputs over this period has raised concerns over the depletion of plant-available S reserves in soils and focused attention on the diminishing supply of S from the atmosphere (Syers *et al.* 1987; McGrath *et al.* 1994). Deficiencies of S are known to occur worldwide in a number of crops, including cereals, although to a lesser extent in Europe because emissions of S from industry into the atmosphere have traditionally been larger than in other continents (Tisdale *et al.* 1986).

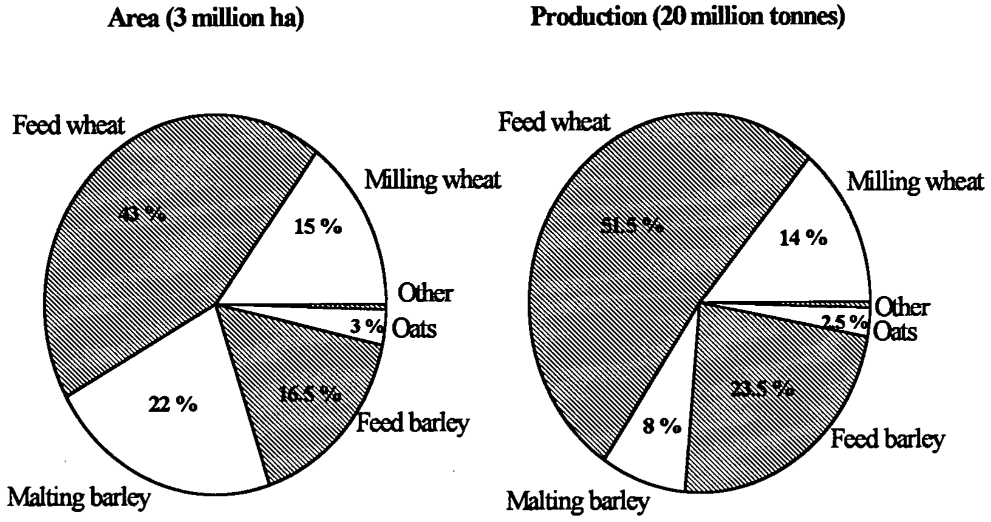


Fig. 1 The home-grown cereal market in the UK in 1993
(Gutsell 1993; Anon 1994; Brown 1994)

The importance of S deposition from the atmosphere in maintaining an adequate S supply for crop yields in the UK has been clearly demonstrated in both pot and field experiments, for example with oats (Scott 1979) and grass (Bristow & Garwood 1984). Reductions in the emissions of sulphur dioxide from industry since 1970 have resulted in smaller inputs of 'wet' and 'dry' S from the atmosphere, especially in remote rural areas (Roberts & Fisher 1985; Unsworth & Fowler 1985; Anon. 1990; McGrath & Goulding 1990). Based on data from the S monitoring network in 1990 supplied by Warren Springs Research Laboratory, 77.1% and 19.5% of the UK land area is now receiving less than 20 and 10 kg S/ha, respectively from the atmosphere (F. Zhao, unpublished). Where atmospheric S deposition is low, deficiency of S most commonly occurs on soils which have a limited ability to retain available sulphate (SO_4-S) against leaching losses, especially in high rainfall areas. Deficiencies of S in field crops in the UK first appeared in multi-cut systems of grassland production (Scott *et al.* 1983; Skinner 1985; Murphy & Boggan 1988) but is now also widespread in winter oilseed rape, which has the highest S requirement of arable crops (Withers 1989; Booth *et al.* 1991; Zhao *et al.* 1991; Withers & O'Donnell, in press).

There is little doubt that the incidence of S deficiency in winter oilseed rape is increasing (Zhao *et al.* 1991; Chalmers *et al.* 1992; Withers 1993a) and there is now concern within the agricultural industry about the effect of S shortages on the yield and quality of cereals. Although extensive field experimentation up to 1986 indicated that cereal crops in the UK were generally not responsive to S fertilizer (Syers *et al.* 1987), S deficiency symptoms in field crops have increasingly been observed in the last few years by the agricultural consultants of ADAS and SAC. This paper reviews the role of S in the nutrition of cereals, reports on previously unpublished experimental work carried out by ADAS and SAC since 1987, and discusses the future significance of S deficiency to the UK cereal industry.

2. SULPHUR REQUIREMENT OF CEREALS

2.1 Role of sulphur in plant growth

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 (Allaway & Thompson 1966; Stevenson 1986; 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. According to Allaway & Thompson (1966), the S-H group provides the main link between enzyme and substrate. Archer (1980) reviews evidence to suggest that an adequate supply of S-H groups is necessary for cell division and growth and that differences in the cell cysteine content between different wheat varieties maybe genetically controlled. Cysteine-rich proteins and enzymes (eg 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 synthesized 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).

2.2 Crop uptake of sulphur

The amount of S in a cereal crop at harvest is reported to range between 10 and 30 kg/ha depending on yield level and, presumably, on S availability (McGrath & Johnston 1986; Syers *et al.* 1987; Klessa & Sinclair 1989). A very similar range (7-26 kg S/ha) was found in recent HGCA-funded experiments on potentially S-deficient cereal crops at 21 sites in England, Scotland and Wales in 1993, although most of the crops contained nearer 15 kg S/ha, excluding S in roots. According to Beaton (1966) and Tisdale *et al.* (1986), cereals have a low S requirement (<20 kg/ha), and Mnkeni & Mackenzie (1981) report values of <10 kg S/ha in low yielding barley crops in Canada. The total crop requirement for S, however, may be larger than the offtake of S at harvest. Detailed measurements of a winter wheat (cv. *Maris Huntsman*) crop in 1975 showed that maximum uptake of S occurs at, or shortly after, anthesis (GS 65, Tottman 1987) and declines thereafter (Gregory *et al.* 1979a). The loss in S, which occurred from the leaf, stem and root and was continuous over the 7-week period between anthesis and harvest, represented 50% of the total S taken up at anthesis (20 kg /ha). The authors suggested that this loss of S (10 kg/ha) was probably due to leaching losses from senescing leaf tissue and the translocation of S from the shoots and roots back to the soil. Also, the amount of S contained in the roots represented 16-20% of total S uptake except at harvest when it was only 5%. Further studies on the same crop indicated that the supply of S by mass flow between stem extension and anthesis from the 0-30, 30-60 and 60-90 cm layers in the soil was 66%, 17% and 17%, respectively of the total (Gregory *et al.* 1979b). There have been no comparable studies on barley or oats.

Preliminary data from the HGCA-funded experiments in 1993 agrees with the pattern of uptake shown by Gregory *et al.* (1979a). The amount of S in the cereal crop up to the stem extension stage (GS 30/31) is only 1-2 kg/ha or less and most S is taken up during stem elongation. At full flag leaf emerged (GS 39), crops had taken up between 5 and 23 kg S/ha. There was generally a slight decrease in crop S content between GS 39 and harvest, although at some sites, usually those low in S, there was an increase in S offtake over this period. Late uptake of S may explain why S deficiency symptoms often disappear in cereals as the season progresses. Although the supply of S to the crop clearly influences the amount of S in the crop at any given growth stage, it does not appear to influence the relative amounts contained in different plant tissues. Rasmussen *et al.* (1977) found that the amounts of S in ears, stems, green leaves and senescing leaves at ear emergence (GS 65) represented 15, 35, 41 and 9%, respectively of the total uptake in both S-deficient wheat and wheat receiving S fertilizer.

Sulphur is probably translocated to the developing grain as free amino acid (asparagine and glutamine) from which metabolic and storage proteins are synthesized (Shewry *et al.* 1981). The supply of S during grain filling influences the pattern of protein accumulation and ultimate grain quality. In studies on breadmaking wheat (Castle & Randall 1987; Skerritt *et al.* 1988), grain S (but not N) concentrations declined during the later stages of grain development when storage proteins with a larger N:S ratio (glutenins and gliadins) were accumulating in preference to the metabolic proteins (albumins and globulins) rich in S. The metabolic proteins are thought to be synthesized soon after anthesis but probably degrade when the grain is drying out.

The distribution of S between grain, chaff and straw of winter wheat at harvest for two sites in East Anglia in 1993 is shown in Table 1. The yield response at Stetchworth was statistically significant ($P< 0.05$). These sites were low in S and proportionately more S uptake in the straw can be expected at sites well supplied with S. The amount of S harvested in the grain as a percentage of the total S uptake (excluding roots) was, on average, 55% in 21 HGCA-funded experiments in 1993. Uptake of S in straw was more sensitive to crop S supply than uptake in the grain. Chaff contained about 1 kg/ha of S.

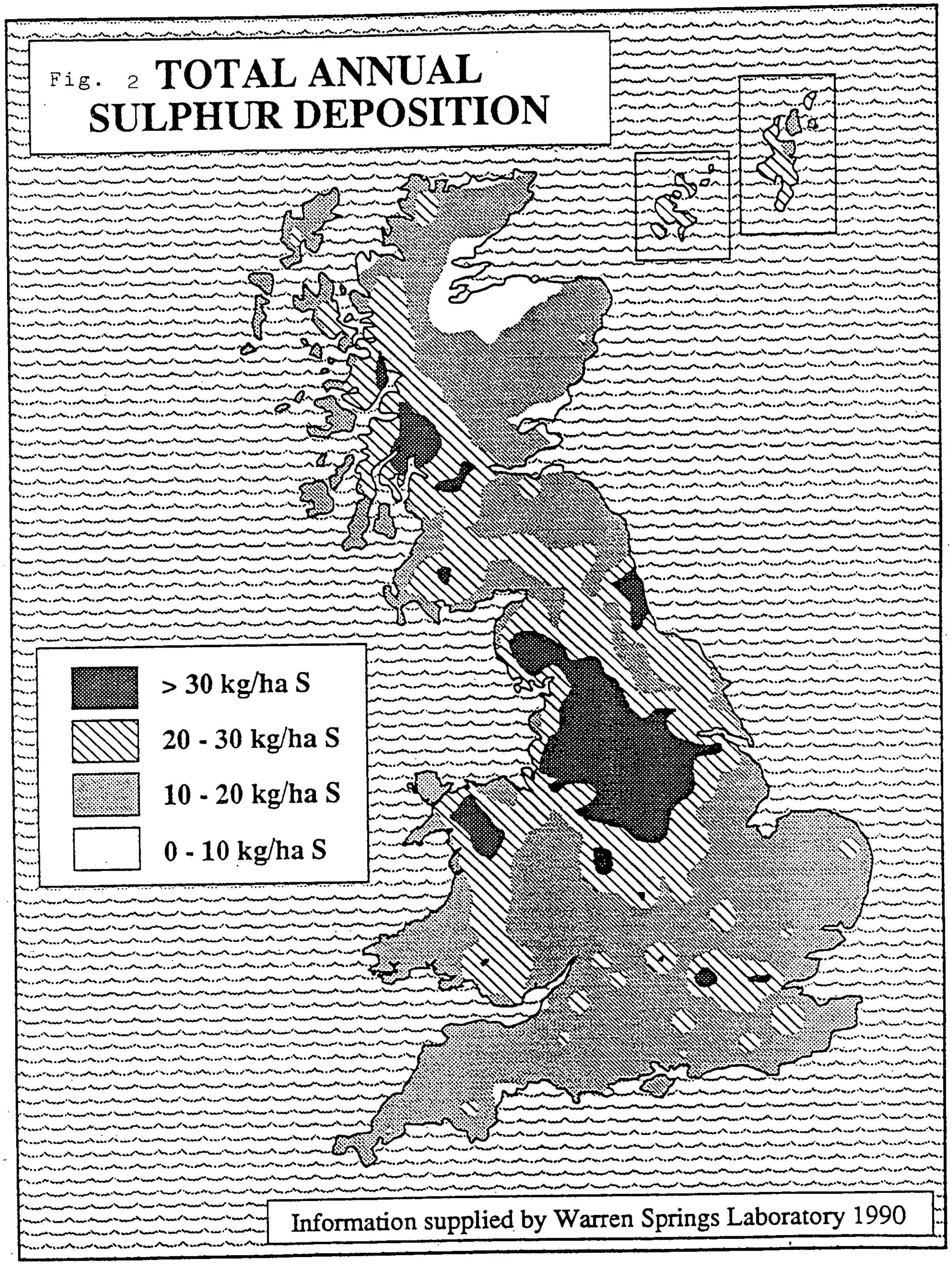
Table 1 The effect of potassium sulphate on the distribution of S in grain, straw and chaff at two sites in East Anglia in 1993.

