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Sulphur status of British wheat grain and its relationship with quality parameters

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SUMMARY

Four hundred samples of wheat grain were collected from the major wheat-growing areas in Britain in 1992 by the Home-Grown Cereals Authority. Total S concentrations in these ranged from 0.054% to 0.209%, with a mean of 0.143%. The range of the N:S ratio in the grain was 13.2-29.6, with a mean of 15.8. Comparison of the results of 1992 with those of 1982 showed a significant decline in the S status of British wheat during the 10 year period. None of the samples in 1982 was found to be S-deficient, whereas in 1992 7% of the samples had a total S concentration smaller than the critical value (0.12%), and 10% of the samples had a N:S ratio greater than the critical value (17.0). Grain from Scotland contained the least S, whereas above-average S concentrations occurred mainly in grain from central England. Bread-making varieties generally had greater N and S concentrations than other varieties. The relationships between grain S concentration and measurements of bread-making quality were not very strong, probably because none of the grain samples of the bread-making varieties were deficient in S, although it is thought that the S deficiency in some samples of non-bread-making varieties may have contributed to the very small protein concentrations in the grain.

INTRODUCTION

Sulphur (S) is an essential nutrient for plant growth and development. Sulphur deficiency in wheat not only reduces grain yield (Byers & Bolton, 1979; Randall, Spencer & Freney, 1981), but also seriously affects bread-making quality of flour (Moss, Wrigley, Macrithie & Randall, 1981; Moss, Randall & Wrigley, 1983; Byers, Franklin & Smith, 1987*a*), because disulphide bonds formed from the sulphydryl groups of cysteine are essential for viscoelasticity of the dough (Frater, Hird, Moss & Yates, 1960; Wall, 1971). Grain with small concentrations of S results in dough with decreased extensibility, and this results in reduced loaf volume (Moss *et al.*, 1981; 1983; Byers *et al.*, 1987*a*).

During recent years there has been growing concern about the possibility of S deficiency in arable crops in the UK, since the inputs of S from the atmosphere and fertilisers have declined considerably (Syers, Skinner & Curtin, 1987). Significant responses to applications of S fertilisers have been reported repeatedly in winter oilseed rape (Withers, 1989; Zhao, Syers, Evans & Bilsborrow, 1991; McGrath, 1992), and less frequently in cereals which have smaller S requirements (Scott, Dyson, Ross & Sharp, 1984). Results of some recent field experiments showed that foliar sprays of either elemental S or ammonium sulphate at flag leaf emergence or milky ripe stage were ineffective in raising the S concentration of wheat grain, and hence the effects of such S applications on bread-making quality were found to be inconsistent (Dampney & Salmon, 1990; Salmon, Greenwell & Dampney, 1990; Griffiths, Kettlewell, Hocking & Wallington, 1990).

Researchers at Rothamsted conducted a survey on the S status of British wheat grain collected in 1981 and 1982 (Byers, McGrath & Webster, 1987*b*). None of the samples were found to be S-deficient (less than 0.12% S in dry matter), although the regional pattern of grain S concentration corresponded closely with the known deposition of S from the atmosphere, with Scottish wheat grain having lowest S. The present work aimed to examine the S status of British wheat from the 1992 harvest and to relate the concentrations of S in grain with some measurements related to bread-making quality.

MATERIALS AND METHODS

Four hundred wheat grain samples were collected by the HGCA in 1992 from major cereal growing areas in Britain. Milling and baking quality was assessed by FMBRA using standard methods (Anon., 1991). Quality parameters used in this paper include protein content (by the Near Infra-red Reflectance method), Hagberg Falling Number, and sodium dodecyl sulphate (SDS) sedimentation volume for all samples, and loaf volume (Chorleywood Bread-making Process; CBP) for bread-making varieties.

For S analysis, subsamples of wholemeal flour were digested with $HClO_4$-HNO_3 in a Carbolite heating block. Ramp rates for temperature increases, dwell temperatures and dwell durations of digestion were controlled by a Eurotherm 818 Controller/Programmer according to Zhao, McGrath & Crosland (1993). Sulphur in the digested solution was determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). This method gave a mean recovery of 99.1% for S in five certified standard plant materials (Zhao *et al.*, 1993). The total N concentration was calculated from the protein content determined by NIR divided by a factor of 5.7 (Osborne, Douglas, Fearn & Willis, 1982). Total N was determined in 25 selected samples by a combustion method (Foss-Heraeus Macro-N). Close agreement between the two methods was obtained with the following regression equation: $N_{combustion} = 0.10 + N_{NIR}$ ($n=25$, $R^2=0.96$). Both N and S concentrations are expressed on a dry matter basis.

