



**PROJECT REPORT No. 142**

**DIAGNOSIS AND PREDICTION  
OF SULPHUR DEFICIENCY IN  
WINTER WHEAT AND BARLEY**

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# DIAGNOSIS AND PREDICTION OF SULPHUR DEFICIENCY IN WINTER WHEAT AND BARLEY

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## ABSTRACT

The sulphur (S) status of winter cereal crops grown at potentially S-deficient sites and their requirement for fertiliser S were assessed in a crop survey and in field experiments by soil and/or crop analysis.

In the crop survey, representative leaf and grain samples were collected from commercial winter wheat and winter barley crops at over 90 locations in England and Wales in 1992 and 1993. Concentrations of total S and sulphate-S either in just fully emerged flag leaves or in second and third leaves at anthesis were significantly related to soil type in the order sands < shallow calcareous  $\leq$  light-textured loams < heavy-textured loams, and were lowest in regions away from industrial activity, but there was no regional or soil type variation in grain S content. Leaf S concentrations were greater in wheat crops than in barley crops although not always significantly so. Similarly, S contents of wheat grain were significantly greater than of barley grain in 1992 only, when they were elevated because of small grain weights. Leaf total S and sulphate-S were significantly lower in malting varieties than in feed varieties of barley, but were not significantly different between breadmaking and feed varieties of wheat. Grain S and N:S ratio contents were generally lower in malting barley varieties and greater in breadmaking wheat varieties compared to feed varieties. There was no relationship between S or N:S ratio in leaves at anthesis and in grain at harvest, and crops which could be classified as S deficient by leaf analysis were not deficient according to grain analysis. Grain S analysis in isolation suggested an unrealistically large number of S-deficient sites and is considered unreliable for diagnosing a deficiency of S. Leaf analysis and grain N:S analysis indicated that only about 5% of sampled crops were short of S during vegetative growth.

Soil and crop samples were taken in autumn (emergence), spring (GS21-25), summer (GS39-65) and/or at harvest from 41 sites evaluating the yield response to 40 kg S/ha applied as potassium sulphate in spring during 1993-94. Grain yield responses estimated by quadrat and/or plot combine of between 4 and 18% were obtained at seven sites and increases in straw (and chaff) or in total dry matter yield of between 5 and 34% were obtained at ten sites. Straw yield responses were obtained more frequently in 1994 and, also, in the absence of grain yield responses. Similarly, grain yield responses were obtained in the absence of straw yield

responses. Distinct S deficiency symptoms were observed at one site in 1993 and seven sites in 1994. At sites showing deficiency symptoms, S application significantly reduced thousand grain weight but did not always increase grain yield. Soil extractable sulphate-S in spring and uptake of S by full flag leaf emergence stage were significantly lower in 1994 than in 1993. Differences in the ratio of N and S uptake during the growing season between 1993 and 1994 also suggested a shortage of S relative to N during early stem extension in 1994, relating to a 30% higher average winter rainfall over the 1993/94 winter compared to the 1992/93 winter. The average recovery of applied S was <10% in both years. Neither soil analysis, whole crop analysis or grain analysis could satisfactorily distinguish yield responsive sites or sites showing S deficiency symptoms. Analysis of individual leaves undertaken in 1994 indicated that yield responsive sites could best be predicted by total S and N:S ratio analysis of second and third leaves at flag leaf emergence or at anthesis, but critical values could not be reliably estimated and were different for the two growth stages. Further work is required to develop a more reliable predictive or diagnostic indicator for S deficiency in cereals.

## 1. INTRODUCTION

Sulphur (S) is an important nutrient for both crop yield and quality in agricultural crops but the need for supplementary fertiliser S in modern methods of crop production has only been recognised comparatively recently in the UK. Inputs of S from the atmosphere and supplied in fertilisers were previously considered to be adequate for crop demands, but reductions in these inputs over the last 30 years have now depleted S reserves on free draining soils to a level where S amendments are required for optimum yields (McGrath *et al.*, 1996).

Deficiency of S in winter oilseed rape has expanded rapidly in recent years, especially in England and Wales, and large yield responses to S fertiliser applications have commonly been obtained in field crops on susceptible soil types. ADAS experiments carried out between 1989 and 1991 indicated that S deficiency was also starting to appear in cereal crops in England and Wales (Withers *et al.*, 1995b) and more recent data from 1993-1994 has confirmed that cereals are susceptible to S deficiency despite their relatively low S requirement (McGrath *et al.*, 1995). A risk assessment model developed at the Institute of Arable Crops Research, Rothamsted indicated that 11% of the total UK land area is at high risk of S deficiency in cereal crops and predicts this will increase to 23% when planned reductions in industrial emissions of sulphur dioxide in Europe are achieved.

The extent to which wheat and barley differ in their susceptibility to S deficiency is not clear since yield responses have been obtained in both wheat and barley in field experiments (McGrath *et al.*, 1996). Barley is more widely grown on the light-textured soils where yield responses to S fertiliser are most frequently obtained and might therefore be more prone to deficiency. However, barley crops generally receive less N and produce less biomass than wheat crops and total S uptake will consequently be lower. Crop S requirements may be less for malting barley varieties, where low protein levels are required, although the balance between N and S in grain protein may affect the malting process (Shewry *et al.*, 1993). Similarly, crop S supply might be more critical for breadmaking wheat varieties which have been genetically manipulated to produce high protein levels in the grain. Sulphur deficient wheat grain contains fewer S-rich gluten proteins and produces a tough dough which gives rise to small crumbly loaves (Byers *et al.*, 1987a; Randall and Wrigley, 1987). Recent HGCA-



funded surveys of British wheat crops have indicated there has been a significant decline in grain S content over the period 1982-1992 (McGrath *et al.*, 1995), but there is no similar information for barley crops. This project compared by survey the S status of winter wheat and winter barley in England and Wales over a two year period.

Various parameters have been identified for the diagnosis and prediction of S deficiency in cereals (Withers and Sinclair, 1994; Zhao *et al.*, 1996), but their applicability to field crops in the UK has not been widely evaluated. Symptoms of S deficiency in cereals are not easily recognised in field crops and can be easily confused with symptoms of nitrogen (N) or trace element deficiency and/or plant stress. Also, grain yield response does not always accompany the appearance of deficiency symptoms and may occur in the absence of any visual response to S fertilisation (Withers and Sinclair, 1994). Reliable diagnosis of S deficiency is therefore needed to avoid yield losses and to ensure that S fertilisers are used efficiently and economically. Utilising an HGCA-funded series of experiments (McGrath *et al.*, 1995) undertaken to determine the effect of fertiliser S on grain yield, this project also investigated soil and crop analysis as methods for identifying the need for S fertiliser in UK cereal crops. Previous HGCA-funded research had indicated that both soil and leaf analysis was useful in diagnosing S deficiency in winter oilseed rape (Withers *et al.*, 1995a).

## 2. MATERIALS AND METHODS

### 2.1 Crop survey

A total of 375 commercial winter cereal crops in England and Wales were sampled over a two year period to determine their N and S status. A relatively large proportion of the fields selected were in areas receiving <20 kg S/ha/year from the atmosphere (information supplied by Warren Springs Laboratory, 1990) and on sandy and shallow calcareous soil types where S deficiency is most likely to occur (Withers *et al.*, 1995b). Wherever possible, wheat and barley samples were taken from the same farm to provide a good comparison and sufficient crops were sampled to ensure that winter wheat and winter barley were equally represented. A total of 193 winter cereal crops were sampled in 1992 and 182 crops in 1993.

In each year, a representative 100 g sample of second and third leaves below the ear was obtained from each field at anthesis stage - GS60-69 (Tottman, 1987) for determination of total N, total S and sulphate-S ( $\text{SO}_4\text{-S}$ ) concentrations. This sampling procedure has previously been successfully used to diagnose S deficiency in cereals (Taureau *et al.*, 1987, Withers *et al.*, 1995b). In an attempt to identify an alternative plant diagnostic parameter at an earlier growth stage, a 100 g sample of flag leaves was also taken in 1993 at full flag leaf emergence stage (GS39) and N, S and  $\text{SO}_4\text{-S}$  were similarly determined. Total N was determined by a Kjeldahl digest. Total S, present as  $\text{SO}_4\text{-S}$  after ashing with magnesium nitrate and dissolution with M hydrochloric acid, and water-soluble  $\text{SO}_4\text{-S}$  were both determined turbidimetrically after the addition of barium chloride (MAFF, 1986).

Samples of the harvested grain, together with a field history questionnaire, were provided by the farmer for about 80% of the sampled crops. Clean grain samples were dried at 80°C overnight and ground to 0.5 mm by a *Retsch* centrifugal mill. Total N was determined by a combustion method (Foss-Heraeus Macro-N) and total S was measured by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) following digestion in a carbolite heating block with  $\text{HClO}_4\text{-HNO}_3$  (Zhao *et al.*, 1994). The number of grains in an approximate 40 g sample were counted using a *Numigral* seed counter and the weight of a thousand grains (tgw) calculated to 100% DM. Grain DM content and specific weight (spw) were

simultaneously measured with a *Sinar Datatec P25* moisture analyser. The spw of wheat was corrected to 85% DM according to the equation of Pushman (1975).

Information on soil type, variety, sowing date, previous cropping, amount and timing of organic manure applications, amount of N applied and estimated crop yield were collated and grouped where necessary for ease of statistical comparison. Fields were identified as being located in northern, midlands and western, eastern, south-eastern and south-western regions of England or in Wales according to ADAS consultancy boundaries, since only small numbers of samples were collected from individual counties. Varieties were grouped into breadmaking, malting or feed categories according to recommended lists compiled annually by the National Institute of Agricultural Botany (NIAB). Soils were divided into sands, light-textured loams, heavy-textured loams and shallow (<40 cm) calcareous types on the basis of their soil texture and classification (Soil Survey of England and Wales, 1993). Sites with clay soils were included as heavy-textured loam soils. Three types of previous cropping were identified; continuous arable, grass-arable and all grass.

Mean values of measured leaf and grain concentrations were calculated and statistical comparison was made by t-test. Relationships between site, soil and crop parameters were assessed using a MINITAB spreadsheet allowing statistical analyses (MINITAB, 1993).

## **2.2 Field experiments**

The responses of winter wheat crops to fertiliser S were tested in field experiments at 21 sites around Britain in 1993 and 1994, respectively. Winter barley was grown at two sites in 1993 and only one site in 1994; winter wheat was the test crop at all other sites. Some sites were common to both years. Two treatments (nil and 40 kg S/ha) were compared in a paired plot design with 5 replicates in 1993 and 6 replicates in 1994. Sulphur was applied as potassium sulphate ( $K_2SO_4$ ) in spring (March/April) and potassium chloride was used to balance the application of K in the plots receiving no S. Both treatments received the same amount of N which was determined according to local farm practice. A locally recommended variety was used at each site and the crops received pesticides according to commercial farm practice. Two sites in 1993 were not taken to harvest due to site problems. The sites were chosen as having a high risk of S deficiency as judged by the conditions required for deficiency in

oilseed rape to occur: sandy or shallow calcareous soils in arable rotations receiving little or no livestock manure and in areas receiving <20 kg S/ha from the atmosphere (Withers *et al.*, 1995b). Site location, soil series and details of atmospheric monitoring of S inputs at each site are given in McGrath *et al.*, (1995) and are summarised in Appendix 1. Rainfall at each site was taken from the nearest meteorological station.

### **2.2.1 Soil analysis**

Soil samples representative of 0-30, 30-60 and 60-90 cm depths were taken from each plot in early winter (emergence), just prior to treatment application in the spring (GS21-25) and/or just after full flag leaf emergence (GS39-53) for the measurement of available S. Six cores were taken from each depth and bulked. Samples were air-dried prior to extraction with 0.016M potassium dihydrogen phosphate (Scott, 1981). Extracted S was measured by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The cumulative amount of S (kg/ha) in the soil profile to 90 cm depth was calculated assuming a soil bulk density of 1.33 g/cm<sup>3</sup>. The amounts of phosphate-extractable inorganic sulphate-S (SO<sub>4</sub>-S) were also measured in selected samples from either autumn or spring sampling times and representing both years using an ion chromatograph (IC) with conductivity detection (*Dionex*).

