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# Variation in grain sulphur concentrations in wheat and barley

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## SUMMARY

To determine the incidence of sulphur (S) deficiency in winter cereals, representative leaf and grain samples were collected from winter wheat and winter barley crops at over 85 field locations in England and Wales during 1992. The fields sampled were located in areas and on soil types where S deficiency was most likely to occur. Milling and malting cultivars represented 30% and 44%, respectively, of the wheat and barley samples taken. Mean total S concentrations in harvested grain were significantly ($P$<0.001) greater in winter wheat (range of 1.07 to 1.81 mg/g) compared to winter barley (range of 0.94 to 1.55 mg/g). The grain from milling wheat contained more S than in feed wheat but S concentrations in feed barley grain were similar to those in malting cultivars. Grain nitrogen (N) content explained 80-85% of the variation in grain S. Grain N and S concentrations in wheat decreased as yield and thousand grain weight increased but there was no such relationship in barley. Grain N and S in barley grain were slightly greater where organic manures had been applied. There was no effect of soil type, sowing date, previous cropping or amount of N applied on grain S. There was no (wheat) or only a weak (barley) relationship between S in grain and S in the second and third youngest leaves at anthesis. Less than 5% of wheat and <10% of barley crops sampled could be considered to be S deficient.

## INTRODUCTION

Sulphur (S) is becoming an important limiting nutrient in crop production in areas of the UK receiving only small inputs of S from the atmosphere. A shortage of S results in pale stunted crops which struggle to achieve satisfactory growth and which produce less seed. The need for S fertilisers on sandy and shallow chalk soils of low S status has been identified in multi-cut systems of grassland production (Syers, Curtin & Skinner, 1987) and for oilseed rape which has a particularily high S requirement (Zhao, Syers, Evans & Bilsborrow, 1991; Chalmers *et al.*, 1992 ). Although less widespread, S deficiency has also been recorded in cereals (Scott, Dyson, Ross & Sharp, 1984; Withers, 1993).

The importance of an adequate grain S content for the formation of sulphydryl (S-H) and disulphide bonds (S-S) in bread-making cultivars of wheat is well established (Archer, 1980; Wrigley *et al.*, 1984). Wheat grain of low S status contains less S-rich proteins and produces an inelastic dough which gives rise to small crumbly loaves (Byers & Bolton, 1979; Moss, Wrigley, MacRitchie & Randall, 1981). Limited work also suggests that low levels of S proteins in barley grain may decrease the value of malting barley cultivars to the maltsters (Shewry *et al.*, 1985). Surveys of British wheat crops indicate there has been a significant decline in grain S status over the 10-year period 1982-1992 (Byers, McGrath & Webster, 1987; McGrath, Zhao, Crosland & Salmon, 1993). However, there is no information on agronomic factors which may influence grain S concentration in wheat and barley. This paper reports on the grain analysis results from a crop survey to determine the extent of S deficiency in winter cereals in England and Wales during 1992.

## MATERIALS AND METHOD

Selected farms in areas of England and Wales estimated to be receiving <20 kg S/ha/year from the atmosphere (information supplied by Warren Springs Laboratory, 1990) were visited during 1992 to identify appropriate winter wheat and winter barley fields for sampling. The majority of the farms were selected on the basis of either having a history of S deficiency in grass/oilseed rape or having sandy and/or shallow calcareous soil types where deficiency is most likely to occur (Withers, 1993). Sufficient farms were selected to ensure that winter wheat and winter barley samples were in similar proportions.

A representative sample of the second and third leaves below the ear was obtained from each field at anthesis stage (GS 60-69, Tottman, 1987) and analysed for total N, total S and sulphate S according to ADAS analytical procedures (Anon., 1986). Samples of the harvested grain together with a field history questionaire were provided by the farmer. 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 $HClO_4$-$HNO_3$ (Zhao, McGrath & Crosland, 1993). The N and S concentrations are expressed on a d.m. basis. 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% d.m. Grain d.m. content and specific weight (sp.wt) were simultaneously measured with a *Sinar Datatec P25* moisture analyser. The sp.wt of wheat was corrected to 85% d.m according to the equation of Pushman (1975).