The exact locations of the collection sites were recorded for 381 samples only, and these form the basic data set.

RESULTS AND DISCUSSION

Varietal differences in total N and S concentrations and N:S ratio

The 381 samples included 28 varieties, half of which were bread-making varieties. The mean N and S concentrations and N:S ratio for each variety are shown in Table 1. Analyses of variance indicated highly significant ($p<0.001$) varietal differences in both total N and S concentrations (Table 1). Generally, the bread-making varieties had higher N and S concentrations than the other varieties. In contrast, there was no significant varietal difference in the N:S ratio.

Table 1 *Mean N and S concentrations and N:S ratios for the 28 wheat varieties in the 1992 survey*

Variety	Number of samples	N%	S%	N:S
Bread-making varieties				
Mercia	57	2.477	0.158	15.8
Hereward	33	2.375	0.146	16.3
Soissons	5	2.314	0.142	16.3
Tonic	4	2.759	0.170	16.3
Estica	3	2.258	0.136	16.6
Urban	3	2.332	0.145	16.1
Avalon	3	2.333	0.149	15.6
Carolus	2	2.662	0.159	16.8
Canon	2	2.632	0.156	16.9
Axona	2	2.387	0.160	15.0
Camp Remy	2	2.265	0.140	16.2
Futur	1	2.611	0.150	17.4
Baldus	1	2.060	0.130	15.8
Talon	1	2.672	0.162	16.5
Mean		*2.438*	*0.153*	*15.9*
Other varieties				
Riband	108	2.074	0.134	15.6
Beaver	52	2.264	0.142	16.0
Haven	40	2.153	0.139	15.4
Apollo	25	2.166	0.140	15.6
Slejpner	17	2.263	0.148	15.4
Galahad	7	2.206	0.140	15.7
Hornet	3	2.122	0.127	16.8
Tara	2	2.101	0.127	16.6
Norman	2	1.796	0.108	16.8
Admiral	2	2.112	0.126	16.7
Longbow	1	1.673	0.122	13.7
Wasp	1	2.162	0.144	15.0
Virtue	1	2.387	0.156	15.3
Soleil	1	2.407	0.148	16.3
Mean		*2.149*	*0.138*	*15.6*
F ratio		7.55	5.61	1.02*
$p<$		0.001	0.001	0.435

* Log-normalised prior to ANOVA

Comparison between the 1982 and 1992 surveys

Results of the 1992 survey were compared with those of the 1982 survey, consisting of 238 samples (Byers *et al.*, 1987*b*). Total N concentration in the 1982 survey ranged from 1.57% to 2.90%, with a mean of 2.26%. The range was slightly wider in 1992, being from 1.35% to 3.18%, but the mean N concentration (2.24%) was very similar to that in 1982. It is clear from Fig. 1*a* that the frequency distributions of the N concentrations were remarkably similar in the two surveys.

The situation for grain S status was very different. In 1982 the total S concentration ranged from 0.133 to 0.214%, with a mean of 0.172% (Byers *et al.*, 1987*b*). This compares to a range of 0.054-0.209% and a mean of 0.143% in the 1992 survey. It is evident from Fig. 1*b* that the S status in wheat has decreased significantly during the 10 year period. In 1982 no samples contained less than 0.12% total S (the critical value for deficiency; Randall *et al.*, 1981), whereas in 1992 about 7% of the samples had a S concentration below 0.12%, and a further 34% were between 0.12% and 0.14% (range of marginal S deficiency).

Grain N:S ratio is sometimes considered to be a more reliable method of assessing S deficiency, and a value of 17:1 has been suggested as critical (Randall *et al.*, 1981; Byers *et al.*, 1987*a*). Fig. 1*c* shows a clear shift in the range of N:S ratio from 8.8-14.5 in 1982 to 13.2-29.6 in 1992. None of the 1982 samples had a N:S ratio greater than the critical value of 17.0, whereas in 1992 10.0% of the samples had a N:S ratio greater than 17.0. Changes in the grain N:S ratio again indicate strongly a substantial decrease in the S status of British wheat.

