FORMS OF SULPHUR IN SOILS AND THE EFFECTS OF ADDED SULPHUR AND PHOSPHORUS ON GROWTH OF BARLEY (*HORDEUM VULGARE* L.) IN THREE QUEBEC SOILS

by

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ABSTRACT

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FORMS OF SULPHUR IN SOILS AND THE EFFECTS OF ADDED SULPHUR AND PHOSPHORUS ON GROWTH OF BARLEY (HORDEUM VULGARE L.) IN THREE QUEBEC SOILS

The study was carried out on three Quebec soils belonging to the St. Bernard, Howick and Bearbrook series. The laboratory study revealed that total S contents of soils ranged from 0.032 to 0.060% and were correlated to total N and organic C contents. Extractable sulphate values decreased with depth and top soil values were above critical levels reported for corn and alfalfa. Mineralization resulted in appreciable contribution to SO_4-S. The top soils showed negative sulphate adsorption but subsoils adsorbed considerable sulphate.

The field plot study showed that added S increased barley yields only on the Bearbrook soil in 1978. Tissue S content was increased with added S and critical S concentrations in grain were estimated to be 0.08% and 0.14% for the Bearbrook and St. Bernard soils, respectively. Added S significantly narrowed N:S ratios in grain and critical N:S ratios were estimated to be 24:1 and 15:1 for the Bearbrook and St. Bernard soils, respectively. Added P increased yields, P concentration and uptake on the Bearbrook and Howick soils. Rain added substantial amounts of S during the growing season at all three sites.

RESUME

M.Sc. P.N.S. Mnkeni Ressources Renouvelables

FORMES DE SOUFRE DANS LES SOLS ET LES EFFECTS DE L'ADDITION DE SOUFRE ET DE PHOSPHORE SUR LA CROISSANCE DE L'ORGE (HORDEUM VULGARE L.) DANS TROIS SOLS DU QUEBEC

L'étude a été menée sur trois sols du Québec appartenant aux séries St-Bernard, Howick et Bearbrook. Les résultats de laboratoire ont démontré que les teneurs en S total des sols varient de 0.032 à 0.060% et qu'elles sont reliées aux teneurs en N total et en C organique. Le contenu en sulfate extractible du sol diminue avec la profondeur et les valeurs obtenues dans les horizons de surface dépassent les niveaux critiques nécessaires au mais et à la luzerne. Une contribution appréciable au contenu en sulfate est fournie par minéralisation. Les sols de surface adsorbent les sulfates négativement, alors que les sous-sols révèlent une adsorption considérable de sulfate.

Les essais en parcelles menés en 1978 ont permis de conclure que l'addition de soufre n'augmentait les rendements en orge que dans le sol Bearbrook. La teneur en S des tissus a augmenté et la teneur critique en S du grain a été estimée à 0.08% pour le sol Bearbrook et à 0.14% pour le sol St-Bernard. Le rapport N:S du grain a diminué de facon significative par l'addition de soufre. Des rapports N:S critiques ont été

estimés à 24:1 et à 15:1 pour les sols Bearbrook et St-Bernard, respectivement. L'addition de phosphore a provoqué une augmentation des rendements, de la concentration en P et de son assimilation sur les sols Bearbrook et Howick.

Les précipitations durant la saison de croissance ont fourni des quantités substantielles de soufre à tous les sites.

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FOREWORD

This thesis is presented as two papers, noted as Chapters 2 and 3, respectively, to be submitted for publication. It contains an overall introduction and literature review to both chapters, and ends with a combined conclusion for both chapters.

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INTRODUCTION

Sulphur deficiencies have been reported in many areas around the world and sulphur fertilization is now required in many places to prevent decreases in crop production (Coleman 1966). The factors responsible for this widespread occurrence in sulphur deficiency have also been discussed by Coleman (1966) and include increased use of high analysis fertilizers with little or no sulphur, decreased use of sulphur as a pesticide, and measures taken to limit atmospheric pollution from industrial and domestic sources.

In Quebec, the trend towards the use of high analysis fertilizers has been the same as elsewhere. The use of normal superphosphates decreased from 68% of all phosphate fertilizers used in the Province in 1972 to 28% in 1975 (Quebec Fertilizers 1975). Further atmospheric S supplies from local sources have also been on the decline as reported in a City of Montreal air quality report for the year 1976.[1] As yet no S deficiency has been observed in the province; however, Martel and Zizka (1977a, b) working with two soil types, recorded significant increases in alfalfa dry matter yields due to S fertilization and significant decreases in barley grain yield due to lack of or low

[1] Communante Urbaine de Montreal. Rapport de Qualite d'Air 1976.

level of S fertilization under greenhouse conditions. These findings along with the continuing trend towards the use of high analysis fertilizers indicate that sulphur could be a potential problem and suggest that further study covering more soils is needed to establish the need of crops for S fertilization under field conditions.

Furthermore, reports of Kamprath et al. (1956), Caldwell et al. (1969) and Aulakh and Parischa (1977) indicate that sulphur and phosphorus interact with one another when supplied together to crops. Since phosphate fertilizers already feature prominently in Quebec agriculture, it was of interest to find out to what extent the sulphur and phosphorus nutrition of the test crop would be influenced by fertilization with the two nutrients.

In response to these concerns, a study was undertaken in 1978 with the following objectives:

(i) to determine the distribution of some sulphur fractions in some cultivated surface soils and subsoils in Quebec.

(ii) to assess sulphate mineralization and sorption potential of the experimental soils.

(iii) to determine barley yield response to S fertilization and the S-P interaction under field conditions.

(iv) to assess the contribution of sulphur from precipitation during the growing period.