	Raynham, Norfolk		**Stetchworth, Cambridgeshire**	
	Untreated	**40 kg S/ha**	**Untreated**	**40 kg S/ha**
Grain				
Yield (t/ha @ 85% D.M.)	10.05	10.10	7.83	8.11
S concentration (%)	0.119	0.134	0.123	0.131
S offtake (kg/ha)	10.2	11.5	8.2	9.0
Straw				
Yield (t/ha @ 85% D.M.)	6.03	6.40	4.54	4.95
S concentration (%)	0.056	0.098	0.086	0.118
S offtake (kg/ha)	2.9	5.3	3.3	5.0
Chaff				
Yield (t/ha @ 85% D.M.)	1.49	1.56	1.59	1.71
S concentration (%)	0.058	0.072	0.066	0.068
S offtake (kg/ha)	0.7	1.0	0.9	1.0
Total S offtake (kg/ha)	13.8	17.8	12.4	15.0
S harvest index	0.74	0.65	0.66	0.60

2.3 Soil and atmospheric sulphur supply

Over the last 30 years, the S demand of cereals has been largely satisfied by supplies of S from the soil and the atmosphere. Soil S supply depends on the amount of SO_4-S in solution and adsorbed onto soil surfaces, and on the mineralization of carbon (C)-bonded and ester-sulphate forms of S in the organic matter. The mineralization of S by soil micro-organisms is a key process which is not fully understood; C-bonded forms of S appear to be the main source of energy-driven mineralization whilst SO_4-S is released from ester-sulphates when hydrolyzed by microbial enzymes, particularly where soil S content is low (Freney *et al.* 1975; McGill & Cole 1981; McLaren *et al.* 1985; Ghani *et al.* 1992).

Fig. 2 **TOTAL ANNUAL SULPHUR DEPOSITION**



Information supplied by Warren Springs Laboratory 1990

The release and transfer of SO_4-S between ester-sulphate and C-bonded forms of organic S is largely responsible for the variation in SO_4-S in soils during the growing season (Castellano & Dick 1990). The amounts of SO_4-S mineralized in UK soils are generally considered to be low, especially in fields in continuous arable rotation, whilst SO_4-S is rapidly immobilized in soils which are accumulating organic matter (Syers *et al.* 1987).

The ability of UK soils to adsorb SO_4-S released by mineralization has also been shown to be very low, except on soils rich in iron oxides (Curtin & Syers 1990). Phosphorus-rich free draining soils with a pH above 6.0 are particularly unretentive and have a high potential for leaching of mineralized S. McGrath & Goulding (1990) calculated that the amounts of S leached at Woburn (19 kg/ha) were similar to the amounts deposited in rainfall. Subsoils with a larger clay content have more capacity to retain SO_4-S and are less prone to S deficiency providing crop rooting depth is not restricted (Buole & Pittman 1984; Oates & Kamprath 1985; Hue & Cope 1987; Zhao & McGrath 1994). 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.

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). The total amount of S deposited per year depends on location and prevailing weather patterns. Campbell *et al.* (1990) report deposition rates of <10 kg/ha/year in northern Scotland and up to 35 kg/ha/year in central England. Sulphur deposition in rainfall has been estimated at between 8 and 16 kg S/ha/year (Unsworth & Fowler 1985) but contributions from sea spray can significantly increase S deposition rates near western coasts. In New Zealand, Ledgard & Upsdell (1991) found that sea spray contributed 80% of S in rainfall near the coast but only 10% of the rainfall inland, and a similar marine influence in the UK is suggested by Unsworth & Fowler (1985).

In the major cereal growing areas of the UK, the majority of S deposited from the atmosphere is as 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. The distribution of total (wet and dry) S deposition in the British Isles is shown in Fig. 2. Where the requirements for S cannot be met from the atmosphere, then soil S reserves will become progressively depleted unless fertilizer S is applied. This is undoutedly the major reason why S deficiency in grass and arable crops is expanding in the UK.

3. SULPHUR DEFICIENCY IN CEREALS

3.1 Deficiency symptoms

Sulphur deficiency symptoms have been recorded in a relatively small number of cereal crops in the UK over the last ten years but the frequency with which they occur is increasing. In Scotland and Ireland, deficiency symptoms have been seen sporadically in winter cereals since 1983 (Scott *et al.* 1984; Conry 1993) but have been observed in England and Wales only since 1989 (Withers 1993b). Symptoms have appeared as a paling or slight yellowing of the youngest leaves during late stem elongation, when a continuing 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 and in this respect it can be distinguished from a N (and also manganese) deficiency with which it can be confused. Symptoms typically vary in intensity across fields, which take on a freckled or patchy appearance from a distance. Australian experience indicates that young leaves turn from pale green to yellow to white with increasing severity of deficiency and eventually the whole plant may turn yellow (Grundon 1979; Randall & Wrigley 1987). Archer (1974) noted a purplish discolouration at the base of tillers when wheat was grown in nutrient solutions starved of S.

In common with other crops, S deficiency results in crop stunting, leaf narrowing and reduced grain yield. Conry (1993) measured reductions of up to 50% in the green leaf area of the top 3 leaves of barley plants suffering S deficiency and Rasmussen *et al.* (1977) noted a higher percentage of non-productive tillers in S-deficient wheat. Taureau *et al.* (1987) found that plant stems were more brittle in cereal crops which were short of S. Reductions in grain yield in field crops appear to be due to reduced numbers of fertile ears (Rasmussen *et al.* 1977; Taureau *et al.* 1987) and/or a reduction in the number of grains per ear (Archer 1974; Scott *et al.* 1984) rather than a reduction in grain size. Deficiency probably initially impairs the normal development of established tillers during stem extension and may result in reduced ear fertility only where the deficiency is severe. Consequently, the vegetative phase may be prolonged although this has not been commonly reported. Castle & Randall (1987) found that protein synthesis in the developing grain started earlier in S-deficient crops compared to crops well supplied with S.

In pots in a greenhouse, S deficiency symptoms can occur within 1 month of emergence (Stewart & Porter 1969; Zhao & McGrath, in press). In the field, the occurrence and severity of S deficiency symptoms is very variable and depends on the seasonal variation in the supply of N and S from the soil, and probably to a lesser extent the atmosphere, and the demand by the crop. Rasmussen *et al.* (1977) observed symptoms soon after the start of stem extension in three out of four seasons, whilst in the fourth season, symptoms did not appear until ear emergence. In the UK, symptoms are more transient in nature; they may coincide with a period of cold or dry weather during stem extension and disappear when the soil has become warm and/or moist. Castellano & Dick (1990) consider that sulphur transformations within the soil organic matter during the growing season clearly have a marked influence on the availability of S for crop uptake. Consequently, a reduction in grain yield does not always accompany the appearance of symptoms and conversely grain yield response to applied S can be obtained in the absence of deficiency symptoms (Ramig *et al.* 1975; Taureau *et al.* 1987; Conry 1993; Knudsen & Pederson 1993; Withers 1993b). Experience with oilseed rape suggests that S deficiency may be more likely after wet winters and in late drilled crops which have not established a well developed root system by the stem extension stage (Chalmers *et al.* 1992).

3.2 Grain yield response

Despite their low S requirement, grain yield responses to applied S have been obtained in a number of experiments on cereals. Much of the early work was reviewed by Beaton (1966), whilst more recent experiments have commonly demonstrated yield increases of 20-30% and up to 100% where the deficiency is severe (Table 2). The data show that yield responses have been largely obtained on coarse-textured sandy soils with small amounts of extractable SO_4-S (<3 mg/kg). Ramig *et al.* (1975) did not obtain a yield response in the first year after ploughing out natural grass but did obtain a yield benefit to applied S in the three subsequent years from applications to the first wheat crop. Other experiments on similar soils low in S have not shown yield benefits, which suggests a significant contribution of S from the atmosphere (Gupta & MacLeod 1984; Reneau *et al.* 1986). Experiments in Canada produced no yield response in barley but the soils contained relatively large amounts of extractable SO_4-S (Mnkeni & Mackenzie 1981). No yield responses have been obtained in many recent experiments on winter wheat and spring barley in Denmark on soils where yield responses in oilseed rape occur (Knudsen & Pederson 1993).

Evidence for a strong interactive effect of crop N and S supply on either dry matter production or grain yield of cereals has been demonstrated in a number of pot and field experiments (Stewart & Whitfield 1965; Stewart & Porter 1969; Ramig *et al.* 1975; Byers & Bolton 1979; Spencer & Freney 1980; Randall *et al.* 1981). When S is limiting, application of N does not influence yield, whilst the yield response to applied S increases with increasing amounts of N applied. A similar N*S interaction has been observed in oilseed rape (Booth *et al.* 1991; Zhao *et al.* 1993).

Table 2 Grain yield response of winter cereals to sulphur fertilizers in field experiments.

Country	Soil Type	Source	Crop	Yield response (%)	Optimum rate of S (kg/ha)	Reference
USA	Silt loam	G	wheat	15-50	14	Rasmussen & Allmaras 1986
	Silt loam	G	wheat	10-20	10	Ramig *et al.* 1975.
	Silt loam	AS	wheat	76-100	28-56	Mailer & Maples 1986
	Loamy sand	G	wheat	20-30	20	Oates & Kamprath 1985
	Sandy loams	AS/G	wheat	25	29	Mitchell & Mullins 1990
	Silt loam	AS	wheat	15	-	Rasmussen *et al.* 1977
Australia	Sandy loam	G	wheat	40	25	Randall *et al.* 1981
Australia	Sandy loam	G	wheat	95	25-50	Spencer & Freney 1980
France	Shallow limestone	AS	wheat	up to 20	10-20	Taureau *et al.* 1987
Germany	Sandy loams	E	wheat	up to 20	-	Schnug 1987
Ireland	Sandy loam	AS	barley	8-31	-	Conry 1993
Scotland	Loamy sand		barley	5-28	-	Scott *et al.* 1984
England	Sandy loam	G	barley	6	10-20	Withers 1993b
	Loamy sand	G	wheat	10	-	Withers 1993b

G = agricultural gypsum
AS = ammonium sulphate
E = elemental sulphur (soil-applied)

The effect of a shortage of S on the grain yield of wheat, barley and oats in the UK has been studied in a number of pot and/or field experiments over the last 15 years. Much of the earlier work was done in pots. Scott (1979) found that the grain yield of oats decreased when S inputs in rain were withheld. There was also a much larger yield response to added S fertilizer and a greater proportional retention of S in the straw in pots kept inside compared to pots kept outside in the rain. Differences in the uptake of S between non-S-fertilized pots kept inside and the same pots kept outside was equivalent to the amount of S supplied in the rain. Atmospheric inputs of S in this experiment represented nearly 50% of the total S uptake in grain and straw. In a classical pot experiment with spring wheat, Byers & Bolton (1979) obtained up to 5-fold increases in grain yield from applied S but such responses are much larger than would be obtained in the field.