### **2.2.2 Crop analysis**

Nitrogen and S uptake by the crop were measured just before S treatment application in spring (March/April, GS 21-25), in early summer (May/June, GS 39-53) and at harvest. In spring and early summer, the plants in six 0.5 m double rows were dug up, weighed after discarding roots and their N and S contents determined (MAFF, 1986). At harvest, yields of grain, straw and chaff were estimated by threshing the plants within four 1 m<sup>2</sup> quadrats from each plot. In 1994, grain yields from each plot were also measured by plot combine. N and S contents in grain, straw and chaff, grain specific weight (spw) and thousand grain weight (tgw) were determined. Additional samples of 100 flag leaves were taken in early summer (GS39-53) for determination of total N, total S and water-soluble S. In 1994, a comparison was made of the N, S and water-soluble S in separately sampled first (flag), second and third leaves between GS39 and GS65 (anthesis) to assess the effect of sampling position on leaf N and S status. Total N in grain was determined by the Macro-N combustion method and total S

was determined by ICP-AES after digestion with fuming nitric acid and potassium nitrate (Zhao *et al.*, 1994). Soluble S in water extracts of leaf tissue was determined turbidimetrically in 1993 and by ICP-AES in 1994. All concentrations are expressed as mg/g in the dry matter. Analysis of variance and regression were performed using Genstat 5 software (Genstat 5 Committee, (1993) and MINITAB, (1993)).

### 3. RESULTS

#### 3.1 Crop survey

The range in N and S concentrations measured in second and third leaves at anthesis and in grain at harvest were very similar in 1992 and 1993. Leaf N and S concentrations in barley and wheat typically ranged from 20-50 mg/g and 1.5-4.5 mg/g, respectively (Table 1). Grain N and S concentrations typically ranged from 13-27 mg/g and from 0.9-1.7 mg/g, respectively in each year. Minimum and maximum values outside these typical ranges usually represented single crops. Significant linear relationships between N and S in the grain and in the leaves were obtained for both wheat and barley, although for leaves the relationships were poor ( $r^2$  0.1-0.2), reflecting site variation in dry matter accumulation. Estimated average yields of 6.4 and 7.3 t/ha were obtained from average applications of 143 and 188 kg N/ha for barley and wheat, respectively. There was no difference in either yield or N applied between the two years. Approximately 85% of fields were in continuous arable rotation and had not received any organic manures in the previous year. On average, winter wheat was sown 11 days later and sampled at anthesis 12 days later than winter barley in both years.

**Table 1.** Range and average concentrations of N, S, and  $SO_4$ -S in second and third leaves of winter cereals at anthesis and in their grain at harvest during 1992-93.

Determinand	No. of samples	Concentration (mg/g)			
		Range	Median	Mean	s.e.
<b>Leaves</b>					
N	366	12.9 - 51.4	34.4	34.2	0.34
S	368	1.10 - 6.30	2.80	2.82	0.035
N:S	366	5.9 - 23.5	12.3	12.6	0.16
$SO_4$ -S	366	0.50 - 3.60	1.20	1.32	0.026
$SO_4$ -S:S	366	0.20 - 0.88	0.44	0.47	0.006
<b>Grain</b>					
N	303	13.4 - 29.6	20.0	20.0	0.16
S	303	0.94 - 1.81	1.26	1.26	0.008
N:S	303	12.5 - 19.6	15.8	15.9	0.08

Concentrations of N and S in second and third leaves at anthesis were lower in barley than in wheat in 1992 but differences between wheat and barley in 1993 were not significantly

different, despite wheat crops receiving 45 kg/ha more N than barley crops (Table 2). Leaf S concentrations were also very similar between wheat and barley in 1993 when sampled at GS39. When averaged over both years, barley crops tended to show lower leaf N and S concentrations than wheat crops. Consequently there was no difference in the ratio of N:S or of SO<sub>4</sub>-S:S between wheat and barley leaves in either 1992 or 1993. When averaged across both wheat and barley, leaf N, N:S and SO<sub>4</sub>-S:S ratios were larger in 1993 compared to 1992, despite similar amounts of N being applied, but there was no difference in leaf total S concentrations between years (Table 2).

Differences in the N and S concentrations of the harvested grain between wheat and barley and between the two years showed a slightly different pattern to those in leaf N and S concentrations. Hence, grain N and S concentrations of barley were lower than in wheat in 1992, but only grain N concentration was lower in barley than in wheat in 1993 (Table 2). Consequently, grain N:S ratio was similar in both barley and wheat in 1992 but was significantly higher in wheat in 1993. Grain N concentration was lower in 1993 than in 1992 for both barley and wheat, but grain S concentration was lower in 1993 only for wheat. When averaged across both wheat and barley, grain N and S concentrations were lower in 1993 than in 1992, and when averaged across both years, they were significantly lower in barley than in wheat. Grain spw and tgw were larger in wheat than in barley, except for wheat crops in 1992, which showed a very low tgw; indeed tgw in barley was greater than in wheat in 1992. In this year, there was a significant negative relationship between grain N or S and tgw in wheat samples (grain S = 2.01 - 0.02(tgw), r<sup>2</sup> 0.41, P < 0.001, 74df), which was absent in barley crops or in wheat crops in 1993. Both crops showed larger tgw in 1993 than in 1992 but spw was larger in 1993 only for wheat crops.

From the information supplied by the farmers, malting varieties represented about 45% and 26% of barley crops sampled in 1992 and 1993, respectively and breadmaking varieties represented about 31% and 40% of wheat crops in each year, respectively. Concentrations of N, S and SO<sub>4</sub>-S in leaves at anthesis were significantly lower in malting barley crops than in feed varieties (Table 3). However, at harvest only grain N was consistently different between barley varieties with grain N:S significantly lower in samples intended for malting. Malting barley crops received 32 kg/ha less N than feed crops and had smaller grain, although grain

**Table 2.** Concentrations of N, S and SO<sub>4</sub>-S (mg/g) in leaves at anthesis and grain at harvest in barley and wheat in 1992 and 1993 and in relation to fertiliser N applied and grain yield.

Determinand	Year		Sig <sup>1</sup>	Crop			Crop					
	1992	1993		Wheat	Barley	Sig <sup>1</sup>	Wheat	Barley	Sig <sup>1</sup>			
Leaf												
N	32.9	35.5	c	35.0	33.3	b	34.5	35.6	NS	31.4 <sup>e</sup>	35.3	c
S	2.81	2.83	NS	2.91	2.73	b	2.95	2.88	NS	2.67 <sup>b</sup>	2.78	NS
N:S	12.2	13.1	b	12.5	12.7	NS	12.1	12.9	a	12.2	13.3 <sup>a</sup>	a
SO <sub>4</sub> -S	1.28	1.37	NS	1.36	1.29	NS	1.34	1.37	NS	1.21	1.37	a
SO <sub>4</sub> -S:S	0.45	0.48	b	0.46	0.47	NS	0.45	0.47	NS	0.45	0.49	a
N (kg/ha)	163	169	NS	188	143	c	186	192	NS	141 <sup>e</sup>	146 <sup>e</sup>	NS
Grain												
N	20.9	19.0	c	21.0	19.1	c	22.3	19.6	c	19.7 <sup>e</sup>	18.5 <sup>b</sup>	b
S	1.30	1.22	c	1.29	1.23	c	1.37	1.21	c	1.24 <sup>e</sup>	1.23	NS
N:S	16.1	15.6	b	16.2	15.5	c	16.3	16.2	NS	15.9	15.0 <sup>e</sup>	c
Tgw	35.0	43.6	c	39.0	39.2	NS	33.5	44.9	c	36.4 <sup>e</sup>	42.4 <sup>b</sup>	c
Spw	68.4	71.2	c	73.2	66.1	c	70.4	75.3	c	65.8 <sup>e</sup>	66.3 <sup>e</sup>	NS
Yield (t/ha)	6.9	6.8	NS	7.3	6.4	c	7.2	7.3	NS	6.6 <sup>e</sup>	6.2 <sup>e</sup>	a

1 Significance level: NS not significant, a 5%, b 1%, c 0.1%.

2 Significance level between crops within each year: a 5%, b 1%, c 0.1%.



yield and spw were not significantly different (Table 3). In contrast to barley, both feed and breadmaking wheat varieties contained similar S and SO<sub>4</sub>-S concentrations at anthesis. Leaf N concentrations were lower in breadmaking varieties in 1992 but the difference was relatively small averaged across the two years. Contents of N and S tended to be greater in breadmaking wheat than in feed wheat with only small additions of fertiliser N and had a greater specific weight (Table 3), although differences in grain S were statistically significant only in 1992. The increase in N was slightly greater than the increase in S, causing a slightly higher N:S ratio in breadmaking wheat varieties but the differences were small. Grain S in malting varieties was less than in feed varieties but the differences was not always significant at the 5% level (Table 3).

**Table 3.** Differences in N, S and SO<sub>4</sub>-S concentrations (mg/g) in leaves at anthesis and in grain at harvest between feed varieties of barley and wheat and varieties grown for malting or breadmaking and in relation to fertiliser N applied and grain yield.

Determinand	Barley			Wheat		
	Feed	Malting	Sig. <sup>1</sup>	Feed	Breadmaking	Sig. <sup>1</sup>
<b>Leaf</b>						
N	34.6	29.5	c	35.6	33.0	c
S	2.90	2.45	c	2.90	2.85	NS
N:S	12.5	12.5	NS	12.8	12.1	NS
SO <sub>4</sub> -S	1.36	1.14	b	1.35	1.31	NS
SO <sub>4</sub> -S:S	0.47	0.47	NS	0.46	0.46	NS
N (kg/ha)	158	126	c	185	194	NS
<b>Grain</b>						
N	19.8	17.8	c	20.6	22.3	c
S	1.25	1.21	NS	1.28	1.35	b
N:S	15.9	14.7	c	16.1	16.5	a
Tgw	40.8	35.8	c	39.4	37.6	NS
Spw	66.4	66.4	NS	71.5	76.6	c
Yield (t/ha)	6.4	6.3	NS	7.4	7.1	NS

<sup>1</sup> Significance level: NS not significant, a 5%, b 1% and c 0.1%.

**Table 4.** *The percentage of winter wheat and winter barley crops sampled and average concentrations of N and S in leaves at anthesis and in grain at harvest within each region.*

Region	No. of crops sampled	Winter barley		Winter wheat		Concentration (mg/g)							
		1992 % of crops	1993 % of crops	1992 % of crops	1993 % of crops	Leaves		Grain		Grain			
						N	S	N:S	SO <sub>4</sub> -S	SO <sub>4</sub> -S:S	N	S	N:S
Northern	69	16	23	16	19	36.1	2.97	12.7	1.48	0.50	20.0	1.23	16.2
Midlands and Western	53	15	14	13	15	35.8	3.29	11.2	1.50	0.45	20.3	1.29	15.8
Eastern	78	23	17	24	19	30.9	2.54	12.7	1.43	0.56	19.6	1.27	15.4
South-eastern	90	24	24	24	25	34.9	2.93	12.3	1.30	0.44	20.3	1.27	16.0
South-western	71	19	19	19	19	33.6	2.50	13.8	0.99	0.39	19.8	1.25	15.8
Wales	14	4	3	4	3	35.0	2.74	13.3	1.20	0.43	20.0	1.24	16.1
Significance <sup>1</sup>						c	c	c	c	c	NS	NS	a

<sup>1</sup> Significance level: NS not significant, a 5%, b 1% and c 0.1%.

### *3.1.1 Site variation*

The numbers of winter wheat and winter barley crops sampled within each region is shown in Table 4. Slightly fewer samples were taken in Eastern region and slightly more samples were taken in Northern England in 1993 compared to 1992, but otherwise very similar numbers of wheat and barley crops were taken from each region in both 1992 and 1993. Leaf S concentrations at anthesis were smallest in samples from south-west England and greatest in samples from midlands and western region (Table 4). Leaf N:S ratios were correspondingly largest and smallest from these two regions, respectively. This was a generally consistent effect for both crops and across both years. In eastern region, both leaf N and S concentrations were low, especially in barley crops which received significantly smaller average amounts of fertiliser N (122 kg/ha) compared to other regions (144-163 kg/ha), reflecting a greater proportion of malting varieties on light soils in eastern region.