The information generated from this study is presented in two chapters. Chapter 2 is concerned with the characterization of the experimental soils in terms of the distribution of the various S fractions, and their potential for sulphate mineralization and sorption. Chapter 3 deals with the effects of S and P fertilization on the yield and quality of the barley crop as well as the contribution of S from rain.

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CHAPTER 1

LITERATURE REVIEW

1. Sulphur Status of Soils

1.1. Sulphur Gains and Losses by Soil

The sulphur status of a soil is a result of the interplay of a number of factors including the initial sulphur content of the parent material, the rate at which sulphur is added to the soil and the rate at which it is lost.

The lithosphere contains about 0.06% S which is present mainly as sulphates in sedimentary rocks or as metallic sulphides in igneous rocks, much of which is transformed to sulphate during the process of weathering (Jordan and Ensminger 1958). This native sulphur is supplemented by variable additions from the atmosphere and agricultural practices. The principle source of atmospheric S is SO_2 released in urban and industrial areas by burning sulphurous fuels (Coleman 1966). Accessions of S from the atmosphere can vary from less than 1 kg/ha/year in remote rural areas to more than 130 kg/ha/year near industrial centres. Agricultural practices such as application of superphosphates (12% S) or ammonium sulphate (24% S), manuring, use of sulphurous fungicides and irrigation also add

significant quantities of S to the soil (Mehring and Bennet 1950; Jordan and Ensminger 1958).

Much of the S lost from the soil is accounted for by leaching and to a much less extent by production of volatile S gases. Losses of S from the soil by leaching as measured in lysimeter percolates have been reported by a number of workers (Driebelbis 1947; Pratt and Chapman 1961; Volk and Bell 1945). These losses were found to vary from insignificantly small amounts to as much as 285 pounds per acre per annum. Production of volatile S gases has been demonstrated both in anaerobic and aerobic soils (Lewis and Papavizas 1970; Banwart and Bremner 1975). However, Banwart and Bremner (1976) working with 25 different Iowa soils under aerobic and waterlogged conditions, found that where S was volatized, the amounts were so small (<0.05% of total S) that gaseous losses of S from soil would be insignificant under conditions likely to be encountered in the field.

1.2. Total S in Soils

Various workers have reported values for the total sulphur content of soils (Evans and Rost 1945; Williams and Steinbergs 1955; MacKenzie *et al.* 1967; Tabatabai and Bremner 1972b; Bettany *et al.* 1973). Generally it has been found that soils have a total S content ranging from 0.002 to 3.5% S. In non-

calcareous mineral soils, total S content values range between 0.01 and 0.1% and have been found to be closely correlated with organic matter contents (Tabatabai and Bremner 1972a).

1.3. Inorganic S in Soils

Most noncalcareous soils contain very little inorganic S, usually less than 5% of the total S (Freney et al. 1962; Tabatabai and Bremner 1972b; Bettany et al. 1973). Sulphate and sulphide are the most common forms in soils. Under aerobic conditions the inorganic S fraction consists almost exclusively of sulphates (Freney et al. 1962; Neptune et al. 1975). Sulphide accumulation is known to occur only in soils developed under strongly reducing conditions and in poorly drained subsoils (Whitehead 1964). Other inorganic sulphur compounds that have been reported include elemental S, thiosulphates, tetrathionates, and other polythionates (Smittenberg et al. 1951).

1.4. Organic S in Soils

Over 90% of the total S in most noncalcareous surface soils is present in organic forms (Freney et al. 1962; Lowe 1964; Rehm and Caldwell 1968; Tabatabai and Bremner 1972a; Bettany et al. 1973; Neptune et al. 1975; Scott and Anderson 1976). Although much of it remains uncharacterized, it has been subdivided into broad fractions which are considered to be a useful preliminary for further identification (Anderson 1975).

These fractions include HI-reducible-S, carbon-bonded S and residual or inert S.

The HI-reducible S fraction contains S compounds that are not directly bonded to carbon and it is thought to consist primarily of sulphate esters and ethers in the form of phenolic sulphates, sulphated polysaccharides, choline sulphate, and sulphated lipids (Freney 1967; Tabatabai and Bremner 1972b). In most mineral soils it is the dominant form of organic S constituting between 33 and 78% of the total soil organic S (Lowe 1965; Freney et al. 1970; Tabatabai and Bremner 1972b). Since the S in this fraction can be readily hydrolyzed to inorganic sulphate by acid or alkali, HI-reducible S is considered to be the most labile fraction of soil organic S (Spencer and Freney 1960; Lowe 1965; Cooper 1972). Despite its lability it is generally considered to be too large a fraction to provide a suitable index of plant available S. Nevertheless, Spencer and Freney (1960) reported significant correlation between this fraction and both S uptake and yield on several Australian soils.

The S directly bonded to carbon accounts for between 5 to 35% of the total soil organic S (Lowe 1964; Tabatabai and Bremner 1972; Neptune et al. 1975). Organic soils contain a much higher proportion of C-bonded S(47 to 58%) (Lowe and DeLong 1963). Based on analyses of soil hydrolysates it has been estimated that about half of the C-bonded S occurs as amino acids (Freney

et al. 1972). The nature of the remainder of this fraction is unknown.

The presence of an exceptionally stable fraction of organic S was suggested by Lowe (1964) and later supported by results from other studies (Freney 1967; Bettany et al. 1973; Tabatabai and Bremner 1972b), which indicated that it accounted for between 3 to 59% of the total organic S in mineral soils. According to Lowe (1964) this fraction is so stable that it is unlikely to be of any significance as a potential source of S to plants.