Information on soil type, cultivar, 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 (Byers *et al.*, 1987) since only small numbers of samples were collected from selected counties. Cultivars were grouped into milling, malting or feed categories according to NIAB recommended

Table 1. *Percentage of winter cereal crops on different soil types*

| Soil type | Texture class | Winter wheat | Winter barley |
|---|---|---|---|
| Sand | S, LS | 11 | 15 |
| Light loam | SL, SZL | 35 | 35 |
| Heavy loam | SCL, ZCL, CL | 26 | 19 |
| Shallow calc. | All textures | 28 | 31 |

Table 2. *Sulphur (mg/g) in winter cereal grain by region in 1992*

| Region | Samples | Mean | Range | SE |
|---|---|---|---|---|
| Northern | 25 | 1.25 | 1.09 - 1.59 | 0.026 |
| Midlands & Western | 20 | 1.36 | 1.23 - 1.57 | 0.022 |
| Eastern | 39 | 1.30 | 1.03 - 1.66 | 0.025 |
| South-eastern | 38 | 1.34 | 1.06 - 1.81 | 0.025 |
| South-western | 27 | 1.26 | 0.94 - 1.61 | 0.029 |
| Wales | 8 | 1.22 | 1.07 - 1.53 | 0.054 |

Table 3. *Differences in selected parameters between wheat and barley*

| | leaf | | | grain | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | N | S mg/g | N:S | N | S mg/g | N:S ratio | tgw g | sp.wt kg/hl | yield t/ha |
| wheat | 34.49 | 2.95 | 12.2 | 22.27 | 1.37 | 16.3 | 33.5 | 70.4 | 7.2 |
| barley | 31.36 | 2.67 | 12.1 | 19.69 | 1.24 | 15.9 | 36.4 | 65.8 | 6.6 |
| S.E.D. | 0.899 | 0.094 | 0.42 | 0.385 | 0.018 | 0.17 | 0.68 | 0.55 | 0.15 |
| d.f. | 188 | 189 | 188 | 155 | 151 | 151 | 155 | 81 | 151 |

lists. Soils were divided into sands, light-textured loams, heavy-textured loams and shallow (<40 cm) calcareous types. Three fields with clay soils were included as heavy-textured loam soils. Three types of previous cropping were identified; continuous arable, grass-arable and grass.

Variation in leaf and grain N and S concentrations with site, soil and crop parameters was assessed by regression analysis. Mean values were calculated and statistical comparisons were made by analysis of variance.