Leaf SO<sub>4</sub>-S concentrations were lowest in south-west England and highest in midlands and western region only in 1992. In 1993, samples from northern and eastern England contained the most SO<sub>4</sub>-S and the ratio of SO<sub>4</sub>-S:S was consequently significantly greater in these two regions compared to other areas (Table 4). When averaged across both crops and years, there were no statistically significant regional differences in N or S content in the grain. Small differences within individual crops or years were obtained but these were not consistent and only small differences were obtained in the grain N:S ratio between regions (Table 4). Grain yields were not significantly different between the regions.

The majority of crops sampled were on light-textured loam and shallow calcareous soil groups but other soil types were also reasonably well represented (Table 5). A larger number of crops on sand and shallow calcareous soils, and correspondingly fewer crops on heavy-textured loam soils, were sampled in 1993 compared to 1992, especially for winter wheat. There was a highly significant effect of soil type on leaf S but not on grain S content. Concentrations of S and SO<sub>4</sub>-S in leaves at anthesis increased in the order sands < shallow calcareous ≤ light loams < heavy loams and leaf N:S ratio decreased in the same order (Table 5). This was a consistent effect except for wheat crops in 1993. There was no similar effect of soil type on grain S

**Table 5.** The percentage of winter wheat and winter barley crops sampled and the average concentrations of N and S in leaves at anthesis and in grain at harvest on different soil types.

Soil type	No. of crops sampled	Winter barley		Winter wheat		Concentration (mg/g)							
		% of crops		% of crops		Leaves			Grain				
		1992	1993	1992	1993	N	S	N:S	SO <sub>4</sub> -S	SO <sub>4</sub> -S:S	N	S	N:S
Sand	58	15	17	10	20	32.8	2.52	13.6	1.21	0.48	19.6	1.24	15.8
Light loam	130	33	35	36	35	34.9	2.85	12.7	1.34	0.47	20.1	1.25	16.0
Heavy loam	77	23	17	27	15	34.6	3.08	11.8	1.45	0.47	20.5	1.29	15.9
Shallow calcareous	110	29	31	27	30	33.7	2.76	12.6	1.28	0.48	19.9	1.27	15.7
Significance <sup>1</sup>						NS	c	a	a	NS	NS	NS	NS

<sup>1</sup> Significance level: NS not significant, a 5%, b 1% and c 0.1%.

content, except for barley crops in 1993 which showed low grain S concentrations on sandy soils. Small but significant differences between soil groups were measured in grain spw, with highest values on sandy soils and lowest values on heavy-textured loam soils. Amounts of fertiliser N applied and grain yields were similar across all soil groups.

### 3.1.2 Effect of sampling time

There was no significant difference in average leaf N and S concentrations between wheat and barley in 1993, either when sampled at GS39 or at GS65, except for a slight increase in leaf N in barley at GS 39 compared to wheat (Table 2); differences between sampling periods are therefore averaged across both crops. Average values of leaf N and N:S were larger and leaf SO<sub>4</sub>-S and SO<sub>4</sub>-S:S lower in samples taken at GS39 than in samples taken at GS65, but leaf total S concentrations were not significantly different (Table 6). Significant but poor positive linear relationships ( $r^2$  0.3) were obtained for both N and S between the two sampling periods, which were, on average, 18 days apart. The relationships for leaf total S was GS39 = 1.36 + 0.499 (GS65) and for N:S ratio was GS39 = 8.74 + 0.512 (GS65).

**Table 6.** Differences in the concentration of N, S and SO<sub>4</sub>-S (mg/g) in flag leaves at GS39 and in second and third leaves at GS65.

Parameter	GS39		GS65		Sig. <sup>1</sup>
	Mean	s.e.	Mean	s.e.	
N	41.7	0.04	35.5	0.05	c
S	2.77	0.005	2.83	0.005	NS
N:S	15.5	0.23	13.1	0.25	c
SO <sub>4</sub> -S	1.15	0.003	1.37	0.004	c
SO <sub>4</sub> -S:S	0.41	0.009	0.48	0.010	c

<sup>1</sup> Significance level: NS not significant, a 5%, b 1% and c 0.1%.

### 3.1.3 Extent of sulphur deficiency

The proportions of crops which could be classed as S deficient by either leaf analysis at anthesis or by grain analysis after harvest are summarised in Table 7. In isolation, leaf S, N:S and grain N:S diagnosed relatively small numbers of deficient crops (<15%) within individual years but grain S analysis suggested a much higher proportion of deficient crops, except for

wheat in 1992. There was no significant relationship between grain S and grain N:S ratio, but there was such a relationship between S and N:S in leaves at anthesis ( $r^2$  0.45). Also there was an almost total lack of agreement between the two methods of diagnosis. Hence, crops which were classified as deficient by leaf analysis were not deficient according to grain analysis. The numbers of crops classified as deficient by having both low S and high N:S ratio were very low. However, both methods indicated that almost all of S deficient crops were on sand, shallow calcareous and light loam soils in areas receiving small amounts of S from the atmosphere, especially East Anglia, north Northumberland and counties in southern and south-west England.

**Table 7.** Percentage of barley and wheat crops exceeding critical S and N:S values<sup>1</sup> in leaves at anthesis and in grain at harvest in 1992 and 1993.

Crop/Year	Leaves			Grain		
	S < 2 mg/g	N:S > 17:1	Both criteria	S < 1.2 mg/g	N:S > 17:1	Both criteria
Barley 1992	12	7	2	25	11	3
Barley 1993	12	15	7	21	5	4
Wheat 1992	4	1	0	8	8	0
Wheat 1993	9	7	5	35	11	8

<sup>1</sup> Critical values for S and N:S were taken as < 2.0 mg/g (Taureau *et al.*, 1987) and  $\geq 17.5:1$  (Withers *et al.*, 1995b) in leaves, respectively and as < 1.150 mg/g and  $\geq 17.5:1$  (Randall *et al.*, 1981) in grain, respectively. If critical values for S and N:S ratio were taken as 1.20 and 17.0, the number of deficient grain samples increased dramatically.

### 3.2 Field experiments

#### 3.2.1 Yield response

Grain yield response estimated by quadrats in 1993 and by plot combine in 1994 are detailed in McGrath *et al.* (1995). These data are summarised in Appendix 1 together with quadrat yield estimates in 1994, which have not been previously reported. Significant ( $P < 0.05$ ) increases in grain yield to applied S fertiliser were obtained at 3 sites in 1993 (Langston, Shifnal, and Elrick) and at 1 site in 1994 (Eastleach). In 1994, significant increases in grain yield assessed by plot combine were also obtained at Bridgets, Wimborne, and Fakenham, but

increases in grain yield assessed by quadrats at these three sites were either much smaller (Bridgets) or statistically significant at only the 10% level. At one site in 1993 (Garblies) and at two sites in 1994 (Clibburn and Borders), the S treatment significantly reduced quadrat grain yields but not combine grain yields (1994 only). Maximum yield increases obtained either by quadrat or plot combine at responsive sites ranged from 0.29-0.77 t/ha or 4-18%. Similar or greater grain yield responses from applied S at other sites were not statistically significant (Appendix 1) because of the generally large variability in quadrat estimates within and between plots.

Statistically significant increases in straw (plus chaff) yields were obtained at 3 sites in 1993 (Stetchworth, Gupton and Langston) and 7 sites in 1994 (Kennington, Eastleach, Wimborne, Sidmouth, Fakenham, Clibburn, and Woburn). The responses ranged from 0.4-2.0 t/ha or 5-34%. At Sidmouth, Clibburn and Woburn in 1994, the increases in straw yield were large (>1 t/ha) and sufficient to significantly ( $P < 0.05$ ) reduce the crop harvest index. There was no significant effect of the S treatment on harvest index at other sites. Visible colour differences between treated and untreated plots were observed at most of the sites showing a significant S effect on straw yield in 1994, but were generally absent in 1993 with the exception of Woburn. Sites in 1994 which showed the most distinctive colour differences between plots gave the largest increases in straw yields but no significant grain yield response (ie Woburn, Clibburn, Kennington and Sidmouth). At these sites, the colour differences were observed at the start of stem extension and disappeared by GS65. At Bridgets and Fakenham, which gave significant increases in grain yield by plot combine, colour differences were still evident at GS65. At Shifnal in 1994, distinct colour differences were observed between plots, but without either straw or grain yield response and at Eastleach, the significant yield response was obtained without any apparent deficiency symptoms.

Where colour differences were observed, young fully expanded leaves on untreated plots looked pale green or yellow compared to the darker green leaves on S-treated plots. Total S and N:S concentrations in affected leaves ranged from 1.5-2.5 mg/g and were  $\geq 16:1$ , respectively. Transient colour differences were also noted at other sites. At Sessay in 1993 and Sessay, Wimborne and Hempstead in 1994, yellowing or necrosis of leaf tips was more prevalent on some untreated plots, but this was judged to be due to stress effects rather than

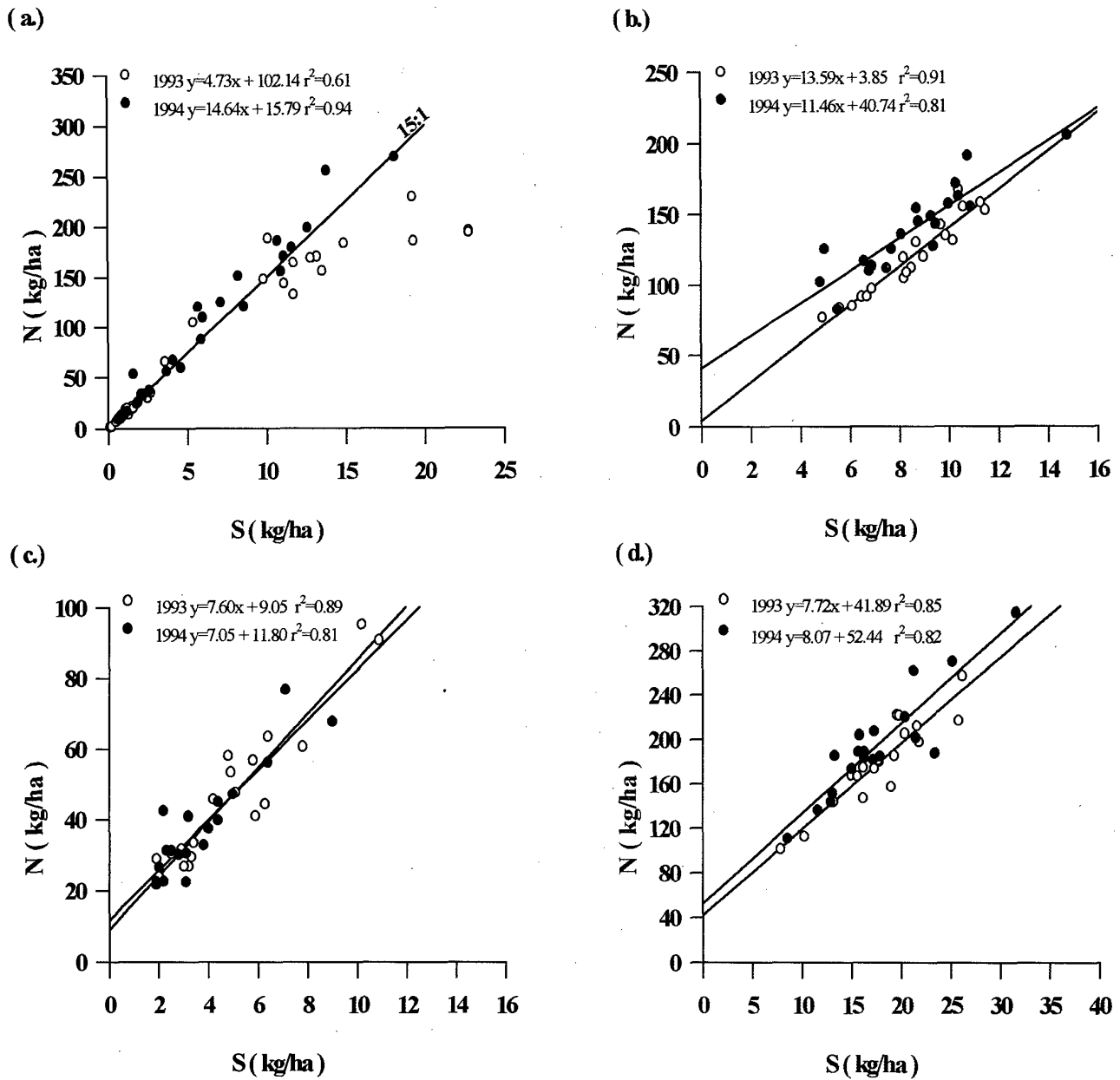
solely S deficiency on the basis that the whole leaf was not affected or that only a few plots showed colour changes. Sulphur application significantly reduced *tgw* at all sites showing colour differences in 1994 and at Eastleach. These reductions in *tgw* were large (10%) and generally accompanied by reductions in grain *spw*, but this was by no means consistent. This suggests that S application increased yield by increasing tiller numbers or the number of grains per ear, the former being consistent with increased straw yields. There was no effect of S on grain *tgw* or *spw* in 1993, when distinct colour differences were absent (the plots at Woburn were not harvested).