1.5. Organic S Mineralization in Soils

The fact that most of the sulphur in soils is present in the organic fraction and that the amounts of sulphate S in well drained soils are often too small to provide adequate sulphur for plant growth, points out the importance of the conversion of organic sulphur to inorganic forms. The mechanisms of the mineralization of sulphur in soils are still largely unknown. However, since much of the soil organic S is present in the form of sulphate esters, it has been suggested that sulphatases (enzymes which hydrolyze sulphate esters and release inorganic sulphate: $R.O.SO_3^- + H_2O = ROH + HSO_4^-$) may play an important role in the processes whereby organic soil sulphur is mineralized and made available for plant growth (Freney 1967; Skujins

1967). Some evidence to this effect was provided by the work of Houghton and Rose (1976) in which they incubated a variety of synthetic sulphate esters with various soils and found that they were readily hydrolyzed by indiginous enzymes. Apparently many soils are known to contain sulfohydrolysases capable of releasing sulphate from alkyl-, aryl-, and sugar-sulphates (Biederbeck 1978).

The aryl-sulphatases hydrolyze sulphate esters with an aromatic radical (phenolic esters of sulphuric acid) and were the first sulphatases to be detected in soils (Tabatabai and Bremner 1970a). They have been reported from a number of U.S., African and Canadian soils (Tabatabai and Bremner 1970a; Cooper 1972; Kowalenko and Lowe 1975). In the U.S., Tabatabai and Bremner (1970b) examined 27 Iowa surface soils and found that activity of this enzyme was significantly correlated with organic C content but not with pH, S content, N content or texture of the soils. However, Cooper (1972) working with 20 Nigerian soils found a significant correlation between aryl-sulphatase activity and total C, organic S, and HI-reducible-S ($r = 0.878$). This latter correlation was considered most important since HI-reducible sulphate esters are thought to be the natural substrates of sulphatase enzymes in soils. In four Canadian soils aryl-sulphatase activity declined sharply throughout a 14-week incubation period and although there was a slightly significant

correlation between aryl-sulphatase activity and $CaCl_2$-extractable sulphate ($r = 0.49$), Kowalenko and Lowe (1975) suggested that this enzyme was not a major factor in the release of sulphate from these soils.

Despite the uncertainty in mechanism, mineralization of small amounts of sulphate from soil organic matter has been reported by several workers (Barrow 1961; Freney and Spencer 1960; Nelson 1964; Haque and Walmsley 1972; Singh et al. 1978), although some workers (Barrow 1961; White 1959) have also reported soils in which no mineralization occurred during incubation. When soils contain very low amounts of sulphate, the amounts mineralized may be critical in preventing S deficiency in plants. Thus a survey by Hamm et al. (1973) has shown that if the contributions of the mineralized-S are neglected 53% of the soils tested in the Grey Soil Zone and 18% of those from the Black Soil Zone in Saskatchewan can be considered as potentially S-deficient. The importance of the mineralized-S has also been emphasized by Bettany et al. (1974) who found that most of the S taken up by alfalfa from several Saskatchewan soils was obtained from S mineralized during plant growth.

1.6. Sulphate Sorption by Soils

Sulphates which are added to soil or released through organic S mineralization are subject to loss by leaching.

Lysimeter studies reported by Lyon and Bizzelli (1916) show that the removal in drainage water was three to six times as much as was removed by crops. One of the major factors affecting the loss of sulphur by leaching is the extent to which it is retained by soils. S, in the form of sulphate (SO_4^{2-}) or the bisulphate (HSO_4^-) ion, is retained by various colloids in forms resistant to leaching by water. The strength of retention, however, varies in different soils and minerals (Chao et al. 1962a; Gebhardt 1973; Haque and Walimsley 1973). Sulphate so retained is referred to as "adsorbed" (Ensminger 1954).

The mechanisms of sulphate adsorption by soil colloids and model systems have been discussed by various workers (Harward and Reisenauer 1966; Aylmore et al. 1967; Hingston et al. 1967,1968,1972; Mekaru and Uehara 1972; Parfitt 1978). The theory that seems to have gained wide acceptance is that developed by Hingston et al. (1967,1968,1972), which identifies two types of anion adsorption, specific and non-specific. In non-specific adsorption the anions are retained as counter ions in the outer Helmholtz layer or the diffuse layer opposite a net positively charged surface. Specific adsorption on the other hand, occurs when the anion enters into coordination with an oxide metal ion which involves displacement of one anion (ligand) by another. In such systems, the adsorbed anion exchanges for OH or OH_2^+ groups in the inner Helmholtz layer

(Hingston et al. 1972). Sulphate and other anions including fluoride, phosphate and molybdate are adsorbed, specifically in this manner. Evidence for ligand exchange by sulphate with surface OH groups comes from observations that higher pH values are obtained when K_2SO_4 is added to soil suspensions than values obtained with KCl of equal normality (Chao et al. 1965; Bornemisza and Llanos 1967; Mekaru and Uehara 1972).

Sulphate adsorption in soils has been shown to be strongly dependent on pH. Most studies have shown that retention increases with decreasing pH of the equilibrating solution within the pH range 6.5 to 4.0 approximately (Chao et al. 1962; Kamprath et al. 1956; Harward and Reisenauer 1966). Liming soils with sulphate retention properties have been shown to desorb some of the adsorbed sulphate and reduce the amount of sulphate retained (Volk and Bell 1948; Ensminger 1954; Aylmore and Karim 1968). This liming effect is considered to be a direct effect of pH in which Sulphate is displaced by hydroxyl groups (Harward and Reisenauer 1966). By contrast, Mokwunye (1975), working with some Nigerian soils, reported increased retention with increase in pH and suggested that liming activated surface hydroxy-aluminium species.