## RESULTS

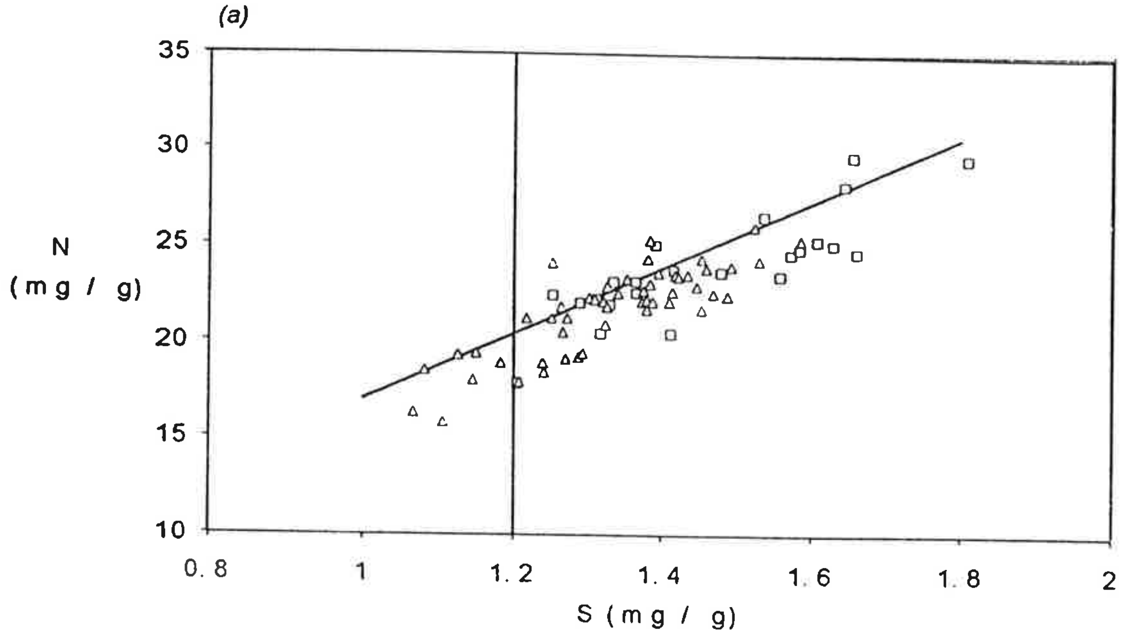
Grain samples and yield estimates were received from 80% of the 195 fields sampled, reflecting the large degree of co-operation obtained from the farmers contacted. Estimated yields ranged from 4.0 to 10.0 t/ha in winter wheat and from 4.9 to 9.8 t/ha in winter barley. The proportion of winter barley and winter wheat crops grown on different soil types is shown in Table 1. A slightly lower proportion of winter barley was grown on heavier-textured soils but the majority of both barley and wheat crops sampled were grown on sand, light loam and shallow calcareous soils on which a S deficiency is most likely to occur (Withers, 1993). Approximately 85% of the fields sampled were in continuous arable rotation and had not received any organic manures in the previous year. Winter wheat was sown, on average, 11 days later than winter barley.

The mean and range of grain S concentrations between the different regions is given in Table 2. Lowest mean values in both barley and wheat samples were from northern and south-west England and Wales. Winter wheat showed greater concentrations of N and S in both leaf and grain samples compared to winter barley but there was no difference in the N:S ratio between the two crops (Table 3). In contrast to grain sp.wt, tgw was less in winter wheat than in winter barley. Further results will be reported separately for the two crops.

### *Winter wheat*

Grain S and N:S ratios varied from 1.07 to 1.81 mg/g and from 14.3 to 19.2, respectively. Greater grain N and S concentrations were found in milling cultivars compared to feed cultivars (mean +2.2 and +0.14 mg/g, respectively). Milling cultivars, which represented 30% of the wheat fields sampled and which received an average 11 kg/ha more N, also showed a greater mean sp.wt. The mean tgw was, however, less than in feed cultivars. There was a negative linear relationship between grain S (or N) and tgw ($r^2$=-0.4, 74 d.f.). A similar, but much weaker, negative correlation ($r^2$=-0.13, 65 d.f.) was also obtained between grain S and yield level. Grain N accounted for 87% of the variation in grain S (Fig. 1). The linear relationship indicated a N:S ratio in the sample population of 15.8:1. There was a positive linear relationship between leaf N concentration and grain S (and N) (Table 4). Multiple regression did not improve the percentage of the explained variation. There was no effect of soil type, sowing date, previous cropping, organic manures or amount of N applied (Table 4).

There was also no linear relationship between grain S at harvest and leaf S at anthesis. Grain N:S ratio was not related to any parameter.