In reviewing a large number of field experiments on winter wheat, winter barley and spring barley in England and Wales up to 1985, Syers *et al.* (1987) concluded that fertilizer S was not required by cereals. Statistically significant positive responses to foliar sprays of elemental S were obtained in only 3 of the 61 comparisons made. In 1989, a visual response to applied S was obtained in winter wheat (cv *Mercia*) on a loamy sand soil in Somerset (Withers 1993b). 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 (Table 3). A yield increase of 0.61 t/ha (10%) at this site was not, however, statistically significant. The effect of a single rate of S on grain yield in winter cereals was similarly tested at 11 other sites in south-west England over the period 1985-1989 but no significant positive responses were obtained (ADAS, unpublished).

Table 3 The effect of 30 kg S/ha of S fertilizer (gypsum) on grain yield (t/ha @ 85% dry matter) and on total S concentration (%) and N:S ratio in leaves and grain of winter wheat (cv. *Mercia*) in Somerset, England in 1989.

		Leaf		Grain	
	Yield (t/ha)	Total S %	N:S ratio	Total S %	N:S ratio
Control (Nil S)	6.33	0.14	29	0.09	30
Gypsum (30 kg S/ha)	6.94	0.33	12	0.13	19
S.E.D.	0.461				

Further MAFF-funded experiments during 1987-1990 tested the effect of increasing rates of agricultural gypsum (10, 20, 30, 40, 60 and 80 kg S/ha) and ammonium sulphate (24 and 48 kg S/ha) and of foliar-applied elemental S (10 kg S/ha) on crop response in spring barley (5 sites), winter barley (5 sites) and winter wheat (2 sites) in England and Wales (ADAS, unpublished). Averaged across all treatments, significant positive yield responses of 0.4 t/ha (6%) were obtained in 1990 at 2 sites in Wales and one site in south-west England (Table 4). No symptoms of S deficiency were recorded at these sites. A visual response to the S treatments was recorded at the site in south-west England the previous year but there was no grain yield response. In 1992, a grain yield response to soil-applied sulphate was obtained in winter wheat on a sandy soil in northern England (E. J. Evans, personal communication) but there was no yield response in a similar experiment on a shallow chalk soil in southern England (ADAS, unpublished).

Table 4 Yield response of cereals to fertilizer sulphur at sites in England and Wales during 1987-1990 in relation to crop sulphur content in leaves at anthesis and in grain at harvest

Year	Site location	Crop	Yield response		Leaf		Grain	
			+S t/ha	- S t/ha	S (%)	N : S ratio	S (%)	N : S ratio
1987	Ashcombe, Devon	spring barley	+ 0.26	4.82	0.38	8.5	0.12	17.1
1988	Downderry, Cornwall	spring barley	+ 0.01	2.29	0.31	9.3	0.12	17.6
1989	Clibburn, Cumbria	winter barley	+ 0.11	4.24	0.14	10.7	0.12	17.9
	Yeavering, Northumberland	winter wheat	- 0.15	6.16	0.38	8.2	0.15	16.8
	Penallt, Gwent	winter barley	- 0.06	7.26	0.28	10.7	0.11	14.8
	Colaton, Devon	winter barley	+ 0.01 (a)	7.13	0.15	24.0	0.09	22.0
	Churchland, Dyfed	spring barley	- 0.02	3.84	0.29	13.4	0.12	20.0
1990	Little Corby, Cumbria	spring barley	- 0.05	5.46	0.32	15.5	0.11	19.4
	Charminster, Dorset	winter wheat	- 0.07	8.21	0.22	14.0	0.11	16.8
	Colaton, Devon	winter barley	+ 0.39 (b)	6.92	0.25	17.9	0.10	20.4
	Marlies, Dyfed	spring barley	+ 0.40 (b)	3.82	0.28	12.1	0.15	17.1
	Penallt, Gwent	winter wheat	+ 0.37 (b)	7.32	0.22	16.6	0.09	21.7

(a) A visual response was obtained at this site.

(b) Statistically significant, $P < 0.01$.

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 1988-1990, 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) on grain yield and baking quality in winter wheat was tested. 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 & Salmon 1990). In 1993, 21 field experiments in England, Wales and Scotland tested the effect on grain yield of a single rate of S applied in spring as potassium sulphate. Preliminary results from HGCA-funded experiments indicate grain yield responses ranging from 3-18% (McGrath *et al.* 1994). A visual response was obtained at 3 further sites which either did not give a yield response or where yield was not recorded. Yield responsive sites were confined to sandy or shallow soils. There was no yield response at two further sites cropped to winter barley.

In 1983, 'tramline comparisons' at four sites in north-east Scotland on sandy soils developed over fluvioglacial gravel showed yield responses in winter barley of between 5 and 28% (Scott *et al.* 1984). A summary of a further 33 fully replicated field experiments carried out during 1982-1985 in Scotland is given in Appendix 1. These experiments, which included at least one S fertilizer treatment as part of the experimental design, tested either foliar-applied elemental S (5, 10, 15 or 20 kg S/ha) or agricultural gypsum (80 kg S/ha). Potassium sulphate (20 kg S/ha) was compared with foliar-applied elemental S at two of the sites. Significant grain yield increases were obtained at only 6 of the sites which were all in north-east Scotland (Table 5). There were no significant N x S interactions at those sites which tested this aspect. One further site in north-east Scotland in 1988 showed a visual response to 10 kg S/ha applied as potassium sulphate but there was no grain yield response.

Table 5. Cereal sites in Scotland showing a significant ($P<0.05$) response in grain yield (t/ha @ 85% dry matter) to S fertilizers during 1982-1985.

Year	Site	Crop	Yield Response (t/ha)	pH (units)	Soil OM (%)	SO_4-S (mg/kg)
1983	Kindcardineshire	spring barley	+0.26	6.6	6.0	-
1983	Morayshire	winter barley	+0.55	6.2	4.0	6.4
1984	Aberdeenshire	winter barley	+0.58	6.2	10.0	8.0
1984	Morayshire	winter brley	+0.48	6.2	3.0	4.1
1984	Morayshire	winter barley	+1.05	6.0	3.0	7.3
1984	Aberdeenshire	winter wheat	+0.66	6.1	9.0	-

The response of cereals to applied S in Ireland has recently been summarised by Conry (1993). In 1981, the yield of spring barley grown on a light-textured gravelly soil was increased by 14% upon application of gypsum but there was no yield response in winter wheat at the same site the following year. Subsequent field experiments on winter wheat at other potentially S deficient sites in Ireland over the period 1983 to 1985 showed no yield benefit to soil-applied or foliar-applied S, even at one site showing deficiency symptoms. In 1986, 1989 and 1990, the effect of foliar-applied elemental S (10 kg S/ha) and soil-applied soluble sulphate (86 kg S/ha) on the yield of winter barley was compared on two contrasting soil types; a gravelly sandy loam and a free-draining clay loam. Statistically significant grain yield increases (averaging 14 and 21% for foliar-applied and soil-applied S, respectively) were obtained in each year on the light textured soil; in 1989 and 1990 the yield benefit was about 2 t/ha (30%). Smaller yield increases (a maximum of 0.4 t/ha) on the heavier-textured soil were not significant (P <0.05). An expanded research programme is planned to examine the effect of S on both the yield and quality of Irish cereals (Murphy 1990).

The pattern of grain yield response to S fertilizers in the UK and elsewhere has clearly not been consistent. This is largely due to seasonal variatons in crop N and S supply but may also indicate that deficiency in cereals is not yet severe. At currently recommended rates of N application, the majority of cereal crops are probably able to obtain sufficient S from the soil and the atmosphere to maintain satisfactory crop growth. However, the experimental data clearly shows that S deficiency may occur on sandy or shallow soils in areas where the amounts of S deposited from the atmosphere are low (<20 kg/ha), especially where large amounts of N are applied. As has been shown for winter oilseed rape (Zhao *et al.* 1993), the correct balance of N to S is an essential requirement for the satisfactory growth and development of cereals.

4. DIAGNOSIS AND PREDICTION

4.1 Plant analysis

Accurate diagnosis and prediction of S deficiency is important if S fertilizers are to be used economically and sensibly. It is generally recognised that plant analysis is the most reliable means of diagnosing S deficiency because it reflects the crop's response to variation in the supply of S from various sources. The concentration of total S, SO_4-S, N:S ratio and SO_4-S:S ratio in plant tissue have all been suggested as indices of deficiency for diagnostic purposes and their drawbacks discussed (Jones 1986; Syers *et al.* 1987). Following on from some preliminary work by Freney *et al.* (1978) under greenhouse conditions, Spencer & Freney (1980) evaluated these indices in a comprehensive field experiment on spring wheat at three sampling times (Table 6).

Table 6 Effect of plant age on critical values of four crop parameters for diagnosing sulphur deficiency in spring wheat. (The critical value is that which produces 90% of maximum yield)

	Sampling			
	t_1	t_2	t_3	Mean
Days from sowing	61	92	134	-
Sulphate S : total S	0.14	0.12	0.11	0.13
Sulphate S (ppm in the DM)	460	360	190	-
Total S (% in the DM)	0.30	0.28	0.15	-
Total N : total S	15	16	19	16

t_1 = fourth leaf expanding
t_2 = fully tillered (20 cm tall)
t_3 = jointing

Source : Spencer and Freney (1980).

Whole plant concentrations of S and SO_4-S decreased and N:S ratio increased as the plant matured. Time of sampling had the least effect on the SO_4-S:S ratio and the N:S ratio and these authors calculated critical values of 0.13 and 16, respectively. Although crop N supply had little effect on the critical values identified for each sampling time in this experiment, the authors indicated that the N:S ratio would be more affected by crop N supply and therefore less appropriate. Whole plants were taken for analysis because no difference was found in the concentration of total S between main stem and tillers when the wheat crop was fully tillered (20 cms tall). Scott (1985) also considered the SO_4-S:S ratio as the best index for assessing S deficiency in grass, values above 0.2 reflecting an adequate S status. Schnug (1987) found a critical SO_4-S:S ratio of 0.25 for cereals in northern Germany.

The data of Freney *et al.* (1978) was critically re-evaluated by Scaife & Burns (1986) who showed that the concentration of SO_4-S on its own was just as good a measure of satisfactory crop growth as the SO_4-S:S ratio, despite its variability with plant age. They concluded that the SO_4-S:S ratio was insensitive and analytically time consuming, and recommended a critical SO_4-S concentration of 250 ppm below which S is deficient. The concentration of SO_4-S might be considered more appropriate because when S is limiting, all absorbed SO_4-S is converted into protein with little remaining free (Roberts & Koehler 1965; Stewart & Porter 1969). In Scotland, this critical concentration is routinely used in advisory work to confirm S deficiency symptoms in both cereals and oilseed rape but field experiments in England and Wales have not found either the SO_4-S concentration or the SO_4-S:S ratio to be useful in predicting whether a yield response will occur (Withers & O'Donnell, in press). Schnug (1987) reports a critical SO_4-S concentration of 0.1% for whole cereal plants at the stem extension stage in northern Germany.