Phosphate ions have also been shown to affect sulphate adsorption. Kamprath et al. (1956) observed that adsorption of sulphate from solution was reduced by the presence of phosphate

ions dramatically. This was in agreement with findings that the order of adsorption for different anions is phosphate > molybdate > sulphate > nitrate = chloride (Chang and Thomas 1963). This conclusion has been further supported by field and laboratory evidence in which it has been demonstrated that when single superphosphate is applied, phosphate tends to be retained in the upper top soil while sulphate tends to be adsorbed further down in the profile (Ensminger 1954; Aylmore and Karim 1968). However, it should be mentioned that while this distribution pattern may result from the displacement of sulphate by phosphate, other factors may also contribute. Competition from organic matter for anion adsorption sites, for instance, is thought to limit retention of sulphate by topsoils (Fox 1974). Further, in long-term field experiments in Poland, Boratynski and Zietecka (1974) found that differences in sulphate retention could also be attributed to soil texture. They found that in a moderately heavy soil, sulphate was retained in both topsoil and subsoil layers; in a medium soil, sulphate was not retained to a significant extent in the topsoil but large amounts were retained in the subsoil; in a light soil no sulphate remained in the topsoil and measurable retention in the subsoil was observed only at the highest rate of superphosphate application.

The tendency for sulphate to accumulate in subsoil horizons has important consequences for plant nutrition. In some

parts of the U.S.A. where topsoils are lighter in texture and have high pH and phosphate status, sulphur deficiencies have been reported in shallow-rooting crops and in deeper-rooting crops during establishment, but not in established deep-rooting crops which have access to subsoil S supplies (Kamprath et al. 1957; Anderson and Webster 1959; Stanford and Lancaster 1962). However, Metson (1978) cautions that the large accumulations of adsorbed sulphate sometimes found in subsoils may not be necessarily available to plants, as these high sulphate levels may be associated with pH levels so low that aluminum toxicity may be restricting root growth.

2. Sulphur in Plant Nutrition

2.1. Crop Response to S Fertilization

Sulphur plays an important biological role in plant nutrition because it is a constituent of some irreplaceable amino acids and is involved in some metabolic processes (Coleman 1966). Thus addition of sulphur-containing fertilizers to S deficient soils increases their yields and improves their quality. Responses to direct applications of S have been reported in several crops including cereals which are generally regarded as having low S requirements. In Canada, S favourably influenced barley yields in Alberta (Bentley et al. 1955; Nyborg 1968) and in the United States similar responses have been reported in several

states (Conrad 1947; Powers 1923; Anonymous 1964). Beneficial effects of S to corn and other cereals have also been reported and are summarized in a review by Beaton (1966).

2.2. Sulphur-Phosphorus Interaction

Interaction between sulphur and phosphorus has been reported by a number of workers. Aulakh and Parischa (1978) reported a significant negative interaction between S and P on the yield, grain quality, concentration and total removal of sulphur and phosphorus by Moong crops. Caldwell et al. (1969) reported consistent decrease in P content in alfalfa and corn tissue with increasing rates of sulphur. Similar results were reported by Coic (1962) who found that S deficiency encouraged P absorption in a barley experiment. Antagonistic effects of sulphate sulphur on per cent P have also been reported in oats by Nielsen et al. (1967).

2.3. Sulphur Status of Crops

The content of total S in plants has been used as a diagnostic criterion for S adequacy in plants by several workers. Harward et al. (1962), in greenhouse work with alfalfa, obtained highly significant correlation between per cent yield and S content. On the basis of this relationship, they suggested a critical level of 0.22% S for alfalfa. In barley and wheat Gupta (1976) found sulphur concentrations of less than 0.12% in

kernels and boot stage tissue (BST) to be associated with S deficiency in the two crops, while concentrations greater than 0.14% were in the sufficiency range. This was in contrast to the value reported by Ward et al. (1973) in which S levels of less than 0.15% in wheat and barley were considered to be low.

The N:S ratio has also been suggested as a means of defining the S requirements of crops (Dijkshoorn 1960). This index has been shown to be relatively stable for individual crops because sulphur and nitrogen form part of the plant proteins in fixed proportions. Pumphrey and Moore (1965) found the N:S ratio in alfalfa to be relatively constant over a wide range of growth stages and suggested a ratio of 15:1 or above to be indicative of S deficiency. With a normal nutrient regime Dijkshoorn and Wijk (1967) reported N:S ratios of 15:1 in the leaves of many species of field crops, 14:1 in grasses and 17:1 in legumes.

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CHAPTER 2

FORMS OF SULPHUR IN SOILS AND SULPHATE MINERALIZATION AND SORPTION POTENTIAL OF THREE QUEBEC SOILS

4. INTRODUCTION

Generally sulphur deficiency symptoms have not yet been reported in the Province of Quebec. However, the possibility that sulphur might be limiting in crop production has been indicated by recent greenhouse work by Martel and Zizka (1977a,b) in which they reported significant increases in alfalfa dry matter yields due to S fertilization and significant decreases in barley grain yields due to lack of or low level of sulphur. The purpose of the work reported here was to provide information on the sulphur status of some Quebec soils chosen for a field study designed to provide more information on the potential nature of sulphur as a soil fertility problem in Southwestern Quebec. Some information on the sulphur status of Quebec soils is already available from some early work by Lowe and DeLong (1961) and MacKenzie et al. (1967), but was restricted to the distribution of the different forms of sulphur in a few soil types. An additional objective of this work was to obtain information on sulphate sorption and mineralization potential of the experimental soils hitherto unavailable on any Quebec soils.