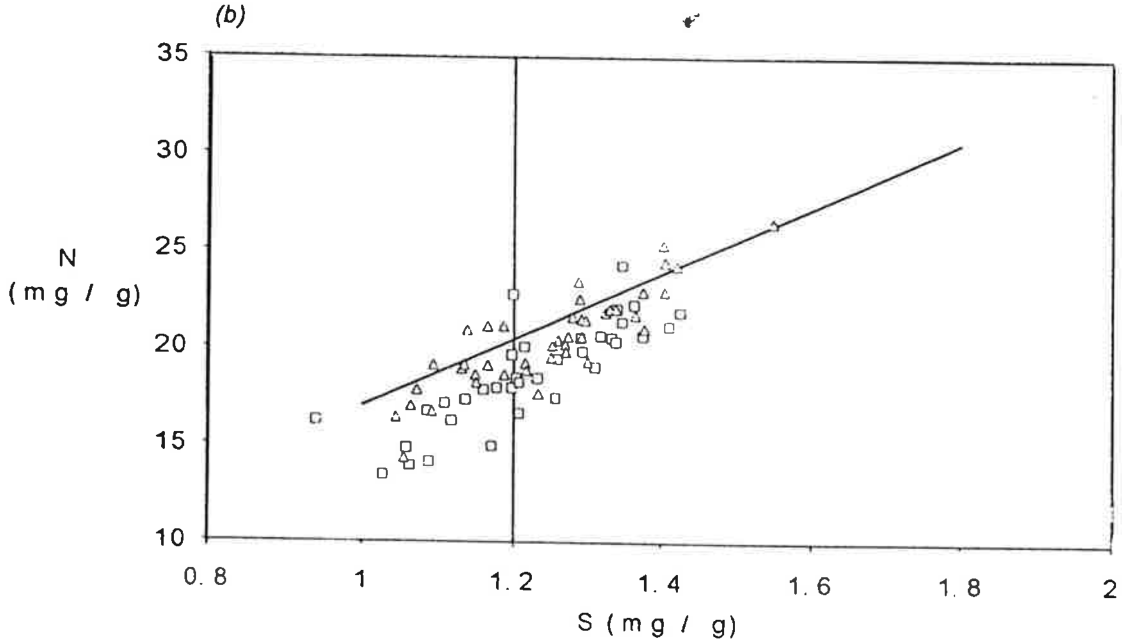




Fig. 1. Grain N and S relationships in milling and malting cultivars (□) compared to feed cultivars (∇) in *(a)* wheat and *(b)* barley. (1.2 mg/g total S and 17:1 N:S ratio lines drawn)

*Winter barley*

Grain S and N:S ratios varied from 0.94 to 1.55 mg/g and from 12.7 to 18.9, respectively. As with winter wheat, there was a highly significant positive linear relationship between grain N and grain S (Fig. 1). This relationship explained 81% of the variation in grain S and indicated a N:S ratio in the sample population of 18.7:1. Grain S was also related to leaf N concentration and the amount of N applied (Table 4). However, malting cultivars, which represented 44% of the barley fields sampled, did not show lower grain S despite lower grain N. The N:S ratio in the grain of malting cultivars was consequently lower (Fig. 1). The N:S ratio was positively correlated to the amount of N applied ($r^2$=0.3, 75 d.f.) but was otherwise an independant variable. Higher amounts of N applied in northern England resulted in grain with a larger grain N:S ratio compared to other regions. Slightly greater grain S concentrations were observed where organic manures had been applied but there was no effect of soil type, previous cropping, sowing date or estimated yield level (Table 4). Grain S at harvest was weakly correlated to leaf S concentration at anthesis. Multiple regression did not improve the percentage of the explained variation.

Table 4. *Explained variation in grain N and S concentrations*

| | Winter barley | | Winter wheat | |
|---|---|---|---|---|
| | N | S | N | S |
| Cultivar | 0.003[1] | ns | 0.001[1] | <0.001[1] |
| Soil type | ns | ns | ns | ns |
| Sowing date | ns | ns | ns | ns |
| Previous cropping | ns | ns | ns | ns |
| Manure | 0.053[1] | 0.028[1] | ns | ns |
| N applied | 0.22[2] | ns | ns | ns |
| Yield | ns | ns | 0.06[2] | 0.13[2] |
| Tgw | ns | ns | 0.39[2] | 0.41[2] |
| Sp.wt | ns | ns | ns | ns |
| Leaf N | 0.17[2] | 0.07[2] | ns | ns |
| Leaf S | ns | 0.07[2] | ns | ns |
| Leaf SO4S | ns | 0.06[2] | ns | ns |

[1] denotes *P* value. [2] denotes regression coefficient ($r^2$). ns denotes no significant (*P* <0.05) effect.