The concentration of total S and the N:S ratio in crop tissue is most commonly used to distinguish between S deficient and normal crops. Total S is analytically convenient but critical concentrations vary depending on the part of the crop sampled (whole plant or leaf) and the time of sampling. Schnug (1987) identified a critical concentration of 0.4% total S in whole plants at stem extension stage whilst Taureau *et al.* (1987) advocated a critical concentration of 0.2% total S in the second and third leaves at anthesis. In pot studies where the crop is harvested after about 35 days, dry matter accumulation in wheat was reduced when the total S concentration fell below 0.14% (Goodroad *et al.* 1989) or 0.2% (Stewart & Porter 1969). Analysis of the crop at such an early stage is, of course, inappropriate because a lack of deficiency at the seedling stage is no guarantee that the crop will not suffer deficiency at a later stage. In field experiments, critical concentrations have been usually assessed at about the ear emergence stage (GS 45-59) with critical values of 0.06-0.09% in whole plants indicating deficiency (Oates & Kamprath 1985; Rasmussen *et al.* 1975; Rasmussen *et al.* 1977). Gupta (1976) considered a critical value of 0.12% more appropriate at this growth stage whilst Mailer & Maples (1986) found a critical level of 0.27% at full flag leaf emergence. Advisory experience in the UK suggests that leaves showing deficiency symptoms generally contain <0.2% total S (e.g. Table 3) whilst concentrations between 0.2 and 0.25% S may suggest borderline status.

Rasmussen *et al.* (1977) found large seasonal variation in the total S concentration of S-deficient tissue (0.08-0.15% in whole plants) during early growth and favoured the use of the N:S ratio for diagnostic and predictive purposes. The N:S ratio is considered more useful because leaf protein does not vary in its composition and has a constant N:S ratio of 15:1 (Stewart & Porter 1969). Where S is limiting, N accumulates as non-protein N (NPN) such that the total N:total S ratio widens. Where N is limiting, S accumulates as SO_4-S and the N:S ratio narrows. In most studies, a N:S ratio of 16-19 has been found to be critical for S deficiency to occur (Stewart & Whitfield 1965; Stewart & Porter 1969; Rasmussen *et al.* 1975; Spencer & Freney 1980; Mailer & Maples 1986), although critical values of 20-22:1 have also been reported (Oates & Kamprath 1985; Mailer & Maples 1987; Goodroad *et al.* 1989). Rasmussen *et al.* (1977) found that the N:S ratio in whole plants decreased from about 16:1 at the tillering stage to 10:1 at ear emergence. This does not agree with the data of Spencer & Freney (1980) as shown in Table 6. Differences probably reflect differences in the S content of the soils used. Rasmussen *et al.* (1977) suggest that decreases in the N:S ratio may be due to re-mobilization of N from older tissue since whole plants were taken for analysis. Large N:S ratios do not necessarily indicate a shortage of S but may simply reflect a large rate of applied N.

These data indicate that it is best to sample only actively growing tissue during a period of maximum demand (GS39-65), when a total S concentration of 0.25% S or above *and* a N:S ratio of 17:1 or below would indicate a satisfactory S supply. Advisory experience in the UK indicates that visible symptoms are usually associated with N:S values well in excess of 20:1. There is comparatively little data on critical threshold values in spring cereals but Rasmussen *et al.* (1977) found N:S ratio values for spring wheat similar to those for winter wheat. In contrast, total S concentrations were generally higher than in winter wheat at a comparable growth stage reflecting the quicker growing habit of spring cereals.

4.2 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. Total S concentrations below 0.12%, and especially below 0.1%, in cereal grain have been associated with S deficient plants (Roberts & Koehler 1965; Archer 1974; Rasmussen *et al.* 1975; Byers & Bolton 1979). In field and pot experiments with spring wheat, grain yield response to S fertilizer was associated with a grain S concentration of <0.12% *and* a N:S ratio wider than 17:1

in the grain (Randall *et al.* (1981) and these critical values are now generally accepted for breadmaking wheat. These workers found that reliance on grain S alone can be misleading because shortages of N can also depress protein formation. In pot studies, Byers & Bolton (1979) found that the N:S ratio in grain from plants well supplied with both N and S was fairly constant at 15:1 but was well in excess of this value when S was in short supply, and Byers *et al.* (1987b) considered the N:S ratio in the grain was a better indicator of S deficiency.

However, in field experiments grain N:S ratio has been shown to vary depending on the crop N and S supply because grain metabolic, storage and functional proteins have a varied composition. The proportion of the different proteins present in the grain will govern the final N:S ratio in the grain. According to Wrigley *et al.* (1984b), S-rich proteins will have N:S ratios nearer 10:1 whilst S-poor proteins will have N:S ratios over 30:1. Grain N:S ratios in field crops well supplied with S are commonly 9-12:1 (Salmon 1984; Randall & Wrigley 1987). Wide N:S ratios in cereal grain do not necessarily indicate that crop S supply is sufficiently low for grain yield to suffer even though breadmaking quality may be poorer. A high N supply and /or yield limitation (eg lodging) during the grain filling period may result in an accumulation of N in grain with adequate S (Timms *et al.* 1981). It is for this reason that consideration of both the S concentration and the N:S ratio are required to diagnose S deficiency in the grain (Randall *et al.* 1981).

Moss *et al.* (1982) suggested that S deficient crops could be more simply diagnosed by soaking cereal grains in a 4% glutaraldeyde solution, buffered to pH 6.8, at 40°C for 48 hours. Grains with adequate S remain straw yellow in colour whilst S-deficient grain turns a yellow-brown, light purple brown or dark purple brown depending on the severity of the S shortage. The colours are based on the well-known Munsell colour chart for describing soils and samples are scored on the basis of the percentage of grains in each of the four colour classes. In a comparative test with samples from pot and field experiments, Moss *et al.* (1982) found scores ranging from 0 to 300 with S-deficient samples having scores less than 100. There was a good correlation between the glutaraldehyde score and the N:S ratio and total S concentration in the grain. This method has obvious advantages in terms of simplicity but Randall & Wrigley (1987) consider the scoring process tedious for large numbers of samples and the reason for the colour change is not known. They report on an alternative diagnostic method which measures the turbidity of the gluten fraction after the flour has been firstly dispersed in a 12% urea solution and then precipitated by centrifugation and the addition of a dilute bicarbonate buffer (Skerritt & Martinuzzi 1986).

4.3 Soil analysis

Analysis of plant-available S in the topsoil has been found less useful as an indicator of S shortage because of fluctuations in the amount of S mineralized through the growing season and the now well established need to take account of S in the subsoil and the crop rooting depth. A number of soil extractants have been evaluated and SO_4-S extracted by phosphate (Scott 1981) appears the most reliable (Warman & Sampson 1992; Zhao & McGrath, in press). This method is found useful in diagnosing potentially S deficient soils in Scotland (Scott 1981) and New Zealand (Jones 1986), with <3 mg/kg indicating potential yield response (Table 7). However, Hue *et al.* (1984) obtained a good correlation between yield of wheat and water extractable SO_4-S and Blair *et al.* (1991) advocates the use of potassium chloride at 40°C which extracts not only available SO_4-S but also a hydrolyzable organic S fraction which is potentially available to plants. Preliminary results from HGCA-funded experiments in the British Isles in 1993 indicate a good relationship between phosphate-extractable S in the top 30 cm of soil and the crop S content (as measured by N:S ratio in flag leaves) but not necessarily with grain yield. Mahler *et al.* (1993) found that the amount of water-extractable SO_4-S in the soil to 75 cm depth was a good guide to potential crop S supply.

Table 7. Classification and interpretation of the S status of soils in Scotland

Extractable S (mg/l air-dry soil, <2 mm)	Status	Interpretation
<3.0	VL (Very Low)	Response to applications of S likely in sensitive crops.
3.0-6.0	L (Low)	Response possible in sensitive crops.
6.1-10.0	M (Moderate)	Response unlikely except in oilseed rape grown in areas where atmospheric supply of S is low.
>10.0	H (High)	Toxic effects possible at very high levels.

4.4 Modelling

Syers *et al.* (1987) considered that a modelling approach is the only viable option for estimating the need for S fertilizer, because of the limitations of soil and plant analysis. Plant analysis comes too late to treat the current crop and soil analysis may not predict crop yields. A simple model describing the inputs and outputs of S in an agricultural system can be a useful predictive tool provided soil organic S transformations, sulphate leaching and uptake of S from the subsoil can be reliably estimated across a range of soil types. Using soils information from the National Soil Inventory in England and Wales and assumptions regarding the amount of S mineralized each year, such a modelling approach is being developed in the form of a deficiency risk index. Data collected to date indicates 10-15% of the land area in England and Wales is at high risk of S deficiency, located mainly in East Anglia, Hereford and Worcester and south-west England (Zhao & McGrath 1993). The model highlights the high risk of S leaching on sandy soils and it is on these soil types that S deficiency is most often observed.

5. CORRECTION OF SULPHUR DEFICIENCY

5.1 Amount of sulphur

Understandably, there is very little information available in the UK on the amount of fertilizer S required to prevent or correct S deficiency in cereals. In view of their relatively low S requirement, it is unlikely that large amounts of fertilizer S are needed for optimum yield response, although the efficiency with which potassium sulphate fertilizer was utilized by cereal crops in 1993 was less than 10% (Table 1). Recommendations may need to vary depending on the severity of the deficiency as predicted by soil/crop analysis or modelling. In ADAS experiments in England and Wales in 1990, there was no apparent yield benefit to application of more than 10 kg/ha at three responsive sites which did not show deficiency symptoms (Withers 1993b). Yield responses to 10 and 20 kg S /ha applied as foliar elemental S were obtained in Scotland in 1984 at Cushnie, Aberdeenshire and at Bailliesland, Morayshire, respectively (Appendix 1). Commercial literature reports worthwhile yield responses from up to 50 kg/ha of S based on a single field experiment in northern England. The current recommendation for potentially S deficient cereal crops in England, Wales and Scotland is 10 kg S /ha, but if S deficiency becomes more widespread these recommendations will need to be revised. Similar recommendations apply in the USA, although slightly larger amounts are needed where S deficiency regularly occurs (Table 2). Yield response in cereals on sandy coastal plain soils in Alabama was optimal when 20 -30 kg S/ha was applied as soluble sulphate fertilizer at stem extension stage (Oates & Kamprath 1985; Mitchell & Mullins 1990), but larger amounts were required where applications of S were split between planting and stem extension stage. Schnug *et al.* (1993a) recommends an application of 50 kg S/ha to prevent deficiency but provides no yield data to substantiate this recommendation.

Residual effects of S fertilizer applications have not been widely investigated. A yield response to residual S in gypsum has been obtained in semi-arid climates (<500 mm/year), where unused S accumulates in the subsoil (Ramig *et al.* 1975; Rasmussen & Allmaras 1986), but where the annual rainfall is larger than this, residual effects are considered to be small (Jones *et al.* 1968). In the UK, the recycling of straw may make a significant contribution to reducing the amount of fertilizer S required, although, in the short term, soil SO_4-S may be immobilized 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 fertilizer applications to this break crop and the potential mineralization of S from the straw residue.

5.2 Timing of sulphur

In the USA, Mitchell & Mullins (1990) compared S applications at planting, stem extension and a split application between these two timings (Table 8). The largest yield response was obtained when ammonium sulphate was applied at stem extension stage, but this was not consistent within each year. A late corrective application of ammonium sulphate at flag leaf emergence gave only 82% of the grain yield that was produced when ammonium sulphate was applied at stem extension stage. Mailer & Maples (1987) recommend application of soluble sulphate in early spring and in reviewing work in France between 1979 and 1985, Taureau *et al.* (1987) also concluded that applications of S during mid-late tillering were more effective than applications after stem extension. This is consistent with the large demand for S once stem extension starts (Gregory *et al.* 1979 a, b). Foliar applications of magnesium sulphate at ear emergence are reported to increase grain yield in cereals but whether this effect is due to a magnesium or a S effect is uncertain.

Table 8 Mean grain yields of winter wheat on a Benndale sandy loam during 1987-89 as affected by rate and timing of ammonium sulphate.