5. MATERIALS AND METHODS

5.1. Soils

The soils under study were all cultivated soils from each of three field experiment sites each located on a different soil series. The soils included a St. Bernard sandy loam at the Macdonald College Seed Farm, a Bearbrook clay at Hudson and a Howick silty clay loam at Riverfield; all in the Province of Quebec. Samples were obtained from three sampling depths: 0-15 cm, 15-30 cm and 30-45 cm, respectively. The samples were air dried, ground and sieved to less than 2 mm before analysis. Samples which were used for total N, total S and HI-reducible S analysis were ground to pass a 100-mesh screen.

5.2. Chemical Analyses

5.2.1. Total Sulphur

Total sulphur was determined by the alkaline oxidation method of Tabatabai and Bremner (1970) using hydriodic acid reduction and the bismuth sulphide end-point (Dean 1966).

5.2.2. HI-Reducible-Sulphur

This was determined by the method of Freney et al. (1969) using the apparatus described by Tabatabai and Bremner

(1970) and the bismuth sulphide endpoint (Dean 1966).

5.2.3. Inorganic Sulphate

Two forms of inorganic sulphate were extracted. The readily soluble-SO_4 was extracted using 0.01 M $CaCl_2 \cdot 2H_2O$ in a 1:2 soil/solution ratio (Bettany and Halstead 1972). The readily soluble plus adsorbed sulphate was extracted using 0.01 M $Ca(H_2PO_4)_2$ (Fox et al. 1964) in a soil/solution ratio of 1:5. KH_2PO_4 was not used because it results in a very turbid extract (Fox et al. 1964).

Sulphur in the extracts was determined turbidimetrically as outlined by Chensinin and Yien (1950) but the turbidity readings were taken using a Zeiss P.M.Q. II Spectrophotometer at a wavelength of 490 nm.

5.2.4. Total Organic Sulphur and Carbon-bonded Sulphur

Total organic sulphur was calculated as the difference between total sulphur and sulphur extracted by 0.01 M $Ca(H_2PO_4)_2$ solution.

Carbon-bonded sulphur was calculated as the difference between total organic sulphur and HI-reducible sulphur.

5.2.5. General Analytical Methods

Total nitrogen was estimated by the micro-Kjeldahl method as described by Bremner (1960). Organic carbon was

estimated by the wet combustion method of Walkley and Black (Allison 1965). Soil pH was determined in a glass electrode assembly in a 1:2.5 soil/water ratio (Peech 1965).

Extractable phosphorus was determined by the Bray No. 2 method (Bray and Kurtz 1945). This consisted of shaking 2.5 g of soil for one minute with 25 ml of the extracting solution (0.03 N NH_4F and 0.1 N HCl). The phosphorus in the soil extracts was measured on the "Technicon" auto-analyzer using the chlorostannous reduced molybdo-phosphoric blue colour method described by Jackson (1962).

Dithionite-extractable iron and acid ammonium oxalate extractable iron were determined following the methods outlined by McKeague and Day (1966) and modified by Raad, Protz and Thomas (1969). A Perkin-Elmer model 303 atomic absorption, spectrophotometer was used to measure iron in the extracts.

5.3. Incubation Experiment

Ten-gram samples of air dried surface soil were weighed into 250 ml Erlemeyer flasks. Distilled deionized water was added to the soils to bring the moisture content to field capacity followed by mixing which resulted in a loose well aerated sample. The flasks containing the moistened soils were sealed with Saran Wrap[1] and incubated at 30° C. Flasks were

[1]Dow Chemical of Canada Limited, Toronto, Ontario.

weighed periodically and brought to field capacity. After each incubation period soil samples were extracted and analyzed for sulphate sulphur using the same methods that were used for inorganic sulphate in soils.

5.4. Sulphate Sorption

Two and one-half grams of soil were equilibrated with K_2SO_4 solutions (25 ml) ranging in concentration from 5 to 250 μg S ml^{-1}, in 0.01 M $CaCl_2$ solution. Soil suspensions were shaken for one hour, left to equilibrate overnight at 25° C and shaken for another hour the next morning for a total of 24 hours in suspension. Chao et al. (1962a) found no significant difference between continuous and occasional shaking. After equilibration the suspensions were filtered and sulphate determined from an aliquot of the filtrate using the method of Chensinin and Yien (1950). The amount of sorbed sulphate was determined by difference.

6. RESULTS AND DISCUSSION

6.1. Total Sulphur

The total S contents of the three surface soils studied ranged from 0.038 per cent to 0.060 per cent (Table 2) and were within the range of analyses reported in other studies 0.013 to 0.094% S for some Minnesota soils (Rehm and Caldwell 1968), 0.057 to 0.062% S for some Iowa soils (Tabatabai and Bremner 1972) and 0.0088 to 0.076% S for some Saskatchewan soils (Bettany et al. 1973). They also compared very well with those for two other Quebec soils, a Greensboro (0.044% S) and a Sherbrooke (0.053% S) reported by Lowe and DeLong (1961). The total S content decreased appreciably with depth in all three soils. The Bearbrook soil had the highest amounts of total S throughout the three sampling depths followed by Howick and the St. Bernard soil (Table 2). There was a strong correlation between total S content and organic carbon ($r = 0.96$, $p = <0.01$) and total N contents ($r = 0.98$, $p = <0.01$), indicating that most of the sulphur in these soils was organically bound. This is confirmed by the data in Table 2 which show that organic S in these soils ranged from 0.03 to 0.055 per cent and accounted for over 90% of the total S in each soil. Like total S, organic S was significantly ($P = <0.01$) correlated

to organic carbon (r = 0.79). Tabatabai and Bremner (1972a,b) and Harward et al. (1962) reported similar results for Iowa and Oregon soils, respectively.