### ***3.2.2 Crop uptake***

Amounts of N and S measured in the above-ground crop on control (nil S) treated plots during the growing season are shown in Fig. 1. Uptake of N and S was significantly correlated on each sampling occasion but the slope of the regression varied through the growing season and between years. Prior to the application of the S treatments in spring, N and S was taken up at a ratio of 15:1 with no difference between years (Fig 1a). Uptake of S during this period varied from < 1 to 6 kg/ha (mean 1.8 kg/ha) depending on dry matter accumulation over the winter. Most crops were sampled in early March but at some sites, samples were taken in April when considerably more growth had occurred. At one site (Lydeard St Lawrence) there was insufficient growth to take a sample.

When the crop was sampled in May/June, there was a clear difference in the ratio of N and S uptake on control (nil S) plots between 1993 (10:1) and 1994 (16:1), Fig. 1a. Average uptake of S by crops at this stage in 1993 was 14.2 kg/ha (range 5-23 kg/ha) but was significantly lower at 9.1 kg/ha (range 2-18 kg/ha) in 1994. Average crop dry matter (DM) production and uptake of N were also lower in 1994 than in 1993 because the median crop sampling date was 12 days later in 1993 (8 June) than in 1994 (27 May), although the differences were not significant (Table 8). Application of S increased the uptake of S in May/June at all sites except Flodden in 1993, where the nil S plots became contaminated with S applied by the farmer. The average increase in S uptake on S-treated plots was 5.5 kg/ha (ranging up to 14.4 kg/ha), but the significant difference in S uptake between 1993 and 1994 was maintained on S-treated plots at approximately 5 kg/ha. At three sites in 1994 (Wimborne, Sidmouth and Woburn), N





**Figure 1.** Uptake of N and S by cereal crops without fertilizer S in 1993 and 1994 up to May/June (a) and in grain (b), straw (c) and in total (d) at harvest. Drawn lines represent a fixed N:S ratio in (a) and regression fits in (b-d).

uptake in May/June was also significantly increased (+20, 15 and 35 kg/ha, respectively) on S-treated plots, but there was no effect of S on N uptake at other sites.

At harvest, the difference in the ratio of N and S uptake in straw between 1993 and 1994 on nil S plots was less apparent (Fig. 1c) but was still statistically significant for the grain and total crop. However the greater ratio of N:S uptake in the grain in 1994 was not due to a lower grain S offtake but because of greater N uptake in 1994 compared to 1993 (Table 8). There was no significant difference in the offtake of N or S in straw (and chaff) between 1993 and 1994. Total S removal at harvest averaged 14 kg/ha (range of 7-23 kg/ha) on untreated plots and 17 kg/ha (range 8-32 kg/ha) where S was applied. Application of S increased total S removal at harvest at all but one site, although this was not always statistically significant. Removal of N was significantly increased on S-treated plots at Stetchworth in 1993 and at Eastleach and Woburn in 1994. There was an apparent decrease in both N and S uptake at harvest at the Borders site in 1994.

**Table 8.** Mean uptake (kg/ha) of N and S by cereal crops without added S in 1993 and 1994 at each sampling date.

Sampling date	1993	1994	Significance <sup>1</sup>
Spring (March/April)			
N	20.5	30.7	NS
S	1.4	2.2	NS
Summer (May/June)			
N	169.2	151.6	NS
S	14.2	9.1	b
Harvest			
N (grain)	119.2	139.2	a
S	8.5	8.6	NS
N (straw + chaff)	58.9	51.1	NS
S	6.2	4.9	NS
N (total)	178.1	190.0	NS
S	14.7	13.4	NS

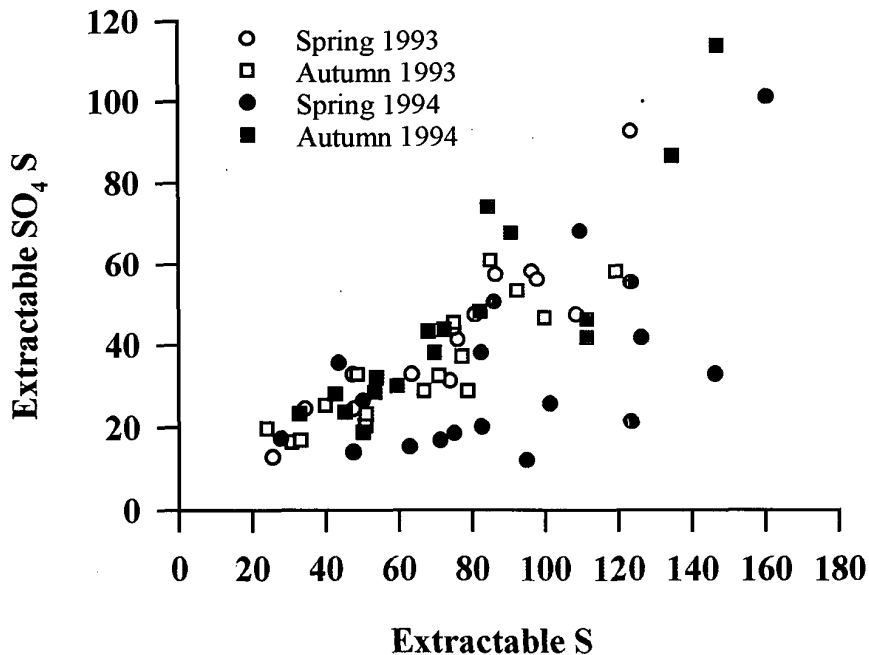
<sup>1</sup> Significance level: NS not significant, a 5%, b 1% and c 0.1%.

Sulphur application reduced the sulphur harvest index (SHI - the proportion of the total S uptake at harvest in the grain) from 65% to 55% but had no effect on the N harvest index. This effect was consistent, but not always significant, across all sites except for some sites in Scotland (Elrick in 1993, Kildrummie and Borders in 1994) where there was no effect. SHI was also significantly greater in 1994 than in 1993 reflecting better assimilation of S in the grain in the generally higher yielding crops in 1994. The recoveries of fertiliser S by the crops at harvest were generally very low (range -5% to 35%, median 7.2%, mean 9.3%, s.e. 1.11) in both years. Sites showing the largest recoveries (>10%) were those where a yield response was obtained and/or where deficiency symptoms were seen.

### **3.2.3 Soil sulphur**

Concentrations of extractable S in the soil on untreated plots typically ranged from 2-15 mg/kg in both 1993 and 1994. The S was uniformly distributed through the soil profile to 90 cm depth except at two sites (Penallt in 1993 and Kildrummie in 1994), which showed a two-fold increase in extractable S below 30 cm depth associated with heavier-textured subsoils. Also, at Sessay in 1994, plot differences in soil S between 60 and 90 cm depth were significantly related to the variable amounts of clay within this horizon (soil S = 0.168 (% clay) + 7.15,  $r^2$  0.57,  $p < 0.001$ , , 37 df). Over 70% of the sites contained < 10 mg S/kg of soil averaged over 0-90 cm depth in both autumn and spring. Flodden in 1993 contained 19 mg S/kg in autumn but this site subsequently became contaminated with fertiliser S and is omitted from the analysis. Concentrations of extractable-SO<sub>4</sub>-S determined on selected samples by IC (Dionex) ranged from < 1 - 10 mg/kg in both autumn and spring (Figure 2).

Differences in the amounts of extractable SO<sub>4</sub>-S and S in the soil between autumn and spring varied between sites and between the two years. In 1993, soil SO<sub>4</sub>-S and S contents were very similar between autumn and spring but in 1994, significantly lower amounts of SO<sub>4</sub>-S and greater amounts of S were measured in spring than in autumn (Fig. 2). In spring 1994, inorganic sulphate-S represented < 40% of the total extractable S content in the soil profile, whilst at other sampling times in both 1993 and 1994, 50-60% of extractable S was present as sulphate-S.



**Figure 2.** Average amounts (kg/ha) of extractable  $SO_4$ -S (Dinoex) and S (ICP-AES) in the soil to 90 cm depth on nil S treated plots in autumn and spring in 1993 and 1994.

Differences in soil extractable S content to 90 cm, or to the sampling depth for shallower soils over rock, on untreated plots between March and May/June sampling dates ranged from -58.9 to +20.3 kg/ha (mean -14.3 kg/ha) in 1993 and -101.2 to + 5.8 kg/ha (mean -35.1 kg/ha) in 1994. The mean difference between the two years was significant at the 10% level ( $P=0.06$ ). Balance sheet calculations on a limited number of sites showed that the loss in soil S between these two sampling dates in 1993 was equivalent to the amount of S taken up by the crop (Table 9).

**Table 9.** Balance sheet for S in autumn, spring and summer (May/June) on untreated and S-treated plots averaged across sites in 1993 and 1994.

Sampling date	S balance sheet (kg/ha)			
	1993		1994	
	Nil S	40 kg S/ha	Nil S	40 kg S/ha
Autumn soil S		70 (19) <sup>1</sup>		77 (18)
Spring soil S		72 (20)		87 (19)
Spring crop S		1 (20)		2 (17)
Spring-Autumn (mineralised soil S over winter)		+3 (18)		+13 (17)
Summer soil S	53 (12)	77 (12)	58 (16)	92 (16)
Summer crop S	14 (14)	20 (14)	9 (15)	14 (15)
Summer-spring (mineralised soil S over early summer)	-3 (10)	+30 (10)	-22 (10)	+16 (10)
Overall balance (Amount of the applied S (40 kg/ha) in soil and crop)		33 (10)		38 (10)
Unaccounted		-7 (10)		-2 (10)

<sup>1</sup> Figures in parenthesis indicate number of sites with available data for calculating means.

However, in 1994, an average of 21.5 kg S/ha was lost from the soil profile during this period. Net balances of S on untreated plots over this period ranged from -71.9 to +28.9 (mean -12.5, median -3.7) at 20 sites where it was possible to estimate. Only a small number of sites showed any net mineralisation in either 1993 or 1994. Changes in the soil S content to 90 cm depth and uptake by the crop at GS39 accounted for over 90% of the fertiliser S applied, when averaged across sites. Soil extractable S concentrations significantly increased in the 0-30 and 30-60 cm horizons on S-treated plots, but there was no difference in soil S at 60-90 cm depth.

### 3.2.4 Effect of sampling stage and leaf sampling position

Highly significant interactions in leaf N and S concentrations were observed between sampling stage and leaf sampling position but concentrations of water-soluble S remained constant

(Table 10). Changes in leaf N were large relative to S, causing significant differences in the leaf N:S ratio. Concentrations of N in all leaves were lower when sampled at GS39 than at GS65, but reductions in S between the two sampling dates were significant only in the second and third leaves. The reductions in S in second and third leaves between GS39 and GS65 were much smaller than for leaf N, and leaf N:S ratio was correspondingly larger at GS39. At GS39, N was greater in second and third leaves than in the flag leaf (leaf 1) but leaf S was similar in all leaves. At GS65, leaf N and S were sequentially lower from leaf 1 to leaf 3 with relatively small differences in the leaf N:S ratio.

**Table 10.** Mean concentrations (mg/g) of N and S and water-soluble S (WSS) in individual leaves from nil S treated plots at GS39 and GS65 for 19 sites (18 winter wheat sites and 1 winter barley site) in 1994.