		S applied (kg/ha)			
Timing	0	11	22	44	Mean
Plant	1.92	1.97	2.27	2.15	2.13
Stem extension	1.92	2.27	2.34	2.32	2.31
Flag leaf emergence	1.92	2.17	2.24	2.03	2.15
Split	1.92	2.15	2.10	2.24	2.16
Mean	1.92	2.14	2.24	2.18	2.19

Source : Mitchell & Mullins (1990)

There have been no comparisons of timing effects in the UK. More information is required on the extent to which yield can be recovered by application of S fertilizers once symptoms appear after stem extension. Measurements of plant-available S in the soil at GS 39 after application of S during early tillering indicate considerable movement of fertilizer S within the profile (P.J.A. Withers, unpublished). Clearly there is a risk that soluble sulphate fertilizers applied too early in the spring can be readily leached before active crop growth has commenced, as is the case with N applications to cereals. Applications during autumn are not recommended for similar reasons.

5.3 Form of sulphur

Sulphur can be added to the soil-plant system either in the form of organic manures or as inorganic S fertilizers. The amounts of S contained in organic manures and animal slurries are very variable, application rates are often difficult to gauge in practice and there is little information on their availability during the growing season (Syers *et al.* 1987). Unpublished data from samples collected by ADAS are given in Table 9.

Table 9 The content of sulphur in animal manures at spreading

Manure type	S kg/m^3
Cattle FYM	0.7
Pig FYM	0.7
Poultry FYM (layers)	1.5
Poultry FYM (broilers)	3.0
Dairy cow slurry	0.4
Beef cattle slurry	0.4
Pig slurry	0.2

An application of 50 m^3/ha of cow slurry can, therefore, be expected to contain approximately 20 kg/ha of S and this broadly agrees with results reported by Watson & Stevens (1986). The plant-availability of S in urine is high (70%) but organic S in dung is relatively resistant to mineralization (Williams & Haynes 1993). The contribution of livestock manures to the S nutrition of cereals is therefore probably small, especially since most cereal crops are in continuous arable rotation and do not receive regular applications of organic manures. Where these are applied, it tends to be in autumn before the crop is sown and any SO_4-S released by mineralization will be leached in free draining soils. Where organic manures are regularly applied the need for inorganic S fertilizers will be greatly diminished, although yield responses in grass to inorganic S fertilizers have been obtained even where livestock manures have also been applied (R.J. Skinner, unpublished).

The range of inorganic S fertilizers which are available for the treatment or prevention of S deficiency can be broadly divided into two groups: insoluble elemental S formulations and soluble sulphate-containing fertilizers. Elemental S products must first be oxidized by specific microorganisms (mainly *Thiobacillus* species) to sulphate before being taken up by the plant. In comparing leaching losses from different fertilizer products, Rhue &

Kamprath (1973) found that it took 150 days for elemental S applied in October to completely oxidize in a loamy sand soil. In experiments in Northern Germany, a smaller yield response in wheat obtained with elemental S compared with sulphate fertilizer when applied at the rate of 100 kg/ha was found to be due to initially low populations of *Thiobacillus* (Schnug 1987). With regular elemental S fertilization, the populations of these organisms should increase so improving the efficiency of conversion to sulphate. However, McCaskill & Blair (1987) found that provided elemental S fertilizers contained particle sizes below 0.5 mm, the presence or absence of microbial S oxidisers makes little difference to their effectiveness.

Mitchell & Mullins (1990) found that elemental S gave a lower yield response in cereals than ammonium sulphate when applied at the same time. Mixtures of molten elemental S and sodium bentonite applied to the soil in prill form have also been investigated but are generally ineffective because of inadequate dispersion in the soil (Nuttall *et al.* 1990). The effectiveness of elemental S fertilizers therefore depends not only on temperature and the numbers and activity of the oxidizing organisms but also on the range of particle sizes in the fertilizer and its adequate dispersion in the soil (Jansen & Bettany 1986; McCaskill & Blair 1987; Syers *et al.* 1987; Chapman 1989). Sulphate oxidised from elemental S may also be immobilized in soil organic matter (He *et al.* 1994).

Elemental S is most commonly applied to agricultural crops in the UK in micronised form (particle size of 5-8 μm) as a foliar suspension. Foliar elemental S (80-90% S) can act as a broad-spectrum fungicide as well as a source of nutrient and it is not always clear in field experiments whether any yield benefit derived from its application is due to a fungicidal or a nutrient effect. At manufacturer's recommended rates, only small amounts of S are applied (8 kg S/ha). The nutrient value is obtained when the material is washed into the soil, since only the SO_4-S component (usually about 2-3% of total S) is actually absorbed by the leaf (McGrath & Johnston 1986). Pot experiments have shown that micronised S is rapidly oxidised in the soil (Jansen & Bettany 1986; Chapman 1989) but field experiments in the UK have generally shown foliar elemental S to be a less effective nutrient source than other soluble sulphate fertilizers when applied at the same rate (Withers & O'Donnell, in press; Withers 1993b). Inadequate dispersal within the soil of the foliar S as it lands on the soil surface may be responsible. In Ireland, the mean yield response in winter barley was 21% where granular ammonium sulphate nitrate (supplying 86 kg S/ha) was used but 14% where foliar elemental S (10 kg S/ha) was used (Conry 1993), although the differences in the amounts of these two fertilizers applied was large.

In view of their mode of action, elemental S fertilizers probably need to be applied earlier and in larger quantity in order to obtain a similar nutrient benefit to soluble sulphate fertilizers. Mitchell & Mullins (1990) found that elemental S (22 kg S/ha) applied at planting was as effective as the same amount of ammonium sulphate applied at the end of tillering to winter wheat but less effective when applied at the same time as the ammonium sulphate. In experiments with oilseed rape in Scotland, foliar elemental S has been as effective as ammonium sulphate when applied at double the rate (Chalmers *et al.* 1992). As pointed out by Syers *et al.* (1987), elemental S fertilizers 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 fertilizers. The oxidation of elemental S is also an acidifying process which may help to mobilize and improve crop uptake of trace elements in high pH soils (Schnug, 1987). If S deficiency becomes more severe in the UK, these aspects would merit investigation.

Inorganic soluble S fertilizers include sulphate and thiosulphate compound salts which can be applied to the soil or to the crop in either solid or liquid form. The majority of the commonly used trace element formulations contain sulphate although the amounts applied are generally small (<3 kg S/ha). Sulphate-containing fertilizers, such as ammonium sulphate, potassium sulphate and magnesium sulphate, dissolve quickly in the soil and become rapidly available for plant uptake. However, they have little residual value on high pH, sandy soils because of the ease with which sulphate is leached (Rhue & Kamprath 1973, Syers *et al.* 1987). Agricultural gypsum (calcium sulphate) is slightly less soluble and has been shown to be not always as effective as ammonium sulphate in field trials (Withers & O'Donnell, in press). This may be a reflection of S losses during application rather than its reduced solubility (20 kg/ha of S will dissolve in 5 mm of rain), since gypsum containing water of crystallization is a fine powder and difficult to spread accurately. Anhydrite calcium sulphate incorporated into granular fertilizers is a more convenient way of utilizing gypsum as a nutrient source (P.M. Sweeney, personal communication). According to Jansen & Bettany (1986), thiosulphate is rapidly oxidised in the soil and therefore comparable to sulphate but a foliar spray of thiosulphate (8 kg S/ha) gave 17% less yield of winter oilseed rape than solid potassium sulphate (30 kg S/ha) in a field experiment in 1989 (Withers 1989). Sulphate-containing fertilizers have the advantage that they contain other useful nutrients although these may not always be wanted or may make the fertilizer prohibitively expensive. Ammonium sulphate, either on its own, or incorporated with ammonium nitrate into prilled N and S products, are most commonly recommended for the prevention and correction of S deficiency in UK agriculture today. The range of S fertilizers available for the correction of S deficiency is shown in Table 10.

Table 10. Range of sulphur fertilizers available in the UK.

		$N:P_20_5:K_20$ Analysis		Sulphur % S
Straight chemicals				
	Ammonium sulphate	21: 0: 0		24
	Single superphosphate	0: 18: 0		11
	Potassium sulphate	0: 0: 50		18
	Gypsum (calcium sulphate)	0: 0: 0		15-18
	Manganese sulphate	0: 0: 0		15-18 + 27-32% Mg
	Epsom salts (magnesium sulphate)	0: 0: 0		13 + 10% Mg
	Kieserite (granular magnesium sulphate)	0: 0: 0		22 + 16% Mg
	Kainit	0: 0: 12-14		5-6 + 4% Mg, 20-22% Na
Solid compound fertilizers				
Kemira	Double Top	27: 0: 0		12
	Sulphur Ten	20: 4:14		2.8
ICI	Sulphur Gold	30: 0: 0		7.6
	Kaynitro gold	24: 0:14		3.2
Hydro	Sulphan	30: 0: 0		6.6
	Sulphur Cut	22: 4:14		3
	Sulphur Grass	24: 5: 5		5
Seabright		30: 2: 0		13.2
Timac	Sulphammo 23	23: 0: 0		23 + 3% Mg.
	Sulphammo 30 Oligomag	30: 0: 0		10 + 5% Mg
J & H Bunns		27: 0: 0		6
	Bittersalz	0: 0: 0		16 + 9% Mg
Liquid fertilizers				
Hydro Chafers (liquid fertilizers)	NS 60	26: 0: 0	15	6
	35 S	35: 0: 0	7.8	3.1
	Nufol 20 S	20: 0: 0	4.3	1.7
Elemental sulphur (selected)				
PBI	Thiovit	0: 0: 0		80
Stoller	Tiger 90	0: 0: 0		90
CCCP	Yellowstone S granules	0: 0: 0		90

6. SULPHUR AND GRAIN QUALITY

6.1 Sulphur in the breadmaking process

The S-containing amino acids methionine and cysteine have an important influence on flour quality in breadmaking wheat cultivars. The amounts of these amino acids in the wheat endosperm influence the proportions of the different types of protein present in the flour. Cysteine, in particular, has an essential role in providing sulphydryl (also called thiol) groups (S-H) for enzymatic oxidation to disulphide bonds (S-S), which bind protein chains (polypeptides) together. The proportion of S-H and S-S bonds within each of the endosperm proteins and their positional availability affects the balance of dough viscosity (extensibility) and elasticity, which determines the functionality for breadmaking and other uses. Whilst S-H bonds allow protein chains to move during dough development and baking, S-S bonds are required to prevent the protein chains from moving too far apart (Fig. 3). The satisfactory interchange of S-H and S-S bonds as the dough is mixed and baked is therefore considered necessary in order to bake a good loaf (Frater *et al.* 1961; Wall 1971; Archer 1980). Oxidants such as ascorbic acid and potassium bromate added to flour may improve baking performance by increasing the ratio of S-S to S-H bonds in the dough. Archer (1980) reviews work showing that, for any given protein content, the optimum ratio of total S-S to S-H bonds in wheat flour is about 15:1; ratios above or below this value producing inferior loaves as measured by loaf volume. However, Jones *et al.* (1974) found that only a relatively small proportion of the S-H (30%) and S-S (12%) bonds present in dough were important during mixing and that these proportions varied for different cultivars.

protein chains held
under tension by
an S-S bond

a protein chain
nearby has a
free S-H bond

the hydrogen atom
changes protein chains
relieving tension
and allowing the dough
to rise

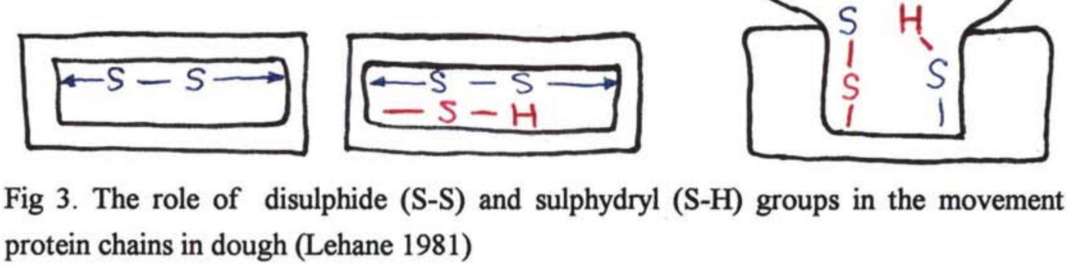


Fig 3. The role of disulphide (S-S) and sulphydryl (S-H) groups in the movement of protein chains in dough (Lehane 1981)

Four types of endosperm proteins have been identified: albumins, globulins, gliadins and glutenins in order of decreasing solubility and increasing molecular weight (Osborne 1924). Albumins and globulins are 'salt-soluble' proteins rich in S but are considered to have a metabolic function rather than a direct influence on breadmaking quality. Gliadins are storage proteins and can be separated into S-poor 'slow' proteins (ω-gliadins) and S-rich 'fast' proteins (α, β and γ-gliadins) according to the speed with which they travel across a gel toward a negative electrode when stimulated by an electric current, a method known as gel electrophoresis. Glutenins are storage proteins which are not soluble in ethanol and have a slightly lower S content than the fast gliadins (Wrigley *et al.* 1984a). Whereas gliadins are monomers with intra-chain disulphide bonds (α, β and γ) or no cysteine (ω), glutenins are polymers with both inter-chain and intra-chain disulphide bonds. Glutenins therefore confer structural stability to dough as it rises. The classification of grain storage proteins according to their S status is discussed by Shewry *et al.* (1986).