6.2. HI-Reducible Sulphur

The content of HI-reducible sulphur ranged from 0.017 per cent to 0.019 per cent for the surface soils (Table 2). These values were considerably lower than those of two other Quebec soils, a Greensboro (0.032%) and a St. Rosalie (0.031% S) reported by Lowe (1963) but were within the range of similar analyses reported by Bettany et al. (1973) for some Saskatchewan soils. The HI-reducible values were significantly P = <0.01) correlated with total S (r = 0.97) and consequently followed a similar distribution pattern in the three soils. Although HI-reducible S values are almost identical for the three soils, considerable differences emerge when these values are expressed as a percentage of total S (Table 2). It is evident that the St. Bernard soil with the lowest total S content had the highest proportion (50%) of HI-reducible S compared to the other soils. These differences in proportion were not related to the levels of organic carbon in the soils. Nevertheless, these proportions were within the range (33 to 78%) normally encountered in mineral soils (Lowe 1965).

6.3. Carbon Bonded Sulphur

Due to lack of a reliable procedure for estimating C-bonded S in soils (Freney et al. 1970; Bettany et al. 1973) it was calculated by subtracting HI-reducible S from total S. Consequently the magnitude, proportions and trend of the values obtained (Table 2) are a reverse of those described for HI-reducible S. The proportions were much higher than those reported by Lowe (1963) for three Quebec mineral soils in which C-bonded S estimated by the Raney-Nickel method accounted for 12, 27 and 32% of total S in the three soils. This finding was not entirely surprising because Freney et al. (1970) found that even under optimal conditions, the amount of Raney-Nickel reducible sulphur was 50% less than theoretical quantities of C-bonded sulphur calculated as above.

6.4. C:S and N:S Ratios of the Soils

The data in Table 2 show that the C:S and N:S ratios of the three surface soils analyzed ranged from 40:1 to 55:1 and 4:1 to 5:1, respectively. The C:S ratios were far lower than the average of 109:1.5 for 37 Iowa soils reported by Tabatabai and Bremner (1972a). The N:S ratios were also very low compared to those reported from other parts of the world: 7.2 for 91 Scottish soils (Williams et al. 1960), 8.0 for 90 Australian soils (Williams and Steinbergs 1958) and 9.9 for 16

Oregon soils (Harward et al. 1962). However, the values compared very well with those reported by Lowe (1963) for two other Quebec soils. The Grenville had a C:S ratio of 36:1 and N:S ratio of 5.4:1, while the Greensboro had C:S and N:S ratios of 62:1 and 5.7:1, respectively. Thus, based on the results of these two different studies it seems logical to suggest that narrow C:S and N:S ratios appear to be a property of most Quebec soils.

The N:S ratios remained virtually constant to the 30 cm level but decreased to less than 3:1 further down in the profile for all three soils. A similar trend has been reported by Harper (1959) for six Oklahoma soils.

6.5. Inorganic Sulphate Sulphur

The data on 0.01 M $CaCl_2 \cdot 2H_2O$ extractable sulphate and 0.01 M $Ca(H_2PO_4)_2$ extractable-SO_4 (Table 2) show that the two reagents extracted different amounts of sulphate S from the experimental soils. The phosphate reagent extracted relatively more sulphate than the chloride reagent in all soils at each sample depth indicating that all soils contained considerable amounts of adsorbed sulphate unlike some Iowa soils which contained virtually no adsorbed sulphate (Tabatabai and Bremner 1972b). Regardless of the extractant used, in all soils, the surface soils had larger amounts of extractable sulphate than

Table 1. Some physical and chemical properties of the experimental soils.

Soil Series	Depth (cm)	Texture	pH	Organic Carbon %	Total N %	C:N	Bray No.2 Phosphorus ppm	Dithionite Extractable Fe %	Oxalate Extractable Fe %
St. Bernard	0-15	Sandy clay	5.4	1.98	0.15	13:1	105.8	0.56	0.55
	15-30	loam	5.6	1.44	0.13	11:1	78.3	0.52	0.50
	30-45		6.0	1.10	0.09	12:1	94.2	0.38	0.38
Bearbrook	0-15	Clay	5.1	2.79	0.25	11:1	21.6	1.62	0.96
	15-30		5.4	1.87	0.18	10:1	15.8	1.36	0.76
	30-45		6.0	0.95	0.09	10:1	42.5	0.98	0.60
Howick	0-15	Silty clay	6.0	2.08	0.23	9:1	86.0	0.98	0.71
	15-30	loam	6.1	1.54	0.16	10:1	78.5	1.07	0.81
	30-45		6.2	0.41	0.08	5:1	50.8	1.13	0.75
Standard error (S.E.)			±0.1	±0.31	±0.02		±3.5	±0.02	±0.01

Table 2 . Different forms of sulphur and C:N:S ratios in the experimental soils.