Determinand	GS39			GS65			SED <sup>1</sup>
	Leaf 1	Leaf 2	Leaf 3	Leaf 1	Leaf 2	Leaf 3	
N	40.0	44.5	42.4	36.9	32.5	27.0	0.96
S	2.63	2.64	2.60	2.55	2.32	2.14	0.104
N:S	15.8	17.7	17.7	15.3	14.9	13.8	0.61
WSS	1.05	0.97	1.13	1.06	1.09	1.16	0.104
WSS:S	0.39	0.36	0.42	0.41	0.46	0.53	0.035

<sup>1</sup> SED values are for the interaction between sampling stage and leaf position.

### 3.2.5 Prediction of yield response

Increases in yields were obtained at too few sites and were generally too small to demonstrate any clear relationship between yield response and the measured soil and crop parameters. Sites were therefore classified as either responsive or non-responsive; responsive sites were defined as those where a significant (P= 5%) response in either the yield of grain, straw (and chaff) or in total was obtained. The few sites which showed colour differences but without response were judged to be non-responsive. On this basis, there were 5 responsive sites in 1993 and 8 responsive sites in 1994. Differences in potentially predictive soil or diagnostic crop parameters between responsive and non-responsive sites were then assessed statistically (Table 11).

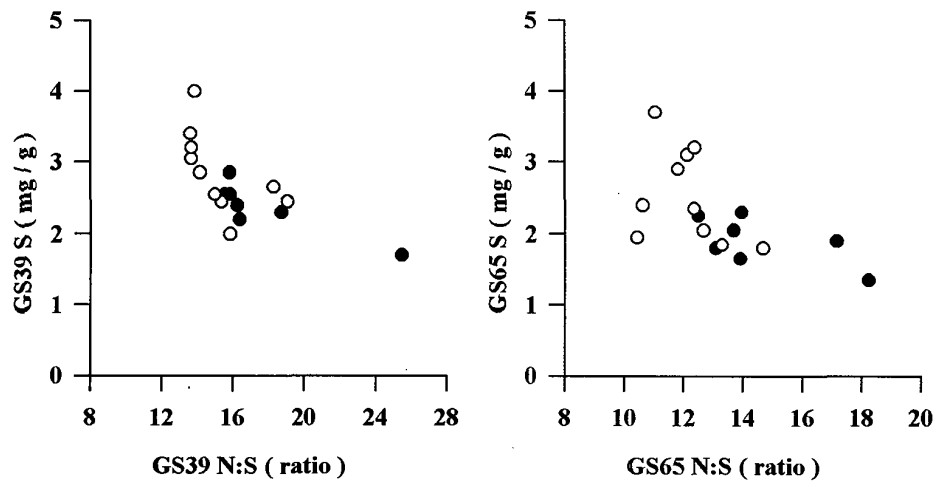
**Table 11.** Prediction and diagnosis of yield responsive sites to fertiliser S by soil and plant analysis.

Soil /plant analysis	Responsive	Non-responsive	Significance <sup>1</sup>
<i>Soil analysis</i>			
Soil SO <sub>4</sub> -S to 90 cm in spring (kg/ha)	31	39	NS
Soil S to 90 cm in spring (kg/ha)	71	72	NS
<i>Crop analysis</i>			
Whole crop S in spring (GS 21-25) - mg/g	3.13	3.15	NS
Whole crop N:S in spring (GS 21-25) - ratio	14.0	15.5	0.06
Whole crop S in summer (GS39-53) - mg/g	1.57	1.64	NS
Whole crop N:S in summer (GS39-53) - ratio	17.2	13.9	0.06
<i>Leaf analysis (1994 only)</i>			
Flag leaf S at GS39 - mg/g	2.47	2.70	NS
Flag leaf N:S at GS39 -ratio	17.2	14.8	NS
2nd/3rd leaf S at GS39 - mg/g	2.23	2.83	0.03
2nd/3rd leaf N:S at GS39 - ratio	20.7	15.2	0.08
Flag leaf S at GS65 - mg/g	2.50	2.78	NS
Flag leaf N:S at GS65 - ratio	14.5	13.2	NS
2nd/3rd leaf S at GS65 - mg/g	1.90	2.52	0.02
2nd/3rd leaf N:S at GS65 - ratio	14.7	12.2	0.01
Grain S - mg/g	1.22	1.26	NS
Grain N:S ratio	16.0	15.1	NS

<sup>1</sup> Significance level: NS not significant at the 10% level, otherwise P value shown.

There was no difference in soil S, whole crop S or grain S content between yield responsive and non-responsive sites. Whole crop N:S ratio at GS39-53 was notably higher at sites with yield responses but this was significant only at the 10% level. Many responsive sites showed low levels of soil extractable sulphate in spring, lower crop S or grain S concentrations but there were also a large number of sites with similarly low levels which did not respond. Two sites with extractable SO<sub>4</sub>-S levels above 10 mg/kg (Plympton and Elrick in 1993) apparently responded to applied S.

In 1994, responsive sites showed significantly lower total S concentrations and greater N:S ratios in second and third leaves sampled either at GS39 or GS65 compared to non-responsive sites (Fig. 3). However, concentrations of S in flag leaves were similar at both growth stages and were not related to crop S content (kg/ha). There was only a poor linear relationship ( $r^2$  0.2) between flag leaf S or N:S at GS39 and at GS65, but S or N:S in second and third leaves was well correlated between the two sampling dates ( $r^2$  0.7). There was also no relationship between crop S content in early Spring and crop S content at either GS 39 or at harvest. Crop S content at GS39 was weakly ( $r^2$  0.3) related to S removal in straw and to total S removal at harvest, but there was no such relationship with grain S removal.



**Figure 3.** Total S and N:S ratio in second and third leaves at yield responsive (●) and non-yield responsive (○) sites sampled at GS39 and GS65 in 1994.

Sites were also classified as S deficient according to whether S deficiency symptoms were observed or not. On this basis, there was only one deficient site in 1993 but 7 deficient sites in 1994. Statistical analysis indicated that sites showing symptoms showed significantly ( $P < 0.001$ ) greater N:S ratios in whole crop at GS 39 and in grain at harvest compared with sites which were not deficient. Total S and N:S in second and third leaves at GS65 was also



selective to a lesser degree and soil extractable sulphate levels were also significantly lower (18 kg/ha) on deficient sites than on sites which did not show symptoms (41 kg/ha). However, these diagnostic parameters could not distinguish between sites sufficiently to indicate a critical threshold value. Neither soil extractable S nor grain analysis could distinguish sites showing S deficiency symptoms.

## 4. DISCUSSION

### 4.1 Crop survey

Although the number of crops sampled was not large in relation to the area of winter cereals grown in England and Wales, the survey provides an opportunity to examine the variation in crop S status between winter barley and winter wheat in areas and soil types where a deficiency of S might be expected based on previous work on oilseed rape (Withers *et al.*, 1995a). Regional effects on leaf S were consistent with differences in the amounts of S deposited from the atmosphere, being smaller in remote rural areas (south-west England) and greater in the more industrial areas of the Midlands. However, crops in northern England were not found to be particularly low in S, despite a relatively high number of samples from Northumberland where deficiency has been observed in oilseed rape (McGrath *et al.*, 1996). The higher leaf SO<sub>4</sub>-S concentrations measured in Eastern England in 1993 suggest larger rates of dry deposition of S in 1993 than in 1992. Dry deposition of sulphur dioxide is the major source of atmospheric S to crops, especially in areas with low rainfall (Campbell and Smith, 1996). However, amounts of dry deposition measured at the field experimental sites in 1993 were not unusually high as compared to 1994 (McGrath *et al.*, 1995) indicating that 1993 was a normal year. Leaf S and SO<sub>4</sub>-S concentrations increased in the order sands < shallow calcareous ≤ light loams < heavy loams reflecting the ability of these soil groups to retain sufficient soluble sulphate to meet crop requirements (Syers *et al.*, 1987). Sand and shallow chalk soils are also the soil types on which yield responses to applied S fertiliser have been most frequently obtained in the UK (McGrath *et al.*, 1996). However, there were no consistent regional or soil type differences in grain S content, although variation in the geographical distribution of grain S has been previously observed in wheat surveys (Byers *et al.*, 1987b; McGrath *et al.*, 1995). This suggests that leaf analysis may be a more sensitive indicator of crop S supply during the growing season than grain analysis after harvest.

Leaf and grain analysis indicated differences in crop N and S status between wheat and barley which were not always consistent within each year. General trends in leaf S averaged across years appeared to be related to crop N supply. Hence, wheat crops contained greater leaf N and S concentrations than barley crops which received, on average, 45 kg/ha less N. Similarly, malting varieties, which received about 30 kg/ha less N than feed varieties, contained smaller

concentrations of N, S and SO<sub>4</sub>-S in their leaves at anthesis, whilst there was no significant difference in leaf N and S concentrations between breadmaking and feed varieties of wheat, which received similar amounts of N fertiliser. Apparently lower leaf N contents in breadmaking wheat crops in 1992 probably reflects late application of foliar-applied N. As the amounts of N applied were very similar in 1992 and 1993, differences in leaf N and S between years were most probably due to differences in the proportions of malting and breadmaking wheat crops sampled in each year and /or the proportion of crops on sandy soils. Hence lower leaf N and S concentrations in barley crops in 1992 compared to 1993 reflects the larger proportion of barley crops grown for malting and on sandy soils sampled in 1992, especially in eastern region. Similarly, this may account for the lack of a difference in leaf N and S between wheat and barley crops in 1993, when the proportion of breadmaking wheat varieties, which showed similar N and S concentrations to feed varieties, was greater and the proportion of wheat crops on sandy soils doubled compared to 1992.

There was no significant relationship between leaf N or S content at anthesis and grain N or S content at harvest for either barley or wheat in either year. Hence, grain S concentrations in barley were not significantly different between malting and feed varieties, despite the large differences in leaf S content. Similarly, concentrations of N and S were generally greater in breadmaking wheat grain than in feed wheat grain, despite little difference in leaf concentrations between the two variety types. Although breadmaking wheat crops represented a greater proportion of sampled crops in 1993, grain N and S content was significantly lower in 1993 than in 1992. Many of the grain samples received in 1992 were small in size, resulting in very low tgw and spw and high concentrations of N and S. In particular, elevated levels of grain S in breadmaking wheat in 1992 were associated with very low tgw (30 g) compared to feed varieties. In contrast, wheat tgw and spw was much larger in 1993 resulting in significantly lower grain N and S contents in that year. The significant negative relationship obtained between grain N or S content and tgw in wheat is consistent with the effect of smaller grain size in concentrating grain protein content and the data indicate that environmental conditions during grainfill may have a large influence on grain S concentrations within individual years. The lack of a similar relationship for barley grain can be explained by the limited scope for changes in grain weight in a closed ear. The larger tgw in barley grain in 1993 compared to 1992 was probably due to the greater proportion of feed varieties sampled

in that year, since feed barley showed consistently higher *tgw* than malting varieties. There was no such difference in *tgw* between wheat varieties.

Differences in leaf N and S concentrations between flag leaves at GS39 and second and third leaves at GS65 are similar to those found by Rasmussen *et al.* (1977), and reflect the greater loss of N relative to S from the crop towards the end of the vegetative growth period. The relative constancy of leaf S, especially for the flag leaves over the two sampling dates, suggests this may be a better indicator of crop S status than N:S ratio if the sampling stage cannot be precisely identified. The regression equations indicate that values of total S and N:S in flag leaves at GS39 corresponding to critical values for S deficiency of 2.0 mg S g<sup>-1</sup> (Taureau *et al.*, 1987) and 17:1 N:S ratio (Withers *et al.*, 1995b) at GS 65 were 2.4 mg S/g and 17.4:1, respectively. This survey casts doubt on the usefulness of the critical threshold values defined by Randall *et al.* (1981) for grain S analysis (1.2 mg/g) to predict the need for S fertilisers to prevent yield loss. Grain S content was not sensitive to differences in S supply in different regions or on different soil types, as defined by leaf S status, and suggested unrealistically large numbers of deficient crops, except in 1992 when wheat grain was elevated because of low grain weights. Withers *et al.* (1995) found that a critical grain S threshold for barley crops showing a yield response to fertiliser S was nearer to 1 mg/g than 1.2 mg/g. Using this criterion, only 2% of crops were short of S. Grain N:S ratio was much more selective than grain S, as was found by Zhao *et al.* (1996) in a pot experiment with winter wheat, but sites diagnosed as deficient by leaf analysis still did not agree with those diagnosed as deficient by grain N:S ratios.