The exact role of the gliadin and glutenin proteins in the breadmaking process is not well understood. Recently, most attention has focused on the glutenin fraction and in particular on the content of high molecular weight (HMW, Mr >81000) glutenin subunits (Fullington *et al.* 1987; Payne *et al.* 1987; Lukow *et al.* 1989; Kolster *et al.* 1991; Shewry *et al.* 1992; Pritchard 1993). These HMW subunits form polymers by the linking of one or more polypeptides by intermolecular S-S bonds and variation in their composition has accounted for a very large proportion of the differences in breadmaking quality between wheat varieties. The ability of the dough to extend without deformation (elasticity) is dependent on the amount and type of the HMW glutenin subunits present in the wheat grain. Hence, Payne *et al.* (1987) found no correlation between the content of HMW subunits and biscuit quality in wheat because resistance to extension is an undesirable quality for biscuit making. The different types of subunits are genetically controlled and can be coded according to their gene location. The proportions of the different subunits appear to be influenced by both genetic and environmental factors (Marchylo *et al.* 1990; Kolster *et al.* 1991).

Whilst HMW glutenin subunits are associated with dough elasticity, the α, β and γ-gliadins and the LMW glutenin subunits, which are comparatively S rich, are related to dough extensibility (Fullington *et al.* 1987). In Australian wheats, the relative amounts of gliadin and glutenin in the flour have a large influence on baking quality (Orth & Bushuk 1972; Archer 1979; MacRitchie 1987). Although Archer (1980) concluded that the final balance between S-S and S-H bonds within the gliadin and glutenin fractions of wheat grain determine the differences in baking quality between different cultivars, the specific role of S-H groups is still unclear. The apparent inferiority of UK breadmaking wheat in the world cereal market has been linked to a low level of HMW glutenins relative to other proteins (Booth & Melvin 1979; Payne *et al.* 1987). The lower content of HMW glutenin subunit 1 in particular gives UK wheat a poor quality 'score' compared to wheat of other countries (Payne *et al.* 1987), although there is substantial variation in the expression of this allelic subunit between different geographical areas. Halford *et al.* (1992) found that the prescence of the allelic subunit 1 (and 2*) increased quantitavely the quality of the flour. The development of more specific and rapid methods of assessing the relative amounts of gliadins and glutenins in wheat should improve our understanding of this complex process. Protein-specific monoclonal antibodies have been successfully used to measure gliadin (Skerritt *et al.* 1987) and glutenin (Mills *et al.* 1993) fractions in wheat flour, and the SDS-insoluble glutenin fraction may become more routinely used as a measure of breadmaking potential within the milling and baking industries (Pritchard 1993).

6.2 Sulphur deficiency and breadmaking quality

The effect of S deficiency on breadmaking quality in wheat was first investigated by Yoshino and McCalla (1966), has been reviewed by Randall & Wrigley (1987) and summary accounts of the changes in grain protein composition upon addition of S are provided by Lehane (1981) and Wrigley *et al.* (1984b). Although breadmaking quality characteristics are genetically predetermined, they are also dependent on environmental factors; in particular the supply of N and S (Byers & Bolton 1979; Moss *et al.* 1981; Byers *et al.* 1987a; Haneklaus & Schnug 1992). When S is in short supply, the formation of protein is inhibited and non-protein N (NPN) accumulates in the grain. According to Byers *et al.* (1987a), the NPN fraction of the total N content can increase from as little as 5% up to 30% when S is limiting, whilst Stewart & Porter (1969) found as little as 25% of the total N in S-deficient wheat grain was in protein form. In addition, the amino acid composition of individual proteins and the proportions of the different storage proteins in the grain alter but the types of proteins present remain the same. These changes involve:

1. A reduction in the quantity of the S-containing amino acids methionine and cysteine and an increase in aspartic acid/asparagine/arginine (Byers & Bolton 1979; Wrigley *et al.* 1980; Byers *et al.* 1987a).

2. A reduction in the quantity of essential amino acids such as lysine, leucine, isoleucine, valine and threonine, which reduces its feeding value to livestock (Byers & Bolton 1979; Wrigley *et al.* 1980).

3. A reduction in LMW S-rich albumin proteins and an increase in HMW ω-gliadins which

contain very little S (Wrigley *et al.* 1980; Moss *et al.* 1981, 1983; Huebner & Bietz 1988).

4. An increase in HMW glutenins which have a low to intermediate S content (Wrigley *et al.* 1984a; Fullington *et al.* 1987).

Table 11 Percentages of densitometric scan areas (A1 to A5) for two samples of wheat flour extracted with SDS in the absence of the reducing agent 2-mercaptoethanol (E), the residue extracted with SDS and 2-mercaptoethanol (R) and for total protein (T).

Flour				Densitometric scan areas					
N : S ratio	S %	Protein %		A1	A2	A3	A4	A5	Total
22 : 1	0.08	10.5	E :	5.5	19.1	13.9	21.8	22.8	83.1
			R :	6.1	2.2	4.5	3.3	1.1	17.2
			T :	12.4	16.8	18.7	27.6	24.6	100
12 : 1	0.18	11.1	E:	4.1	10.8	15.1	27.0	26.5	83.5
			R :	3.7	1.6	6.9	4.5	0.2	16.9
			T :	7.6	9.5	20.0	30.1	32.8	100

Scan areas:

A1 - HMW glutenins of low-intermediate S content.
A2 - ω-gliadins of very low S content.
A3/A4 - LMW glutenins and α , γ & ß gliadins of intermediate to high S content.
A5 - Albumins (and some globulins) of very high S content.

Source: Fullington *et al.* (1987)

Quantitative differences in the proportions of the different proteins present in wheat flour of low and high S content have been obtained by extraction with sodium dodecyl sulphate (SDS) with or without a reducing agent (2-mercaptoethanol) to sever the S-S bonds, followed by gel electrophoresis (Table 11). Increases in the ω-gliadins (A2) in the grain of low S content occur only in the extract without the reducing agent (E) reflecting the low S content of these proteins. The increase in the glutenin fraction (A1) occurs only when the residue (R) remaining after extraction E is further extracted with SDS and the reducing agent, reflecting the high proportion of S-S bonds in these proteins. Smaller reductions in the α, β and γ-gliadins (A4) occur mostly within the first extraction E and suggest lower amounts of S-S bonds relative to S-H bonds, as found by Wrigley *et al.* (1980). These results indicate that increased amounts of HMW proteins either with a high ratio of S-S bonds relative to S-H bonds (glutenins) or containing little S (ω-gliadins) are responsible for the hard, inelastic doughs obtained from S-deficient grain (Wrigley *et al.* 1984a, 1984b; Fullington *et al.* 1987). The gliadin fraction appears more sensitive to differences in S supply than the glutenin fraction (Huebner & Bietz 1988) and van Lonkhuijsen *et al.* (1992) found that the amount of ω-gliadins explained 82% of the variation in loaf volume. The precise role of the ω-gliadins in the baking process is not known.

Similar increases in ω-gliadin content have been observed where high rates of N are applied or where N is applied late to wheat in an attempt to boost protein content (Timms *et al.* 1981; Salmon 1984; Byers *et al.* 1987a). Increases in HMW glutenin were, however, not observed, although this might be expected where a reducing agent was not used (Timms *et al.* 1981) or where the solvent used does not dissolve glutenin (Byers *et al.* 1987). The grain S contents in these experiments were well above the threshold for S deficiency but grain N contents were high (2.2-2.6%). A decline in breadmaking quality at high grain protein levels has been observed by other workers (Finney *et al.* 1957; Tipples *et al.* 1977; Bushuk *et al.* 1978) and the similarity between the protein composition of S-deficient grain and high-N grain suggests a shortage of S relative to N (Timms *et al.* 1981). The effects of an application of N (50 kg/ha) and/or S (20 kg/ha) applied to the soil at ear emergence on baking quality was tested in a field experiment by Randall *et al.* (1990) but the treatments did not increase the N:S ratio and no deleterious effects on baking quality were observed.

An imbalance of N relative to S is most likely to occur where foliar applications of urea are applied late as is common practice in the UK. The effect of this widespread practice on grain quality is currently being investigated but first results from one site indicate that although late urea applications during milky ripe stage increased ω-gliadins this did not result in poorer baking quality when compared to a similar amount of ammonium nitrate applied at GS32 (Salmon *et al.* 1990). Better loaf volume in the urea-treated grain was thought to be due to greater assimilation of the N into glutenin protein. However, in some seasons or at some sites the combined effect of very high fertilizer levels and inherently strong gluten protein may result in wheat flour which does not perform to its full potential in a standard breadmaking process (S. Salmom, personal communication). Foliar application of a small amount (10 kg S/ha) of elemental S at the milky ripe stage slightly reduced the content of ω-gliadins but no measureable differences in loaf volume were observed. Foliar applications of elemental S have been shown to be ineffective in terms of effects on yield and breadmaking quality (Dampney & Salmon 1990; Griffiths *et al.* 1990;

Schnug *et al.* 1993a), although field comparisons in France have demonstrated increased gluten contents in wheat where this type of fertilizer has been applied (Camblin & Gall 1987).

Numerous studies have demonstrated that wheat grain of very low S status produces an inelastic dough which gives rise to small crumbly loaves (Randall & Wrigley 1987). Byers *et al.* (1987a) described loaves made from S-deficient grain as consisting of a rock hard crust surrounding an unbaked interior. The most comprehensive assessment of the relationship between grain S content or N:S ratio and breadmaking quality from field experiments was carried out by Moss *et al.* (1981, 1983). Dough measurements and baking tests were carried out on more than 100 samples of grain with S contents ranging from 0.08 to 0.18%. As grain S content increased, dough extensibility increased and resistance to extension decreased (Fig. 3). The effects on dough extensibility were linear over the range of grain S contents used suggesting that S fertilization may be beneficial to breadmaking quality even though grain S contents are adequate for yield. There was also a positive but weaker and less consistent relationship between loaf volume and grain S.