*Occurrence of deficiency*

Grain total S concentrations below 1.2 mg/g and N:S ratio values above 17:1 are critical threshold values outside which baking quality is considered to deteriorate (Byers & Bolton, 1979; Randall, Spencer & Freney, 1981; Byers *et al.*, 1987). The percentage of grain samples with both <1.2 mg/g total S and a N:S ratio of >17:1 was

4% and 9% for wheat and barley, respectively. Assuming a deficiency threshold of 2 mg/g total S (100% d.m.) in leaf tissue (Withers, 1993), leaf analysis also suggested that only a small proportion of the crops sampled were suffering from a shortage of S during the growing period. However, leaf analysis and grain analysis were not always consistent in diagnosing S-deficient samples. Fields identified as deficient were generally located on sand and light loam textured soils in the south-west and north of England. Samples with low S concentrations in both wheat and barley were also identified at single farms in Norfolk and Kent.

## DISCUSSION

This survey relied heavily on farmer support and this was successfully achieved. The importance of S nutrition in agricultural crops is being increasingly recognised by the farming community and a number of farmers are already applying S fertilisers to their cereal crops. This survey was biased towards S deficient crops and is, therefore, not truly representative of the regions from which the samples were collected. Nevertheless, the majority of grain samples with low or deficient S concentrations came from northern and south-west England and it is in these areas that yield responses to S fertilisation have been previously obtained in cereals (Withers, 1993). Similar regional differences in grain S have been shown in previous surveys of wheat crops (Byers et al., 1987) which have emphasized the importance of atmospheric deposition of S in meeting the S requirement of the crop.

Wherever possible, wheat and barley samples were taken from the same farm to provide a good comparison. The greater S concentrations found in wheat grain are not unexpected considering the strong positive relationship between grain N and grain S. On average, wheat crops received 45 kg/ha more N than the barley crops which resulted in an increase of 2.58 mg/g in grain N. Similarily, greater grain S in milling wheat cultivars compared to feed wheat cultivars is consistent with their genetically determined higher protein content for any given level of N applied. The fitted grain N:S ratio for the wheat sample population (15.8:1) was lower than the critical threshold of 17:1 indicating that S was not limiting for the wheat crops in this survey (Byers & Bolton, 1979, Moss *et al.*, 1981). Indeed very few of the wheat crops sampled could be considered to be S deficient by either leaf or grain analysis. For the barley sample population, the fitted N:S ratio was larger (18.7:1), reflecting the greater proportion of S deficient barley crops compared to wheat. Also, the larger N supply to feed barley (+25 kg/ha) did not result in increased grain S concentrations compared to malting cultivars but simply served to widen the N:S ratio (Fig. 1). The greater number of deficient barley crops despite lower amounts of N applied may reflect the greater proportion of barley crops grown on sand soils (Table 1). These results also suggest that wheat and barley may have different critical S values in relation to grain quality.

The data presented here clearly show that crop N supply has a dominant influence on grain S, with other agronomic factors having no effect. The majority of crops sampled were on soils of inherently low S supply and this lack of diversity may reflect the lack of any significant effect of soil type. Similarily, most crops were in continous arable cultivation and receiving no organic manures. The slight increase in grain S in barley crops receiving organic manures maybe an effect of increased N supply rather than S supply. The wheat harvest was delayed in some areas in 1992 due to wet weather and many of the grain samples received were small in size, resulting in low tgw and sp. wt. The negative relationship obtained between grain N or S and tgw in the wheat samples is consistent with the effect of smaller grain size in concentrating grain protein content. Measurement of the available sulphate in the soil profile was not undertaken in this survey.

According to commonly accepted S deficiency thresholds in leaves (Withers, 1993) and grain (Randall *et al.*, 1981), only a small proportion of the crops sampled would justify S fertilisation. Leaf and grain analysis was also not consistent in diagnosing deficient crops. Fields with low total S in leaves did not always show low grain S and crops diagnosed as S deficient by grain analysis often showed quite adequate leaf S. The second and third leaves were often partly senesced at the anthesis sampling time, especially in winter barley, which may have lowered the N and S concentrations. For example at one site, leaf N and S concentrations were only 15.5 and 1.6 mg/g respectively. An earlier sampling time is planned for a similar survey in 1993.

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