To what extent barley crops are more likely to show S deficiency than wheat crops is therefore not clear because not only do currently used critical threshold values not agree well, but they may be different for wheat and barley and between varieties, depending on the criteria by which the crop is judged. Currently farmers are not paid according to grain S content and so quality effects induced by S shortage are not penalised. Judged on yield considerations alone, leaf analysis indicated that barley crops may be more likely to show S deficiency than wheat crops and that a slightly greater number of crops were short of S in 1993 than in 1992. This may be at least partly explained by the proportion of crops grown on sand soils, which was

greater in barley than in wheat in 1992, and greater in 1993 than in 1992. This suggests that the level of N applied is less important than site in determining crop S supply.

#### **4.2 Field experiments**

Only a relatively small number of sites gave a significant response in grain yield to applied S in either year, despite a large proportion of the sites in 1994 showing distinct colour differences between plots. Although not quantified, these colour differences were consistent with symptoms of S deficiency, with affected leaves containing lower levels of S and higher N:S ratios than unaffected leaves, and many of the sites showing deficiency symptoms in 1994 gave significant increases in straw yield. Since the colour differences between the plots developed during stem extension, the results suggest that a greater number of sites in 1994 were short of S during April and May when the crop was growing most rapidly and that the applied S improved dry matter accumulation during the vegetative stage. However, there was no effect of the S treatment on DM yields in late May (GS39) in 1994 and, by the end of the vegetative growth period in late June (GS65), colour differences had lessened considerably or disappeared. This suggests that the increases in straw DM in 1994 were generated post GS39, probably as a result of continued uptake of N and S during June/July, and explains why many of the sites showing deficiency symptoms in 1994 did not show a yield response. Sites where deficiency symptoms were still evident at GS65 (Bridgets and Fakenham) did give a grain yield response and less of a straw response.

Although leaf colour differences had all but disappeared by anthesis, sites showing deficiency symptoms uniquely showed reduced *tgw* as a result of S application. At Sidmouth, Clibburn and Woburn, which recorded the biggest responses in straw yield and the greatest reductions in *tgw*, deficiency symptoms were recorded at the very beginning of stem extension and were severe during the stem extension phase of growth. A yield decrease in winter barley from applied S was recorded in both years at Clibburn. Symptoms of copper deficiency were observed on S-treated plots during grainfill at this site in 1994. A deficiency of copper was suggested by grain analysis (1 mg/g) and indicates that the soil was not able to supply sufficient copper to meet the crops requirements of the better growing crops on S-treated plots. Similarly, the yield reductions from applied S at Garblies in 1993 and at Borders in 1994 may have been due to yield limiting factors other than S.

Differences in the extent of S deficiency between 1993 and 1994 are also suggested by differences in the uptake of N and S between the two years. In 1993, the majority of the N and S uptake occurred between mid-March and the end of May, whilst in 1994 crops continued to take up significant amounts of N and S after GS39 (June). These differences can only partly be explained by a later mean sampling date in 1993, since the ratio of N and S uptake between sampling dates was significantly different. Hence, in 1994, crops took up more N relative to S prior to GS39 (N:S ratio 18:1) and more S relative to N after GS39 (N:S ratio 9:1) than in 1993 (N:S ratios 12:1 and 15:1 for pre-GS39 and post GS39 uptake, respectively). The significantly lower uptake of S relative to N on nil S treated plots prior to the May/June sampling in 1994 is consistent with the greater incidence of deficiency compared to 1993. Indeed, the uptake of S at this sampling date on S-treated plots in 1994 was the same as the uptake of S on nil S treated plots in 1993. The increased uptake of S relative to N post GS39 in 1994 probably accounts for the disappearance of deficiency symptoms by the end of June and the lack of more widespread grain yield response in 1994 compared to 1993. These results also suggest a shortage of S from mid-March to May and an increased availability of S during June and July in 1994 which was absent in 1993. Soil analysis indicated significantly lower levels of soluble sulphate in 1994 but not lower levels of total available S. Lower sulphate levels in 1994 were probably due to the greater amounts of leaching during a wet winter compared to 1993. Average winter rainfall across the sites in 1993/94 (530 mm) was 30% greater than in 1992/93 (408 mm).

Increased availability of S post summer in 1994, indicated by the greater uptake of S relative to N post GS39, could be due to either greater rates of mineralisation or an influx of atmospheric S. There is no evidence to indicate the latter based on the measurements of dry deposition of S at each site, which were broadly similar across the two years (McGrath *et al.*, 1995). Mineralisation of S from the soil organic S pool during June and July may have been stimulated by a lack of available sulphate in the soil solution. Although sulphate-S was not measured in the soil at the GS39 sampling date, measurements of total available S in 1994 indicated a substantial depletion of S in the soil profile. Balance studies indicated a mean loss of 21 kg S/ha between sampling in spring and summer (GS39-53). Rainfall between spring and summer sampling was 190 mm in 1993 and 143 mm in 1994, whilst rainfall post GS39 to

harvest was 162 mm in 1993 and 104 mm in 1994. However, significant amounts of rain fell at the end of March and in early April in 1994, which may account for the loss of S from the profile over this period. Average mean temperatures over the growing period were similar to the long-term average and not appreciably different between the two years.

Sites which showed a grain yield response were not satisfactorily predicted by any soil or crop analysis parameter, although two of the four sites showing grain yield response in 1994 showed  $< 2.0$  mg/g total S and N:S ratios  $> 17:1$  in second and third leaves at GS65 (Taureau *et al.*, 1987; Withers *et al.*, 1995b). When deficient sites were classified as having a response in either grain, straw (and chaff) or total DM yield, then analysis of total S in second and third leaves, either at GS39 or at GS65, was the best predictor of response in 1994. Analysis of leaf N:S at GS39 was most selective, diagnosing all responsive sites, except Wimborne, but suggesting two sites (Hempstead and Borders) should have responded. Both these sites suffered drought in a dry summer. GS65 analysis was not undertaken in 1993 but there were fewer responsive sites in this year compared to 1994. The N:S ratio in leaves at anthesis was also significantly higher at responsive sites but only two of these sites exceeded the deficiency threshold of 17:1 identified by Withers *et al.* (1995b). The N:S ratio in whole crop was also significantly higher in crops showing deficiency symptoms whilst whole crop S analysis was not particularly useful. For example, crops which had not accumulated much DM by this stage showed elevated concentrations of S, whilst crop S was diluted at sites with very high DM growth. Zhao *et al.* (1996) found that S deficiency in cereals at GS37 in pots was associated with whole plant concentrations of  $< 1.5$  mg/g but, in these field experiments, crop S concentrations at GS39 were below this critical level at 19 of the sites. However, this may be due to the later sampling stage in these experiments since crop S concentrations have previously been shown to decline as crops produce more DM (Rasmussen *et al.*, 1977).

Concentrations of S or N:S ratio in flag leaves at GS39 were not at all related to the uptake of S or N:S uptake ratio at this stage or at harvest; it is therefore doubtful whether this parameter can adequately reflect crop S supply or deficiency risk, even though a shortage of S is seen first in the youngest leaves and that flag leaf total S was not influenced by time of sampling. This may relate to the poor translocation of S within the plant. Leaf sampling post GS39 should therefore concentrate on second and third leaves. Grain S analysis was

insensitive to deficiency risk; this is not unexpected because there is a strict regulation by plants on grain S assimilation. Grain analysis is potentially attractive in two ways: (1) there is no confusion over growth stage as there is with leaf analysis and (2) there is less variation across the field. However, the unrealistic number of deficient crops suggested in the survey by grain analysis and the narrow range in S concentration indicates this is a more unreliable indicator of deficiency than leaf analysis, even though the latter may be affected by slight differences in growth stage. Grain S or N:S status may be important for quality in breadmaking varieties of wheat and malting varieties of barley.



## 5. CONCLUSIONS

### 5.1 Crop survey

1. Co-operation was received from over 80% of the cereal farmers contacted in the survey, reflecting the importance the farming community attaches to the S deficiency problem.
2. Barley crops showed lower average N and S concentrations in second and third leaves at anthesis than wheat crops, although differences were not consistent across years. Leaf N:S ratios were not different between the two crops, indicating that differences in leaf S were largely due to differences in crop N supply. Grain N contents were consistently larger in wheat than in barley but grain S concentrations were greater in wheat only in 1992, when grain weight was unusually low. N:S ratios in wheat grain therefore tended to be greater than in barley grain.
3. Malting barley crops showed consistently lower leaf N and S contents than feed barley but there was no difference in leaf N and S between breadmaking and feed varieties. Grain S contents were lower in malting barley varieties and higher in breadmaking wheat varieties compared to feed varieties. However, the differences were small relative to those of N, and grain N:S tended to be smaller in malting varieties and slightly greater in breadmaking varieties.
4. Leaf S concentrations were lowest on sandy soils and in south-west England. Unlike leaf analysis, grain analysis was not sensitive to differences in site location or soil type. Leaf S concentrations or N:S ratio at anthesis were not related to grain S or N:S and different crops were diagnosed as deficient by the two types of crop analysis.
5. Comparisons of N and S concentrations in flag leaves at GS39 and in second and third leaves at anthesis indicated that crop N declines towards the end of vegetative growth but that leaf S remains relatively constant or declines less rapidly. Leaf N:S ratio therefore declines as the season progresses. Concentrations of S in flag leaves were not influenced by time of sampling.

6. Only a small number of cereal crops (<5%) were judged to be S deficient by either leaf analysis or by grain N:S analysis. Grain S was not a useful indicator of S deficiency in isolation.

## 5.2 Field experiments

1. Application of 40 kg S/ha as potassium sulphate in spring significantly ( $P < 0.05$ ) increased grain yields by between 4 and 18% (0.3 - 0.8 t/ha) at 3 sites in 1993 and 4 sites in 1994. Increases in straw (and chaff) yield or in total dry matter yield at harvest of between 5 and 34% were obtained at 3 sites in 1993 and 7 sites in 1994. However, sites showing a grain yield response did not always show a straw yield response and similarly some sites showed a straw yield or total yield response without any effect of the S treatment on grain yield.

2. Distinct colour differences associated with symptoms of S deficiency were observed during stem extension at 1 site in 1993 and 7 sites in 1994. All sites with S deficiency symptoms in 1994 uniquely showed significantly reduced thousand grain weight when fertilizer S was applied. A straw yield response was obtained at 5 of these sites but only 2 sites showed a grain yield response. Sites with the most distinct colour differences gave the largest responses in straw yields. Symptoms disappeared by anthesis stage at sites which gave a straw yield only but tended to persist at the two sites which gave a grain yield response.

3. Prior to sampling in mid-March (GS 21-25), N and S was taken up in the ratio of 15:1 in both years. In 1994, crops without added S took up less S relative to N between GS2 and GS39 (May/June) and more S relative to N between GS39 and harvest compared to 1993. On average, the S content of crops at GS39 in 1994 was significantly lower than crop S uptake in 1993. Soil analysis also indicated lower levels of extractable sulphate-S ( $\text{SO}_4\text{-S}$ ) in spring 1994 compared to 1993. Differences in S levels in soil and crop between the two years could be accounted for by a 30% higher average winter rainfall in 1993/94 compared to 1992/93.

4. The average recovery of applied S fertiliser was low (<10%) in both years, but greatest at yield responsive sites. Average S removal in crops at harvest was 14 kg/ha on untreated plots

and 17 kg/ha where 40 kg S/ha was applied. The proportion of total S uptake removed in grain averaged 65% on untreated plots and 55% on S-treated plots. Changes in soil S content to 90 cm depth and uptake by crops accounted for over 90% of the fertiliser applied.