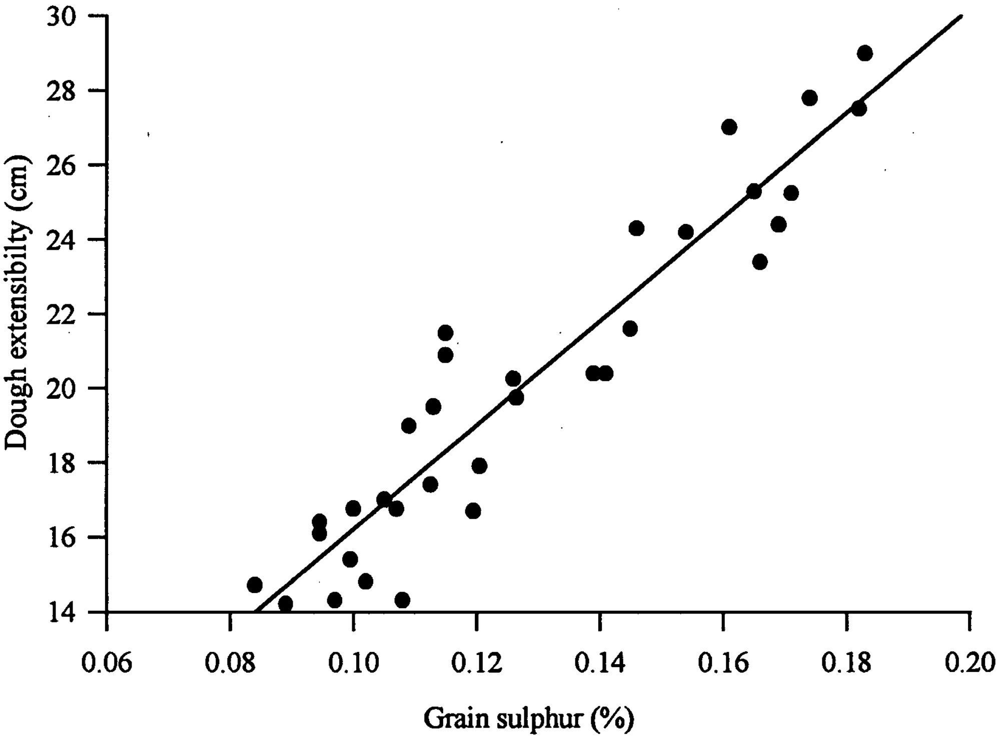


Fig 3. Effect of grain S on dough extensibilty in wheat
(Moss *et al.* 1993)

Byers *et al.* (1987a) found a dramatic improvement in loaf volume, using a small scale breadmaking process, when baking dough mixed from flour with a high S content (930 ml) compared with flour of low S content (475 ml). Additional S at anthesis increased the loaf volume to 1055 ml. Haneklaus *et al.* (1992) found that grain S concentration accounted for 40% of the variation in the loaf volume, obtained using a rapid mix-test, of 23 samples of wheat flour produced from grain grown at different sites in W. Germany. On average, an increase of 0.01% S in the grain corresponded to an increase of 40 ml in loaf volume, which agrees well with the data of Byers *et al.* (1987a). These workers found a N:S interaction effect on loaf volume for grain samples with low N and/or S contents. In recent HGCA surveys (McGrath *et al.* 1993), the correlation between grain S concentration and loaf volume was non-linear and weak, although this may be due to the large number of different varieties and growing conditions and a relatively small proportion of low-S grain. A better correlation ($r^2 = 0.4$) was obtained between grain S concentration and SDS sedimentation volume. Schnug *et al.* (1993a) concluded that grain S content affected Hagberg Falling Number and there has also been work suggesting a link between grain S and Zeleny.

The strong interaction between N and S supply on grain quality has been demonstrated in numerous experiments (Byers & Bolton 1979; Moss *et al.* 1981; Rendig 1986) and Fullington *et al.* (1987) found that differences in protein composition were better correlated to the N:S ratio in the flour than to grain S concentration alone. The grain S or N:S concentration thresholds beyond which changes in glutenin and gliadin are sufficient to cause a large deterioration in breadmaking quality have not been identified or may not be possible to identify because of the dynamic interchange between S-S and S-H bonds. However, albumin contents have decreased sharply in grain containing <0.12% S (Moss *et al.* 1981; Wrigley *et al.* 1984a) and the critical threshold values of <0.12% total S and >17:1 N:S ratio identified for yield may also be appropiate for breadmaking quality.

The relationship between grain S concentration or N:S ratio and breadmaking quality measurements is important because S fertilization of wheat crops may benefit the miller even though a grain yield response is not obtained by the farmer. In ADAS experiments, increasing rates of S as gypsum produced only small increases in grain S content (Withers 1993b). It has also been noted by other workers (Salmon 1984; Randall *et al.* 1990) that when S is not limiting, application of N alone produces larger increases in grain S than when S is applied. When S is limiting, larger increases in grain S are more likely to occur although this will probably depend on the type of S fertilizer applied and its timing (Schnug *et al.* 1993). The largest increases will probably be obtained by application of a combined NS fertilizer.

6.3 Sulphur and malting quality

Similar changes in the amino acid balance and protein composition in barley have been observed when either high rates of N have been applied or under conditions of S deficiency (Eppendorfer 1968; Shewry *et al.* 1985; Rendig 1986). In pot and field experiments, Kirkman *et al.* (1982) found increased amounts of S-poor 'C' hordein proteins (analagous to the S-poor ω-gliadins in wheat) relative to the S-rich 'B' and 'D' hordein proteins (analagous to LMW and HMW subunits, respectively in wheat) where high rates of N had been applied. Using high performance liquid chromatography, Griffiths (1987) also found increased amounts of 'C' hordein in spring barley grain with a high N content. In further experiments by Shewry *et al.* (1983), the proportion of the 'C' hordein increased from 17-29% in grain well supplied with S to 65-74% in S-deficient grain. Contrary to the comparable experiments on wheat, there were no changes in the relative proportions of the albumins, globulins or glutenins. Cysteine, and to a lesser extent methionine, were decreased and glutamine, proline and/or phenylalanine increased in the salt-soluble (albumins and globulins) and hordein proteins but the amino acid composition of the glutelin proteins (mainly structural) was unaffected. Large reductions in grain protein content were accompanied by large increases in NPN (from 7% in normal grain to 30% in S-deficient grain), as reflected in increased amounts of the free amino acids asparagine and glutamine in samples of whole milled grain. This work agrees closely with the earlier studies of Eppendorfer (1968).

The hordein proteins are a poorer source of essential amino acids than the albumins and globulins (Shewry *et al.* 1981) and increased proportions of these proteins in the grain decreases the nutritional value to livestock. To what extent these changes affect the quality of barley for malting and brewing is not known. Shewry *et al.* (1993) briefly reviewed previous work indicating that the amount, distribution and properties of the hordein storage proteins may influence the malting quality of barley. The S-rich 'B' and 'D' hordein proteins occur as polypeptide units linked by disulphide bonds. These protein polymers correspond to the analytically defined 'gel protein' fraction, which has been shown to be inversely correlated with malting quality (Smith & Lister 1983). This negative relationship presumably reflects a poorer breakdown of S-S bonded proteins during the fermentation process and suggests that S deficiency, in reducing the proportions of these polymers in the hordein protein fraction, may actually benefit malting quality. Shewry *et al.* (1993) have also demonstrated that the hordein proteins are unequally distributed within the aleurone layer and endosperm and review evidence to suggest that this may also affect malting quality. Differences in the amounts of 'B' and 'C' hordein proteins between single seeds from the same cultivar can often be considerable (Griffiths 1987) and these storage proteins appear particularily sensitive to environmental conditions during crop growth.

According to Pierce (1987), the amount and type of amino acid present in the grain and resulting wort has a large influence on the brewing process. Free amino acids need to be in sufficient quantity in the wort to support yeast growth during fermentation but without leaving any residue in the final beer which encourage the growth of spoilage organisms and impair the flavour of the beer. The amount of amino acids present is largely governed by the grain N content. The nature of the amino acids present is also important because some amino acids are more efficiently absorbed by the yeast than others (Table 12). Group A amino acids are rapidly absorbed by the yeast, Group B are absorbed more slowly, Group C are absorbed only after supplies of Group A have been exhausted whilst proline is not utilised in any quantity. Amounts of lysine, histidine, arginine and leucine also appear critical in that a shortage of these amino acids reduces fermentation. In the experiments of Shewry *et al.* (1983), the hordein fractions in low S barley grain were enriched in proline and phenylalanine compared to normal S grain, although in the milled samples of whole grain (low S) there were slight reductions in proline and other amino acids in Group C which might remain after fermentation has stopped. Whether grain S status has an effect on malting or brewing quality would therefore appear to depend on the precise role of the different protein fractions and their respective amino acid composition.

Table 12 Classification of amino acids for brewing quality

Group A	**Group B**	**Group C**	**Group D**
Glutamic acid	Valine	Glycine	Proline
Aspartic acid	Methionine	Phenylalanine	
Asparagine	Leucine *	Tyrosine	
Glutamine	Isoleucine	Tryptophane	
Serine	Histidine *	Alanine	
Threonine			
Lysine *			
Arginine *			

* Amino acids whose amount is critical to normal fermentation

Crop S supply may influence other characteristics of the grain which have an influence on malting quality. Reisenauer & Dickson (1961) found that in the presence of N, S fertilization increased the amounts of α-amylase in the grain which is required for starch hydrolysis. Recent experiments have also demonstrated that a protein (friabilin) which adheres to starch granules within the endosperm is responsible for endosperm texture and grain hardness in wheat (Greenwell & Schofield 1986) and barley (Sulaiman *et al.* 1993). Endosperm texture is an important factor in malting quality and there is evidence that concentrations of friabilin in wheat grain may be affected by S supply (Castle & Randall 1987).

7. SIGNIFICANCE OF SULPHUR DEFICIENCY TO THE CEREALS INDUSTRY

Sulphur is considered to be a major nutrient limiting crop production in European agriculture (Schnug 1991) and there seems little doubt that S deficiency is a growing problem in modern UK farming. Deficiency symptoms have been seen in a greater number of oilseed rape crops than ever before and are starting to occur in cereals. The extent of S deficiency in British cereal crops has been estimated by surveys of leaf tissue and/or grain. In a survey of wheat crops in 1981 and 1982 (Byers *et al.* 1987b), none of the grain samples collected by the HGCA contained less than 0.12% total S or showed N:S values larger than 17:1 and could, therefore, be classed as deficient in S. The survey, which was highly representative in terms of the major wheat varieties and areas grown, was repeated in 1992 (Table 13).

Table 13 Ranges and means of grain N and S concentrations and N : S ratio in 1982 and 1992.

		N (%)		S (%)		N : S	
	No. of sample	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
1982	238	1.57 - 2.90	2.26	0.133 - 0.214	0.172	10.7 - 15.0	13.1
1992	400	1.35 - 3.18	2.24	0.054 - 0.209	0.143	13.2 - 29.6	15.8

Source : McGrath *et al.* (1993)

The results show a considerable decline in the S status of wheat grain over this 10-year period and suggest that up to 10% of the samples collected may have been deficient in S (McGrath *et al.* 1993). Regional variation in grain S status corresponded closely to the deposition of S from the atmosphere in these surveys. Deficiency was least likely to occur in the industrial regions surrounding London, the West Midlands and south Yorkshire and most likely to occur in Scotland, northern England, East Anglia and the south coast. The appearance of S deficiency symptoms in isolated cereal crops in Scotland, Wales and northern, south-west and eastern England by the advisory consultants of SAC and ADAS supports these data and a similar decline in crop S status has been observed in oilseed rape (Zhao *et al.* 1991).