Geographical distribution

Regional variation in the grain S concentration occurred. Grain from Scotland contained least S, with most of the samples having less than 0.12% total S. A number of samples from England also had a S concentration below 0.12%, these mainly came from the north of England and East Anglia, and a large number were within the marginal range. Above-average S concentrations occurred mainly in central England, although the distribution of the samples with large S concentrations was not as clearly defined as that shown by Byers *et al.*, (1987*b*) for their 1982 survey. In general, the regional pattern of grain S concentration corresponded with S deposition from the atmosphere estimated by Warren Spring Laboratory (Campbell, Atkins, Bower, Irwin, Simpson & Williams, 1990), indicating the significance of atmospheric S inputs to plant S nutrition. Decreases in the S inputs from the atmosphere during the past 10 years have certainly contributed to the decreased S status in British wheat grain.

As in the previous survey by Byers *et al.* (1987*b*), regional variation in grain N:S ratio was less clear than total S concentration, although the grain from Scotland was more likely to have a greater N:S ratio than the grain from England.

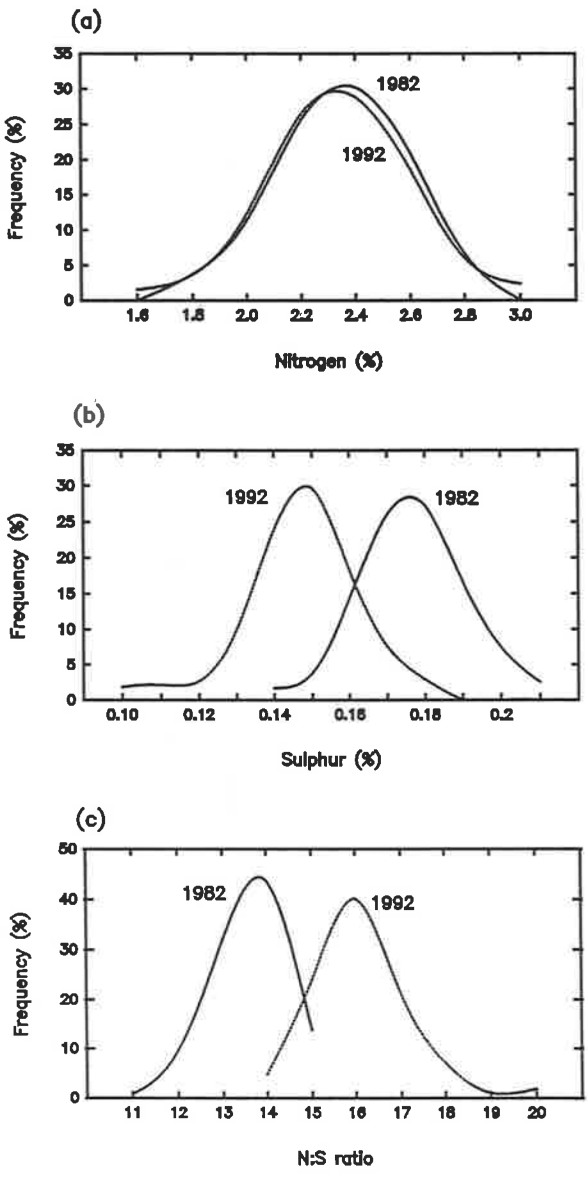

Fig. 1. Changes in the frequency distributions of grain N (*a*), S (*b*) and N:S ratio (*c*) during the 10 year period.