Soil Series	Depth (cm)	Total S (%)	Organic S (%)	HI-Reducible S (%)	HI-Reducible S (% total S)	C-Bonded S (%)	C-Bonded S (% total S)	C:N:S	Extractable-SO_4 0.01 M $Ca(H_2PO_4)_2$	Extractable-SO_4 0.01 M $CaCl_2$
									μg S/g Soil	
St. Bernard	0-15	0.038	0.036	0.019	50	0.017	44.7	55:4:1	24.7	11.3
	15-30	0.034	0.032	0.018	53	0.014	41.0	45:4:1	21.3	9.2
	30-45	0.032	0.030	0.011	34	0.020	63.0	37:3:1	17.9	6.3
Bearbrook	0-15	0.060	0.055	0.017	28	0.039	65.0	51:5:1	41.8	24.2
	15-30	0.048	0.046	0.011	23	0.035	73.0	41:4:1	26.3	13.9
	30-45	0.040	0.037	0.012	30	0.025	63.0	26:2:1	28.9	6.4
Howick	0-15	0.055	0.052	0.019	35	0.032	58	40:4:1	32.2	5.8
	15-30	0.039	0.036	0.015	39	0.021	54	43:4:1	27.9	5.3
	30-45	0.036	0.033	0.011	31	0.023	64	12:2:1	31.7	4.2
Standard error (S.E.)		±0.008		±0.002					±3.2	±1.5

the subsoils in contrast with results from other Eastern Canadian soils (MacKenzie et al. 1967), which showed significant accumulation of extractable-SO_4 in B horizons.

The Bearbrook soil had the highest phosphate extractable sulphate content in the surface soil followed by Howick and St. Bernard soils (Table 2). The same order was followed by the organic carbon and total S contents of the soils (Tables 1 and 2) indicating some relationship between extractable sulphate and organic matter and total S contents of the soils. Harward et al. (1962) also observed that some Oregon soils with high levels of organic matter had high amounts of extractable sulphate. The phosphate extractable sulphate values found in this study were above the critical level of 8 ppm for corn and 10 ppm for alfalfa reported by Fox et al. (1964), indicating that these soils were well supplied with available sulphur.

6.6. Sulphate Sorption by the Soils

Because of the finding that the experimental soils had considerable amounts of adsorbed sulphate an experiment was done to explore the full potential of these soils for sulphate adsorption.

In general the subsoils adsorbed more sulphate than the surface soils (Figures 1 , 2). Similar findings have been reported by other researchers (Williams and Steinbergs 1964,

Ensminger 1954). All the surface soils showed considerable negative adsorption and only started to adsorb when the equilibrium sulphate concentration was in excess of 150 μg S ml^{-1} suggesting that they had very weak sulphate adsorbing properties. During and Martin (1968) reported very similar results for two weakly sorbing New Zealand soils. A number of factors could have contributed to these observations; competition from the more adsorbed phosphate ion (Ensminger 1954, Barrow 1967) can probably explain the lack of substantial sulphate adsorption in the St. Bernard and Howick surface soils which had relatively high extractable phosphorus contents in the surface soils than did the subsoils (Table 1). Competition from organic matter for anion adsorption sites (Fox 1974) is another factor which could have limited the retention of sulphate by the top soils. This is especially true of the Bearbrook soil which had the highest organic carbon content (Table 1).

Free iron oxides have also been associated with sulphate adsorption in soils (Chao et al. 1962b, Scott 1976). In this study the contents of dithionite and acid oxalate extractable iron (Table 1) could only explain the observed differences in sulphate adsorption between surface and subsoils in the Howick soil which had proportionately high amounts of iron in the subsoils relative to the surface soils. However, if only the subsoils are considered, it is evident from the adsorption