A separate survey of potentially S deficient winter wheat and winter barley crops in 1992 found similar regional patterns and confirmed that only a small proportion (<10%) of cereal crops can be considered to be deficient in S (Withers *et al.* 1993). Grain N and S concentrations were significantly larger in winter wheat compared to winter barley when grown on the same farm, reflecting the larger protein contents found in wheat. A greater proportion of winter barley crops (9%) were deficient in S compared to winter wheat (4%), although this is probably because winter barley crops were more often grown on sandy soils, where a S deficiency is more likely to occur (Withers 1993b). However, critical threshold values established for wheat grain (Randall *et al.* 1981) may not be appropriate for barley or oats. It should be noted that these crop surveys were not representative of all cereal growing areas and there is still some uncertainty over the relationship between the S status of leaf and/or grain and the need for S fertilizer.

Experimental evidence in the UK indicates that S deficiency can cause yield reductions in field crops of up to 30%, although much higher yield responses have been recorded in severely S deficient crops outside the UK. The severity of deficiency will clearly depend on the season and the particular site conditions but advisory experience suggests that S deficiency is not yet severe in most of the affected crops in the UK. However, if one assumes that 10% of the UK cereal area is S deficient and will suffer a 5% reduction in average grain yield (Anon. 1994), this represents a loss in revenue of very nearly £10 million (assuming a cereal price of £100/tonne). With the potentially large reduction in yield that S deficiency causes, the risk of deficiency is not something which can be ignored. A farmer looking to reduce growing costs would be better advised to omit phosphate and potash fertilizer than omit S fertilizer, assuming that the deficiency can be accurately predicted. Unfortunately, fields showing a S deficiency in one year may not show the deficiency the next year. A knowledge of soil type, location and retrospective crop analysis is currently the best means of diagnosing whether a deficiency is likely to occur. Once a deficiency has been diagnosed the farmer must assume it will re-occur each year even in reality it may not. A S deficiency is most likely to occur in cereals on free draining, coarse-textured, sandy soils, and to a lesser extent on shallow calcareous soils, in areas receiving <20 kg S/ha/year from the atmosphere. Computer-based modelling suggests that these conditions occur over about 10-15% of the land area in England and Wales (Zhao & McGrath 1993).

Although there is a lack of information on the effect of S deficiency on gluten quality in UK varieties of breadmaking wheat, there is a considerable amount of work elsewhere to indicate that a shortage of S relative to N in the developing grain reduces the elasticity of the dough and results in a poorer loaf. It is not known whether large reductions in grain quality can occur without a reduction in grain yield but there are indications that applications of high rates of N and/or late applications of urea N to boost grain protein content may not have the desired effect on flour quality due to an imbalance of S relative to N. Recent evidence from HGCA-funded experiments indicates that late applications of urea are beneficial to wheat grain quality although whether this is true under a S shortage is not known. This must be of concern to the cereals industry because such practices have been widely recommended in recent years (Sylvester-Bradley 1990; Gooding & Davies 1992). Dampney (1992) reports that 46% of breadmaking wheat crops received an average 50 kg/ha of extra N in 1989. The large amounts of N applied to breadmaking wheat may accentuate the risk of S deficiency on low-S soils. Fertilizer policies which add N and S in balanced proportions were advocated by Stewart & Porter (1969) and seem particularly relevant to modern cereal farming. There is no information on the significance of S deficiency to the malting industry. It has been demonstrated that the protein composition in barley grain changes when S is in short supply but whether this has an impact on the brewing process is not known. Malting barley crops may well be less susceptible to S deficiency on low-S soils because they receive less N.

The potential reduction in grain quality associated with S deficiency is also of considerable 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.

8. CONCLUSIONS

1. Despite their low S requirement (10-30 kg S/ha), cereal crops are susceptible to S deficiency. The incidence of deficiency in field crops has increased in the UK as a result of a reduction in the amount of S deposited from the atmosphere and a depletion of soil S reserves. Recent crop surveys indicate that up to 10% of the UK crop may be sufficiently low in S to impair either grain yield or quality.

2. Sulphur deficiency produces characteristic symptoms of chlorosis in young leaves during stem extension and results in crop stunting, lower ear density and reduced spikelet fertility. Grain yield reductions of up to 30% have been obtained in field crops in the UK but experience outside the UK suggests that larger yield responses to S fertilization may be expected where the deficiency is severe.

3. The occurrence of S deficiency in cereals is very variable and depends on the interaction between crop N and S supply during the growing season. Where S is limiting, effects on grain yield and/or quality may occur only when high rates of N are applied. Grain yield response does not always accompany the appearance of deficiency symptoms and may occur in the absence of any visual response to S fertilization.

4. Experimental evidence from pot and field experiments indicates that S deficiency reduces the quality of cereal grain both for breadmaking and feeding by altering the protein composition and balance of amino acids in the grain. However, the relationship between grain N:S ratio and breadmaking quality in wheat is still poorly understood and there is no information on whether low S (relative to N) in grain affects malting quality in barley.

5. Crop S supply in any one year is governed by the temporal and spatial variability of soil S release and/or atmospheric deposition during the growing season and crop rooting depth. Prediction of S deficiency by soil analysis alone has consequently met with variable success and the integration of soil and crop models are considered more appropriate. Experimental data in the UK indicates that S deficiency is most likely to occur on free-draining, deep, coarse-textured sandy or stony shallow soils, which are not acid, in areas receiving less than 20 kg S/ha /year from the atmosphere.

6. Analysis of the N:S ratio in young fully expanded leaves during stem extension is the most useful way of diagnosing a shortage of S. Normal leaf protein synthesis can be characterised by a total N: total S ratio of 17:1 and values above this indicate S deficiency. However, shortages of S may only be temporary and samples are probably best taken

towards the end of the vegetative growth period. Grain from S-deficient cereal crops generally contains <0.12% total S and a N:S ratio well above 17:1.

7. Sulphur deficiency is best prevented by application of soluble sulphate fertilizers just prior to stem extension. The amount of S required for optimum yield response under UK conditions has not been clearly defined but an application of 10 kg S/ha is currently recommended on the basis of experimental evidence todate. The efficiency of elemental S fertilizers is more variable. The amount, form and timing of S fertilizer for optimum breadmaking quality requires investigation.

8. As emissions of sulphur dioxide from industry become more rigorously controlled, S deficiency in cereals is forecast to expand both in occurrence and severity. Sulphur has become as important a nutrient as phosphorus and potassium in the nutrition of the cereal crop and continuing research effort is needed to better understand the effects of S deficiency on crop growth, grain yield and grain protein composition and provide accurate advice to the agricultural industry on its prevention and control.

9. RECOMMENDATIONS FOR FURTHER STUDY

Compared to other crop nutrients, S has been little studied and there are a number of specific aspects of the S nutrition of cereals where knowledge is lacking:

1. The relationship between crop S status, the expression of symptoms and grain yield response is poor. Uptake of S during the later stages of growth of S-deficient crops is a possible explanation. A very detailed study is required of the uptake of S (in relation to N) from various depths in the soil and its redistribution within the cereal plant during stem extension and especially grain development. Early diagnosis of S deficiency by analysis of SO_4-S in the tissue water requires some preliminary work.

2. The impact of S deficiency on the breadmaking quality of UK wheat varieties requires urgent investigation. There is a need to establish if there is link between grain S (and N:S) content and breadmaking performance under UK conditions and whether S fertilization is beneficial to protein quality even in the absence of a yield response. There is also a limited amount of evidence to indicate that late applications of N to boost grain protein levels in breadmaking wheat may not be beneficial to breadmaking quality where S is limiting and this requires further work.

3. There is no information on the effect of grain S (and N:S) content on malting quality in barley. Simple field experiments designed to provide grain from different varieties with a wide range of N and S concentrations from the same site are initially required to evaluate this in collaboration with UK maltsters.

4. As S deficiency becomes more widespread and severe, there will be a need to evaluate how much, when and in what form fertilizer S should be applied for maximum crop benefit. There has been limited opportunity in UK crops todate. The efficacy of elemental S fertilizers which have a potential residual value in UK soils and of late foliar applications of soluble sulphate to correct deficiency in the crop requires further research effort. Further research will also be required on agronomic and fertilizer practices which influence grain S content when optimum levels in terms of breadmaking quality and or malting quality have been established.

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Appendix 1. Summary of 34 experiments testing the effect of S fertilizers on grain yield (t/ha) in cereals in Scotland during 1982-1988.

A. Spring barley

Year	Site	S applied kg/ha		Yield response	Significance (2)
		Rate	Form (1)	t/ha (85% DM)	
1982	Monboddo, Kincardineshire	10	S	+0.22	NS
1983	Kincorth Estates, Morayshire	10	S	+0.27	NS
1983	Blackiemuir, Kincardineshire	10	S	+0.26	c
1984	Craibstone, Aberdeenshire	5	S	+0.18	NS
1984	Legerwood, Berwickshire	80	G	+0.18	NS
1984	Ballencrieff, East Lothian	80	G	-0.09	NS
1984	Tarrylaw, Perthshire	80	G	+0.06	NS
1984	Halls of Aberuthven, Perthshire	80	G	-0.02	NS
1984	Lacesston, Fife	80	G	_0.18	NS
1984	Boghall, Midlothian	80	G	+0.16	NS
1984	Boghall, Midiothian	80	G	+0.04	NS

B. Winter barley

Year	Site	S applied kg/ha		Yield response	Significance (2)
		Rate	Form (1)	t/ha (85% DM)	
1983	Cassieford, Morayshire	10	S	+0.12	NS
1983	Kearn, Morayshire	10	S	+0.55	c
1983	Craibstone, Aberdeenshire	10	S	+0.14	NS
1983	Oldmeldrum	10	S	-0.01	NS
1983	Ploughlands, Roxburghshire	80	G	-0.11	NS
1984	Elrick Kincardineshire	10	S	+0.03	NS
1984	Cushnie, Aberdeenshire	10	S	+0.58	c
		20	S	+0.55	c
1984	Mains of Fordoun, Kinecardineshire	10	S	+0.05	NS
		20	S	+0.05	NS
1984	Cushnie, Kincardineshire	10	S	+0.08	NS
		20	S	-0.09	NS
1984	Unthank, Morayshire	10	S	+0.29	NS
		20	S	+0.48	c

B. Winter barley (cont'd.)

Year	Site	S applied kg/ha Rate	Form (1)	Yield response t/ha (85% DM)	Significance (2)
1984	Bailliesland, Morayshire	10	S	+0.60	b
		20	S	+1.05	b
1985	Mains of Fordoun,	20	K	+0.07	NS
	Kincardineshire	20	S	-0.25	NS
1985	Unthank, Morayshire	20	K	+0.16	NS
		20	S	-0.20	NS
1985	Cushnie, Kincardineshire	20	S	+0.61	NS
1985	Uppermill, Aberdeenshire	20	S	+0.29	NS
1985	Cushnie, Aberdeenshire	5	S	+0.44	NS
1985	Wardend, Kincardineshire	5	S	+0.26	NS

C. Winter wheat

Year	Site	S applied kg/ha Rate	Form (1)	Yield response t/ha (85% DM)	Significance (a, b, c)
1984	Unthank, Morayshire	10	S	+0.22	NS
		10	S	+0.11	NS
		10	S	+0.16	NS
1984	Mosside, Aberdeenshire	10	S	+0.66	c
1984	North Mains of Turin, Forfarshire	20	S	Lodged	-
1985	Mains of Pitarrow, Kincardineshire	20	S	+0.05	NS
1985	Smiddyhowe, Aberdeenshire	20	S	+0.06	NS
1988	Brahans, Morayshire	10	SvK		NS

1. S = elemental sulphur
G = agricultural gypsum
K = potassium sulphate

2. a, P<0.001
b, P<0.01
c, P<0.05