Correlations with quality parameters

Total S correlated closely with protein content, and hence N concentration (Fig. 2), and regression analysis gave the following equation: $(N\%) = 0.37 + 13.12\,(S\%)$ ($n=381$, $R^2=0.65$, $p<0.001$). Most of the wheat grain from Scotland had very small protein concentrations, smaller than the normal range for the non-bread-making varieties, and it is possible that S deficiency was responsible for this, since the supply of N from the soil and fertiliser applied would probably not be limiting under commercial farming practices. Protein content is one important factor in the bread-making performance of flour. Small protein concentrations in grain also result in poor nutritional value. Other investigations have shown an accumulation of non-protein-N in S-deficient wheat grain (Byers & Bolton, 1979; Wrigley, Du Cros, Downie, Archer & Roxburg, 1980; Byers *et al.*, 1987*a*). In addition, changes in the spectrum of storage proteins due to S deficiency have been observed, with a decreased synthesis of S-rich proteins, such as the α-, β-, and γ-gliadins, and an enhanced production of S-poor proteins, e.g. the ω-gliadins (Moss *et al.*, 1981; Timms, Bottomley, Ellis & Schofield, 1981; Wrigley, Du Cros, Fullington & Kasarda, 1984; Byers *et al.*, 1987*a*). It would be interesting to see if these changes occurred in the grain with small S concentration in this survey.

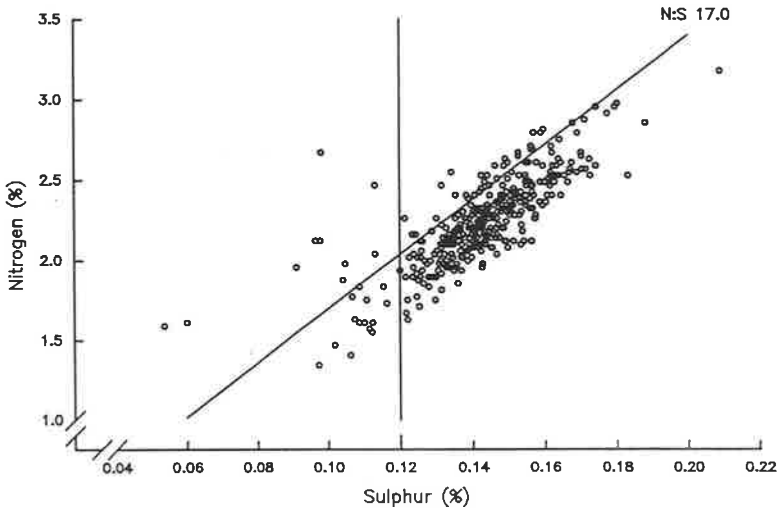

Fig. 2. Relationship between N and S concentrations in wheat grain

Correlation coefficients between grain N and S concentrations, and Hagberg Falling Number and SDS volume are shown in Table 2. The SDS volume is often used to indicate the quality of protein and has been shown to correlate well with loaf volume

(Axford, McDermott, & Redman, 1979). SDS volume correlated with N% better than with S%. The relationship between total S and SDS value can be seen in Fig. 3. Generally grain with a total S less than 0.12% tended to have low SDS values, although to what extent this is caused by a shortage of S is still uncertain, because other factors such as variety and grain protein content are also involved. The relationship did not improve when only bread-making varieties were considered, mainly because these varieties contained greater than 0.12% total S. The correlations between N and S concentrations and Hagberg Falling Number were generally poor.

Table 2. *Correlation coefficients between N%, S% and Falling Number and SDS volume*