5. Soil analysis, whole crop analysis or grain analysis could not satisfactorily distinguish yield responsive sites. Sites showing deficiency symptoms showed significantly lower levels of soil extractable  $\text{SO}_4\text{-S}$  and higher whole crop and grain N:S ratios compared to other sites, but there was not a critical threshold which could be identified for predictive or diagnostic purposes. Individual leaf analysis was not undertaken in 1993, but yield responsive sites in 1994 were best predicted by total S and N:S ratios in second and third leaves at GS39 or at GS65. Although, critical threshold values differed between the two sampling dates, sites with leaf N:S ratios above 17:1 all showed deficiency when sites suffering from drought were excluded.

## 6. FURTHER RESEARCH

This project has highlighted the need for further research on the diagnosis and prediction of sulphur deficiency in cereals. As the deficiency becomes more widespread in cereals, opportunities exist to examine alternative approaches to prediction over a range of field sites on both wheat and barley:

1. The field experiments indicated the importance of winter rainfall in depleting soil sulphate reserves during early stem extension and that this affected the occurrence of deficiency symptoms in 1994. Rainfall is a parameter which is included in S deficiency risk assessment in France and has been included in modelling exercises in the UK (McGrath *et al.*, 1995). A review of yield response data on grass, oilseed rape and cereals in different areas in the UK and in different seasons is required to assess the feasibility of using winter rainfall as an indicator of deficiency risk in individual seasons. This could take the form of a decision support tree.

2. This project evaluated soil and crop analysis at certain key crop growth stages (autumn, early spring, GS39 and GS65). In view of the variation introduced by sampling leaves at the later growth stages, the usefulness of whole crop analysis at an earlier growth stage (in time to correct the present crop) requires investigation. Also as methods of sulphate (and related compounds in the plant) analysis are becoming more precise, their predictive value requires continuing assessment.

3. A number of field crops showed deficiency symptoms but without showing yield response, especially in 1994. This is thought to be related to the mineralisation of S post GS39. The pattern of S mineralisation during the growing season requires investigation in order to identify sites where this soil process is likely to be significant. This should be linked with examination of the residual value of different inorganic and organic S fertilizers (inorganic sulphate, elemental S, livestock manures and sewage sludge), whose application in the rotation (for example to oilseed rape) may have important consequences for the need for S supplementation on following cereal crops.

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APPENDIX 1. SITE AND ASSESSMENT DATA

Year	Site location	Grid reference	Soil series	Soil texture	Sampling depth	Variety	Grain yield by combine		Grain yield by quadrat	
							Ni/S 40 kg S/ha v/ha@85% DM	Ni/S 40 kg S/ha v/ha@100% DM	Ni/S 40 kg S/ha v/ha@100% DM	Ni/S 40 kg S/ha v/ha@100% DM
1993	Raynham, Norfolk	TF904237	Barrow	Sandy loam over loamy sand	90	Riband	10.05	10.10	ND	ND
	Stetchworth, Suffolk	TL669605	Moulton	Sandy loam over chalk	90	Beaver	7.83	8.11	ND	ND
	Lewes, Kent	TQ358094	Coombe	Silt loam over chalk drift	30	Beaver	ND	ND	4.64	4.50
	Adisham, Sussex	TQ210549	Coombe	Silt loam over chalk drift	30	Beaver	ND	ND	7.59	7.66
	Bridgets, Hampshire	SU341518	Andover	Silty clay loam over chalk	30	Admiral	ND	ND	5.70	5.83
	Gupton, Dyfed	SR897989	Milford	Deep sandy clay loam	90	Galahad	ND	ND	4.16	4.41
	Pentyarn, Gwent	SO517098	Oglethorpe	Deep sandy silt loam	90	Puffin <sup>1</sup>	ND	ND	ND	ND
	Penrith, Cumbria	NY600262	Clifton	Loamy sand over sandy clay loam	90	Marinka <sup>2</sup>	ND	ND	3.64	3.17
	Sessay, North Yorkshire	SE448765	Sessay	Loamy sand over clay	90	Haven	ND	ND	5.65	5.33
	Witchampton, Dorset	ST974093	Carstens	Clay loam over shale	45	Riband	ND	ND	6.88	7.26
	Langston, Devon	SX649483	Denbigh	Clay loam over shale	45	Beaver	ND	ND	4.18	4.95 <sup>3</sup>
	Woodmancote, Gloucestershire	SP003089	Sherborne	Silty clay loam over limestone	20	Estica	ND	ND	8.57	8.24
	Devizes, Wiltshire	SU044668	Andover	Silty clay loam over chalk	25	Hereward	ND	ND	6.91	7.15
	Great Tew, Oxon	SP410223	Elmton	Clay loam over limestone	30	Riband	ND	ND	8.27	8.17
	Shinhal, Shropshire	SJ761079	Clifton	Loamy sand over sand	90	Riband	ND	ND	7.17	7.46 <sup>4</sup>
	Ross-on-Wye, Herefordshire	SO631289	Fardislon	Deep sandy loam	90	Mercia	ND	ND	6.39	6.31
	Woburn, Bedfordshire	SP964360	Cotterham	Deep loamy sand	90	Hereward	ND	ND	ND	ND
	Floddan, Scottish Borders	NT863375	Wick	Deep sandy loam	90	Mercia	7.59	7.59	7.69	7.42
	Fdnham, Kelso	NT743375	Whitsonne	Deep sandy clay loam	90	Riband	9.63	9.59	7.43	9.33
	Elrick, Kincardineshire	NH282060	Dess	Sandy loam over granite	60	Riband	ND	ND	5.29	6.03 <sup>5</sup>
	Garbles, Morayshire	NH191554	Forres	Deep loamy sand	90	Riband	ND	ND	7.76	7.42 <sup>5</sup>
	Ross-on-Wye, Herefordshire	SO631289	Fardislon	Deep sandy loam	90	Mercia	6.36	6.16	7.82	7.39
	Bicton, Dyfed	SM838073	Milford	Sandy clay loam over sandstone	80	Beaver	9.43	9.61	8.56	8.67
	Pias, Gwent	SM459615	Wick	Deep sandy loam	90	Zodiac	8.50	8.50	8.29	8.40
	Sessay, North Yorkshire	SE448765	Sessay	Loamy sand over clay	90	Riband	5.93	6.17	6.85	7.10
	Mileoak, Sussex	TQ246089	Andover	Silty loam over chalk	20	Soisson	7.53	7.66	7.58	8.10
	Kennington, Kent	TQ005451	Ryfield	Sandy loam over sand	90	Soisson	8.83	9.06	8.00	8.01
	Bridgets, Hampshire	SU341518	Andover	Silty clay loam over chalk	30	Hunter	7.11	7.12	7.19	7.25
	Shinhal, Shropshire	SJ776076	Newport	Sandy loam over sand	90	Hereward	6.81	6.79	6.51	7.06 <sup>6</sup>
	Eastleach, Gloucestershire	SP194076	Elmton	Clay loam over limestone	20	Hussar	9.87	10.47 <sup>7</sup>	11.95	12.72
	Wimborne, Dorset	ST964123	Andover	Silty clay loam over chalk	35	Riband	6.66	6.82	6.67	6.92
	Sidmouth, Devon	SY082883	Bridgenorth	Sandy loam over sand	90	Spark	6.62	6.87	7.44	7.80
Lydeard St Lawrence, Somerset	ST122321	Bromsgrove	Sandy loam over sandstone	90	Soissons	6.62	6.87	7.44	7.80	
Fakenham, Norfolk	TF905293	Newport	Deep sand with gravel	90	Haven	5.25 <sup>8</sup>	5.22 <sup>9</sup>	4.58	4.86	
Hampstead, Norfolk	TG109362	Newport	Deep loamy sand	90	Riband	6.21	6.06	6.27	5.35	
Stetchworth, Suffolk	TL630598	Moulton	Deep loamy sand over chalk	90	Soissons	9.38	9.29	6.82	6.69	
Cliburn, Cumbria	NY590265	Cranmore	Loamy sand over sand	90	Firfly <sup>1</sup>	3.40	2.97	5.13	4.33 <sup>8</sup>	
Woburn, Bedfordshire	SP964360	Cotterham	Deep loamy sand	90	Hereward	5.08	5.27	4.69	5.30	
Bush Pentaulk, Scotland	NT7230590	Southope	Sandy loam over sandstone	60	Riband	7.53	7.76	ND	ND	
Kildrummie, Scotland	NH880560	Naim	Deep loamy sand	90	Ribbon	7.59	7.49	6.14	5.87	
Scottish Borders	NT863375	Wick	Deep sandy loam	90	Mercia	9.39	9.20	7.79	6.89 <sup>9</sup>	

Site	Straw and chaff yield		Thousand grain weight		Grain specific weight		Symptoms	Soil extractable SO <sub>4</sub> -S (90 cm)		Soil extractable S (90 cm)		Soil S in summer (90 cm)	
	NH S t/ha@100% DM	40 kg S/ha	NH S t/ha	40 kg S/ha	NH S kg/ha@85% DM	40 kg S/ha		Autumn kg/ha	Spring	Autumn kg/ha	Spring	NH S kg/ha	40 kg S/ha
Ravensham	6.38	6.76	43.8	44.0	ND	ND	No	28.8	32.8	66.8	63.5	ND	ND
Stetchworth	5.21	5.66 <sup>b</sup>	43.3	44.4	ND	ND	No	ND	41.2	72.0	76.0	ND	ND
Lewes	5.23	5.38	33.5	30.2	78.7	77.4	No	19.6	12.8	23.8	25.5	20.0	32.4
Adisham	7.16	7.11	42.4	42.7	80.5	80.7	No	16.4	24.4	30.6	34.4	36.4	51.6
Bridges	5.51	5.73	34.8	33.3	74.7	74.3	No	20.4	32.8	50.7	47.4	35.2	70.0
Gulpton	8.60	9.03 <sup>b</sup>	29.6	31.4	71.2	71.3	No	45.2	47.2	74.9	80.7	43.6	80.0
Penygnn	ND	ND	ND	ND	ND	ND	No	ND	92.4	134.2	123.4	ND	ND
Penrith	4.85	5.11	40.2	38.8	71.7	71.4	No	16.8	ND	33.0	55.7	ND	ND
Sessey	5.17	5.45	33.9	30.8	77.2	75.3	No	46.4	58.0	99.7	96.4	67.6	96.8
Witchampton	5.49	5.76	46.7	44.3	75.4	74.8	No	32.4	31.2	70.8	74.0	60.0	87.2
Langston	6.13	6.80 <sup>b</sup>	24.3	26.0	63.4	64.3	No	53.2	56.0	92.3	97.9	92.8	152.0
Woodhacote	10.03	9.73	43.1	38.7	79.6	79.4	No	25.2	24.4	39.9	47.7	31.2	34.0
Devizes	9.74	9.96	36.1	35.7	80.4	79.6	No	ND	ND	73.2	65.2	46.4	74.4
Great Tew	9.02	8.99	44.4	44.5	72.7	71.5	No	32.8	ND	48.6	50.8	ND	ND
Slifhal	5.20	5.45	49.8	47.1	77.3	76.6	No	23.2	ND	51.0	38.6	53.2	76.8
Ross-on-Wye	6.29	6.48	32.5	30.0	79.8	80.4	No	60.8	57.2	85.0	86.5	ND	ND
Woburn	ND	ND	ND	ND	ND	ND	Yes	28.8	ND	78.8	90.0	ND	ND
Flooden	6.58	6.58	39.1	39.5	79.0	78.9	No	ND	ND	ND	ND	ND	ND
Ehnam	6.60	6.81	40.7	43.3	75.7	75.9	No	ND	ND	ND	95.4	ND	ND
Ehick	7.28	7.98	29.5	31.0	70.5	70.7	No	58.0	47.2	119.3	108.5	49.6	49.2
Garthles	7.84	7.86	38.5	35.0	76.7	75.9	No	37.2	44.0	77.1	74.9	95.2	120.0
Ross-on-Wye	10.46	10.31	28.2	28.0	77.7	77.8	No	43.6	35.6	72.2	43.6	ND	ND
Bicton	10.23	11.89	45.4	45.7	69.7	69.7	No	86.4	68.0	134.6	109.6	104.0	128.8
Plas	11.17	10.07	38.0	38.0	78.9	78.6	No	113.6	100.8	147.0	160.4	124.4	178.0
Sessey	7.32	7.93	40.5	39.1	79.4	79.0	No	74.0	41.6	84.2	126.2	58.8	104.8
Mileok	7.33	7.07	41.6	41.0	81.5	81.6	No	32.0	14.0	53.8	47.5	38.8	73.6
Kennington	7.89	8.72 <sup>b</sup>	37.9	36.5 <sup>b</sup>	78.7	78.3	Yes	41.6	21.2	111.3	123.5	46.0	67.2
Bridges	7.22	7.30	42.0	37.8 <sup>b</sup>	79.1	77.8 <sup>b</sup>	Yes	28.0	25.6	42.6	101.4	34.8	53.6
Shifnal	7.09	7.32	42.0	39.0 <sup>a</sup>	82.7	82.2	Yes	30.0	18.4	59.5	75.0	80.8	110.8
Eastleach	6.16	7.10 <sup>b</sup>	36.2	35.1	78.0	77.8	No	23.2	17.2	32.8	27.7	29.2	61.2
Wimborne	10.42	10.98 <sup>b</sup>	46.7	45.9	75.5	75.3	No	48.0	26.4	82.1	50.2	38.8	76.4
Stimouth	7.49	8.69 <sup>b</sup>	36.2	32.2 <sup>b</sup>	78.9	77.7 <sup>b</sup>	Yes	28.4	15.2	53.4	62.8	33.2	70.0
Lydeard St Lawrence	6.70	7.13	38.5	37.8	80.7	80.7	No	23.6	20.0	45.2	82.6	53.6	87.6
Fakenham	4.98	5.60 <sup>b</sup>	43.1	40.8 <sup>b</sup>	72.9	74.3	Yes	18.8	12.0	50.0	94.9	33.2	64.8
Hempstead	5.76	5.66	40.5	39.7	74.3	73.8	No	38.0	16.8	69.6	71.2	40.8	82.4
Stetchworth	6.38	6.47	39.8	40.2	81.8	81.7	No	43.2	32.8	67.9	146.4	45.2	94.4
Cliburn	5.82	7.79 <sup>b</sup>	41.4	39.1 <sup>b</sup>	70.2	68.9 <sup>a</sup>	Yes	ND	ND	ND	33.7	ND	ND
Woburn	5.52	7.40 <sup>b</sup>	30.2	26.9 <sup>a</sup>	77.0	76.2	Yes	ND	ND	ND	ND	ND	ND
Bush Pentuik	ND	ND	43.8	45.1	77.1	76.7	No	67.6	38.0	90.6	82.4	78.8	116.0
Kildrummie	5.51	4.90	42.2	41.6	73.7	73.6	No	46.0	55.2	111.3	123.5	84.0	107.2
Scottish Borders	9.02	8.26	41.7	40.0 <sup>a</sup>	82.2	82.2	No	ND	50.4	81.6	86.1	ND	ND

Site	Crop S in spring		Crop S in summer		Crop S at harvest		S harvest index		Apparent recovery %	Whole crop in spring		Whole crop in summer	
	Nit S kg/ha	40 kg S/ha	Nit S kg/ha	40 kg S/ha	Nit S kg/ha	40 kg S/ha	Nit S ratio	40 kg S/ha		Total S mg/g	N:S ratio	Total S mg/g	N:S ratio
Raynham	2.3	ND	13.8	17.8	0.74	0.64	10.00	2.58	14.8	ND	ND	ND	
Stetchworth	1.3	ND	12.4	15.0	0.66	0.60	6.50	3.30	11.2	ND	ND	ND	
Leves	1.5	ND	8.3	10.2	0.68	0.61	4.75	3.73	13.0	1.44	1.44	11.1	
Atsham	2.5	ND	17.6	19.3	0.56	0.54	4.25	3.80	12.3	2.32	2.32	8.8	
Bridgets	0.8	11.7	10.3	13.2	0.67	0.62	7.25	2.84	15.1	1.56	1.56	11.0	
Gupton	0.9	22.8	18.3	20.4	0.35	0.34	5.25	3.43	15.2	2.12	2.12	8.6	
Penygam	ND	ND	ND	ND	ND	ND	ND	ND	13.4	ND	ND	ND	
Pentlith	1.1	7.4	7.4	7.8	0.66	0.62	1.00	2.80	18.0	ND	ND	ND	
Sesay	1.3	19.2	14.2	17.3	0.60	0.49	7.75	3.09	13.6	1.90	1.90	11.9	
Wichampton	1.1	11.1	13.4	19.0	0.68	0.55	14.00	2.44	16.6	1.76	1.76	13.0	
Langston	1.5	13.5	13.0	17.7	0.52	0.48	11.75	2.54	14.4	1.98	1.98	11.6	
Woodhancote	0.9	13.2	16.7	19.6	0.63	0.54	7.25	2.70	15.0	1.74	1.74	12.8	
Devizes	2.7	22.8	20.7	26.2	0.46	0.42	7.50	3.73	13.2	2.66	2.66	8.5	
Great Tew	1.2	19.3	23.2	25.8	0.57	0.47	13.75	2.91	16.4	2.20	2.20	9.6	
Stiffnal	1.6	9.8	20.3	26.2	0.67	0.61	10.25	3.44	12.8	1.56	1.56	15.2	
Ross-On-Wye	0.1	ND	12.1	16.2	0.56	0.50	6.50	2.48	18.8	ND	ND	ND	
Woburn	0.2	5.4	ND	ND	ND	ND	ND	4.16	10.8	ND	ND	ND	
Flooden	0.5	11.7	19.2	21.6	0.59	0.51	6.00	3.05	15.2	1.56	1.56	13.9	
Edham	3.6	12.8	12.8	15.6	0.65	0.62	7.00	3.28	18.4	1.32	1.32	13.2	
Erick	2.3	14.9	14.1	16.2	0.44	0.44	5.25	3.28	18.4	1.26	1.26	12.3	
Garbles	1.5	15.9	14.9	21.8	0.59	0.41	17.25	3.02	ND	0.98	0.98	18.7	
Ross-On-Wye	2.2	7.1	18.9	21.3	0.57	0.53	6.00	2.35	15.1	0.95	0.95	17.5	
Bieton	1.1	ND	15.4	17.3	0.62	0.60	4.75	3.92	14.5	1.70	1.70	21.1	
Plas	1.1	ND	22.4	25.2	0.46	0.42	7.00	4.27	14.5	1.90	1.90	14.4	
Sesay	0.6	10.9	13.0	15.1	0.62	0.55	6.75	3.24	17.0	1.12	1.12	14.2	
Milcock	1.8	11.1	16.4	21.5	0.67	0.56	12.75	3.71	14.0	1.73	1.73	15.5	
Kennington	2.6	8.2	14.2	17.2	0.67	0.56	7.50	3.07	14.7	1.08	1.08	18.6	
Bridgets	0.8	13.8	14.5	20.4	0.71	0.62	14.75	3.07	12.8	1.48	1.48	18.5	
Eastleach	1.2	10.7	11.7	17.9	0.80	0.62	15.50	2.75	14.1	1.11	1.11	15.0	
Shifnal	1.9	32.5	14.5	17.9	0.71	0.69	12.50	2.70	14.0	1.37	1.37	17.4	
Winborne	4.6	10.7	10.0	15.0	0.68	0.58	12.50	2.92	12.9	1.45	1.45	15.8	
Sidmouth	2.1	12.6	23.1	31.6	0.64	0.64	4.75	2.95	16.6	1.10	1.10	18.4	
Lydeard St Lawrence	0.0	5.9	12.1	13.1	0.67	0.64	4.75	2.95	16.6	1.10	1.10	18.4	
Fakenham	0.9	5.9	12.1	12.9	0.71	0.61	14.00	4.35	14.1	2.92	2.92	20.5	
Hempstead	1.9	ND	7.3	11.6	0.66	0.60	4.25	3.45	14.0	1.27	1.27	20.5	
Stetchworth	0.7	ND	9.9	11.6	0.69	0.60	4.25	3.45	14.0	1.47	1.47	16.3	
Cliburn	ND	1.6	13.4	16.3	0.66	0.55	7.25	3.44	14.0	1.65	1.65	13.3	
Woburn	ND	3.7	8.2	16.3	0.61	0.51	20.25	2.87	15.5	1.15	1.15	33.8	
Bush Pentlith	4.3	6.7	9.4	23.4	0.70	0.41	35.00	3.22	ND	2.99	2.99	15.3	
Kildunnie	4.1	8.6	8.2	ND	ND	ND	ND	3.22	ND	1.23	1.23	ND	
Scottish Borders	5.7	11.6	15.4	13.3	0.65	0.68	-5.25	2.38	16.4	1.42	1.42	14.4	
										21.4	1.07	16.5	

Site	GS39 leaf analysis				GS65 leaf analysis				Grain analysis			
	Flg leaves		Leaves 2 and 3		Flg leaves		Leaves 2 and 3		Total S		N:S	
	Total S mg/g	N:S ratio	Total S mg/g	N:S ratio	Total S mg/g	N:S ratio	Total S mg/g	N:S ratio	Total S mg/g	N:S ratio	Total S mg/g	N:S ratio
Raynham	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.19	12.9	
Stetchworth	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.23	14.6	
Leves	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.22	14.8	
Adisham	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.30	13.7	
Bridgets	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.22	14.0	
Ghpton	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.56	14.2	
Perrygam	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
Perrith	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.36	15.7	
Sesay	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.53	13.0	
Witchampton	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.31	13.3	
Langston	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.62	13.6	
Woodhencote	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.22	16.0	
Devizes	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.53	14.7	
Great Tew	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.39	13.4	
Shibthel	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.14	12.8	
Ross-On-Wye	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.51	14.8	
Woburn	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
Phoddan	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.47	14.0	
Ednam	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.12	13.1	
Ehrck	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.16	13.8	
Garbhis	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.13	14.9	
Ross-On-Wye	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.38	17.8	
Pictou	2.1	14.8	3.05	13.7	3.2	12.5	2.30	13.1	3.1	1.10	15.2	
Phis	2.2	18.2	2.65	18.3	3.1	9.5	2.40	10.6	3.10	1.25	15.7	
Sesay	2.9	13.9	3.20	13.7	3.0	13.5	2.90	12.1	3.10	1.25	15.7	
Milecok	3.4	13.7	3.40	13.6	3.3	13.2	3.20	12.4	3.20	1.39	16.7	
Kennington	2.6	14.6	2.40	16.2	2.5	14.6	2.05	13.7	2.05	1.23	14.0	
Bridgets	2.2	17.5	2.30	18.7	2.4	17.3	1.90	17.2	1.90	1.15	16.6	
Shifnal	3.3	11.1	2.45	15.3	2.5	12.0	1.85	13.3	1.85	1.29	16.0	
Eastleach	2.7	14.4	2.55	15.8	2.2	14.3	1.65	13.9	1.65	1.05	16.1	
Wimborne	3.2	13.7	2.85	15.8	2.7	13.9	2.30	14.0	2.30	1.24	13.9	
Sidmouth	3.3	11.9	2.55	15.5	3.0	11.9	2.25	12.5	3.0	1.12	15.0	
Lydeard St Lawrence	3.6	14.1	4.00	13.9	3.0	13.9	3.70	11.1	3.70	1.16	17.8	
Fakenham	2.2	20.4	1.70	25.5	ND	ND	ND	18.2	1.35	1.04	21.4	
Hempstead	2.1	17.0	2.45	19.1	2.0	15.5	1.80	14.7	1.80	1.10	17.0	
Stetchworth	3.2	13.2	2.85	14.2	2.8	14.3	2.35	12.4	2.35	1.29	16.4	
Cibham	1.4	27.7	1.25	41.4	ND	ND	ND	ND	ND	0.97	25.2	
Woburn	2.2	17.6	2.20	16.4	2.2	14.9	1.80	13.1	1.80	1.41	17.6	
Bush Pentuck	2.4	ND	2.55	ND	2.3	ND	2.60	ND	2.3	1.21	16.2	
Kildunnie	2.1	16.4	2.55	15.0	2.2	14.3	1.95	10.5	1.95	0.88	15.2	
Scottish Borders	2.4	16.0	2.00	15.8	2.8	13.1	2.05	12.7	2.05	1.28	15.8	