	Falling number	SDS volume
N%	0.300	0.509
S%	0.308	0.407

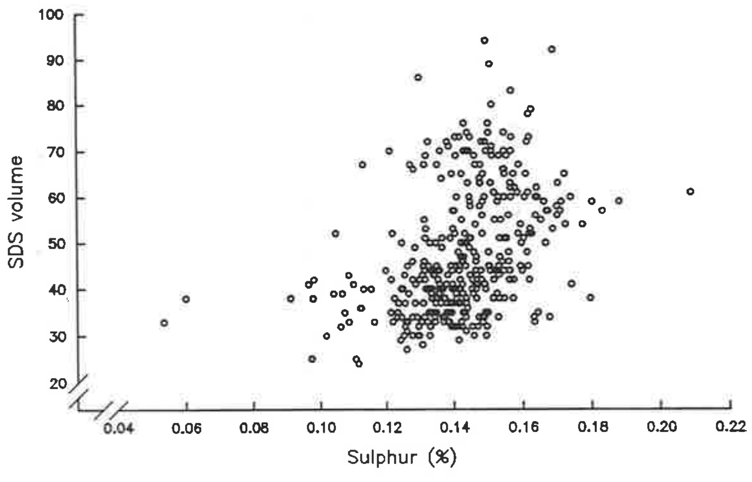

Fig. 3. Relationship between grain S concentration and SDS sedimentation volume

Loaf volume is the most objective measurement of bread-making performance of flour. The relationship between grain S concentration and CBP loaf volume for bread-making varieties is shown in Fig. 4. The bread-making quality of the various varieties under test differed significantly and since none of these particular grain samples were classified as S-deficient, it is not surprising that the relationship between loaf volume and grain S concentration was weak, but statistically significant ($P<0.01$) in a nonlinear regression. However, even within samples of a single variety grain S concentration and protein content did not seem to correlate well with loaf volume in the present study, suggesting that bread-making performance is controlled by complex mechanisms.

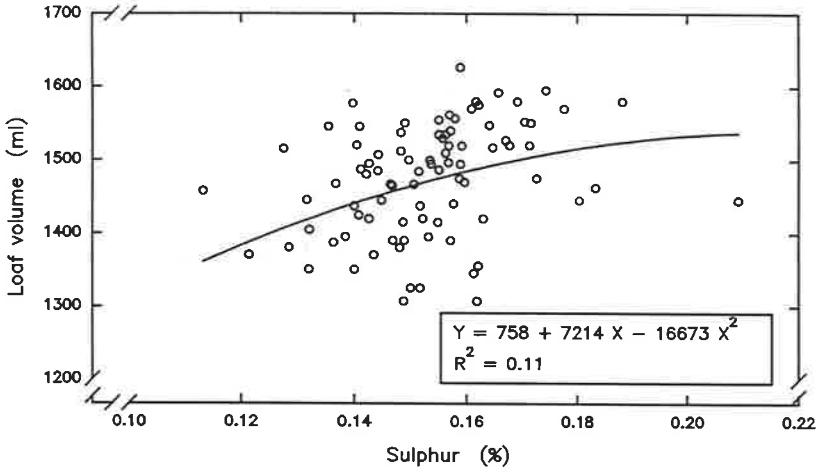

Fig. 4. Relationship between grain S concentration and CBP loaf volume

CONCLUSIONS

Sulphur concentration in British wheat grain has declined significantly during the past 10 years. Approximately 10% of the grain samples collected in 1992 were S-deficient, and a large number were within the marginal range. Bread-making varieties tended to have greater grain N and S concentrations than other varieties. The relationship between grain S concentration and loaf volume was weak, probably because the bread-making varieties were not S-deficient.

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REFERENCES

ANON. (1991). *Flour Testing Panel Methods.* Flour Milling and Baking Research Association, Chorleywood.

AXFORD, D.W.E., MCDERMOTT, E.E. & REDMAN, D.G. (1979). Note on the sodium dodecyl sulfate test of breadmaking quality: comparison with Pelshenke and Zeleny tests. *Cereal Chemistry* **56**: 582-584.

BYERS, M. & BOLTON, J. (1979). Effects of nitrogen and sulphur fertilisers on the yield, N and S content, and amino acid composition of the grain of spring wheat. *Journal of the Science of Food and Agriculture* **30**: 251-263.

BYERS, M., FRANKLIN, J. & SMITH, S.J. (1987*a*). The nitrogen and sulphur nutrition of wheat and its effect on the composition and baking quality of the grain. *Aspects of Applied Biology 15, Cereal Quality*, pp. 337-344.

BYERS, M., MCGRATH, S.P. & WEBSTER, R. (1987*b*). A survey of the sulphur content of wheat grown in Britain. *Journal of the Science of Food and Agriculture* **38**: 151-160.

CAMPBELL, G.W., ATKINS, D.H.F., BOWER, J.S.,IRWIN, J.G., SIMPSON, D. & WILLIAMS, M.L. (1990). The spatial distribution of the deposition of sulphur and nitrogen in the UK. *Journal of the Science of Food and Agriculture* **53**: 427-428.

DAMPNEY, P.M.R. & SALMON, S.E. (1990). The effect of rate and timing of late nitrogen applications to breadmaking wheats as ammonium nitrate or foliar urea-N and the effect of foliar sulphur application. I. Effect on yield, grain quality and recovery of nitrogen in grain. *Aspects of Applied Biology 25, Cereal Quality II.* pp. 229-241.

FRATER, R., HIRD, F.J.R., MOSS, H.J. & YATES, J.R.A. (1960). A role for thiol and disulphide groups in determining the rheological properties of dough made from wheat flour. *Nature* **186**: 451-454.

GRIFFITHS, M.W., KETTLEWELL, P.S., HOCKING, T.J. & WALLINGTON, D.J. (1990). Late-season foliar-applied sulphur and breadmaking quality of winter wheat. *Aspects of Applied Biology 25, Cereal Quality II*, pp. 273-276.

MCGRATH, S.P. (1992). *AFRC Institute of Arable Crops Research, Report for 1991*, pp. 64.

MOSS, H.J., RANDALL, P.J. & WRIGLEY, C.W. (1983). Alteration to grain, flour and dough quality in three wheat types with variation in soil sulfur supply. *Journal of Cereal Science* **1**: 255-264.

MOSS, H.J., WRIGLEY, C.W., MACRITHIE, F. & RANDALL, P.J. (1981). Sulfur and nitrogen fertilizer effects on wheat. II. Influence on grain quality. *Australian Journal of Agricultural Research* **32**: 213-226.

OSBORNE, B.G., DOUGLAS, S., FEARN, T. & WILLIS, K.H. (1982). The development of universal calibrations for measurement of protein and moisture in UK home-grown wheat by near-infrared reflectance analysis. *Journal of the Science of Food and Agriculture* **33**: 736-740.

RANDALL, P.J., SPENCER, K. & FRENEY, J.R. (1981). Sulfur and nitrogen fertilizer effects on wheat. I. Concentrations of sulfur and nitrogen and the nitrogen to sulfur ratio in grain, in relation to the yield response. *Australian Journal of Agricultural Research* **32**: 203-212.

SALMON, S.E., GREENWELL, P. & DAMPNEY, P.M.R. (1990). The effect of rate and timing of late nitrogen applications to breadmaking wheats as ammonium nitrate or foliar urea-n, and the effect of foliar sulphur application II. Effect on milling and baking quality. *Aspects of Applied Biology* **25**, *Cereal Quality II*, pp. 242-253.

SCOTT, N.M., DYSON, P.W., ROSS, J. & SHARP, G.S. (1984). The effect of sulphur on the yield and chemical composition in winter barley. *Journal of Agricultural Science, Cambridge* **103**: 699-702.

SYERS, J.K., SKINNER, R.J. & CURTIN, D. (1987). Soil and fertiliser sulphur in U.K. agriculture. *The Fertiliser Society, Proceedings No. 264.*

TIMMS, M.F., BOTTOMLEY, R.C., ELLIS, J.R.S. & SCHOFIELD, J.D. (1981). The baking quality and protein characteristics of a winter wheat grown at different levels of nitrogen fertilisation. *Journal of the Science of Food and Agriculture* **32**: 684-698.

WALL, J.S. (1971). Disulfide bonds: determination, location and influence on molecular properties of proteins. *Agricultural and Food Chemistry* **19**: 619-625.

WITHERS, P.J.A. (1989). Effect of applied sulphur on yield and quality of winter oilseed rape. *Aspects of Applied Biology* **23**, *Production and Protection of Oilseed Rape and Other Brassica Crops*, pp. 191-197.

WRIGLEY, C.W., DU CROS, D.L., DOWNIE, P.G., ARCHER, M.J. & ROXBURG, C.M. (1980). The sulfur content of wheat-endosperm proteins and its relevance to grain quality. *Australian Journal of Plant Physiology* **7**: 755-766.

WRIGLEY, C.W., DU CROS, D.L., FULLINGTON, J.G. & KASARDA, D.D. (1984). Changes in polypeptide composition and grain quality due to sulfur deficiency in wheat. *Journal of Cereal Science* **2**: 15-24.

ZHAO, F., SYERS, J.K., EVANS, E.J. & BILSBORROW, P.B. (1991). Sulphur and oilseed rape production in the United Kingdom. *Sulphur in Agriculture* **15**: 13-16.

ZHAO, F., MCGRATH, S.P. & CROSLAND, A.R. (1993). Comparison of three wet digestion methods for the determination of plant sulphur by ICP-AES. *Communications in Soil Science and Plant Analysis* (In press).