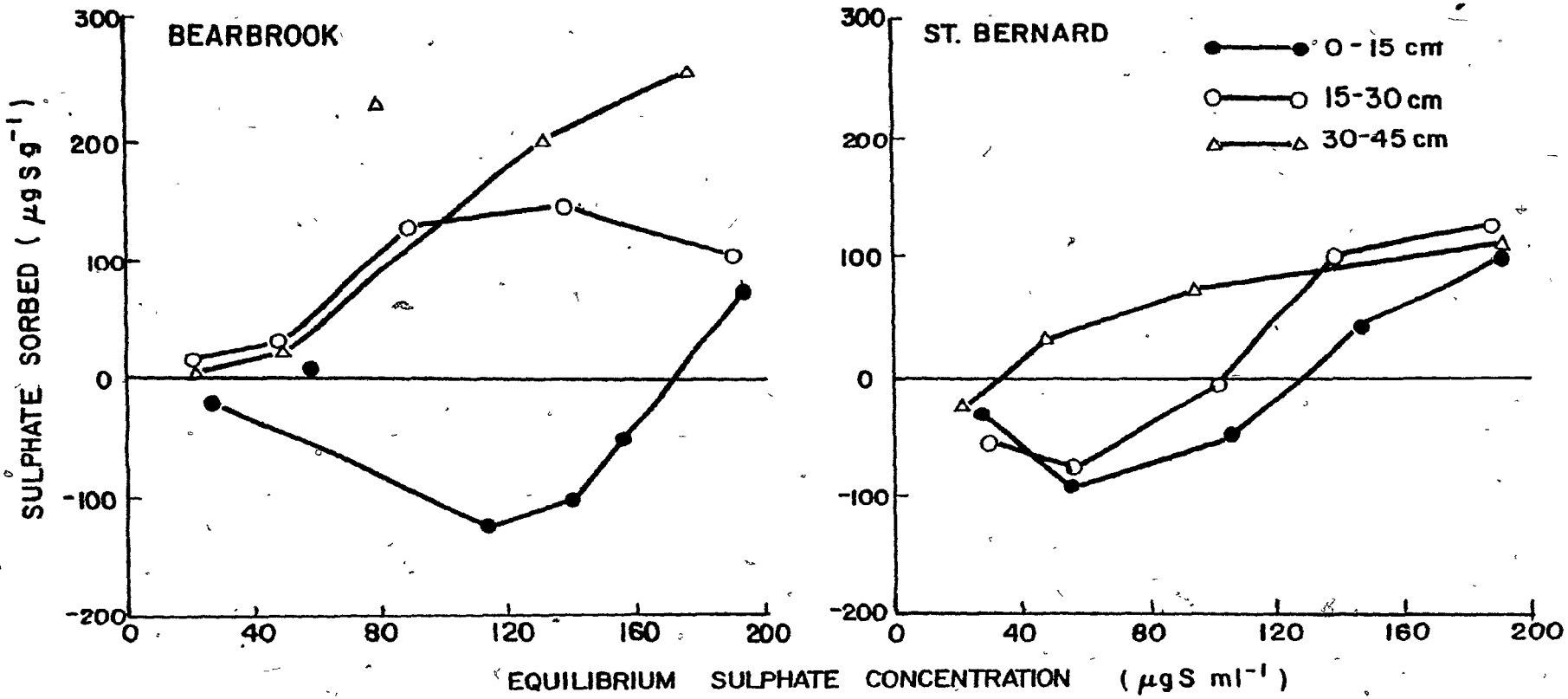

Figure 1. Sulphate sorption isotherms for the Bearbrook and St. Bernard soils.

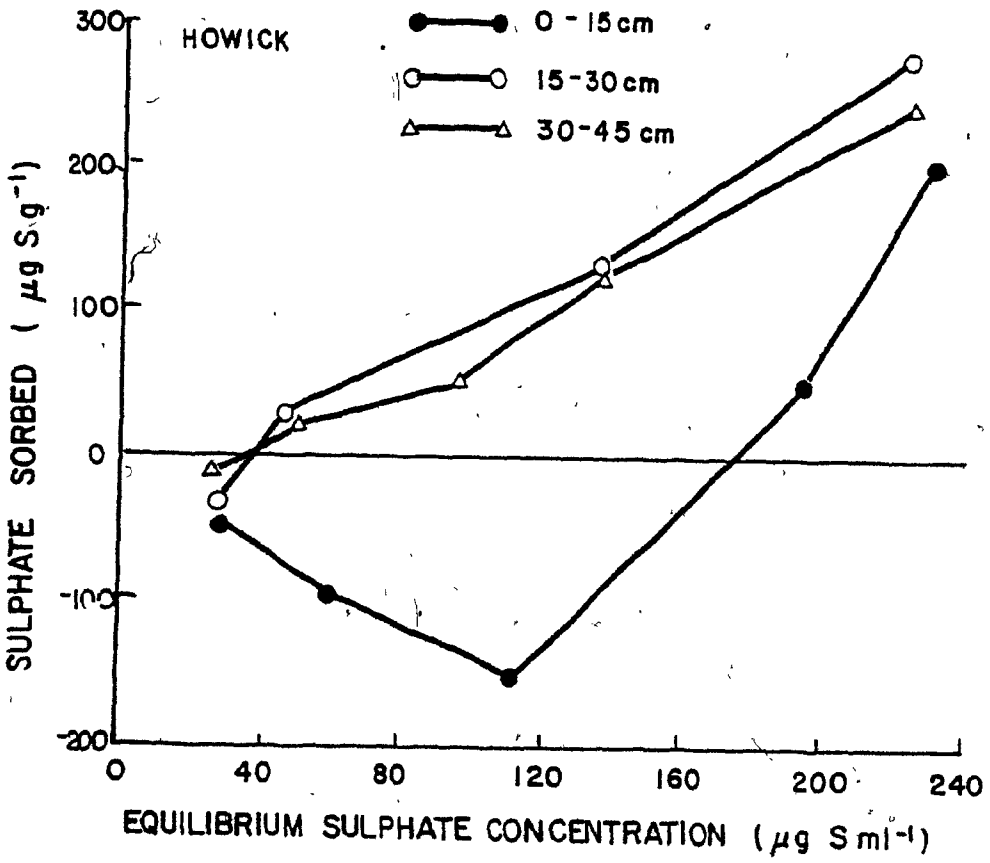

Figure 2. Sulphate sorption isotherms for the Howick soil.

isotherms (Figures 1 and 2) that the St. Bernard soil with the least amounts of the two forms of iron (Table 1) adsorbed less sulphate than the other two soils which had relatively high amounts of iron suggesting that free iron oxides may have contributed to sulphate adsorption to some extent.

Generally, the fact that the surface soils showed such weak sulphate adsorption suggests the possibility that added sulphate could be lost very easily from these soils. This could be especially true for the St. Bernard soil which is a freely draining sandy clay loam.

6.7. Mineralizable Sulphur

The net mineralized sulphate (Tables 3a, 3b) was lower with 0.01 M $Ca(H_2PO_4)_2$ than with 0.01 M $CaCl_2 \cdot 2H_2O$ as extracting reagents in the St. Bernard and Bearbrook soils. This could probably be attributed to the fact that the net sulphate changes involved were too small to be detected by the procedure at the soil/extractant ratio of 1:5 used in this study. Because of this inconsistency, the rest of the discussion will be based mainly on calcium chloride extractable sulphate data.

The levels of net mineralized sulphate fluctuated throughout the incubation period and generally no soil released more than 6.0 ppm of sulphate S (Table 3a). On average each soil mineralized about 3 ppm sulphate S throughout the seven-week

Table 3a . Changes in 0.01 M $CaCl_2$ extractable SO_4-S with time during incubation.

Soil Series	Net Changes in SO_4-S µg /g Soil				
	Days				
	7	14	21	35	49
St. Bernard	3.4	3.0	5.0	2.0	3.0
Bearbrook	4.2	3.6	3.6	2.6	1.5
Howick	4.4	4.0	5.5	1.0	1.5

Table 3b. Changes in 0.01 M $Ca(H_2PO_4)_2$ extractable SO_4-S with time during incubation.

Soil Series	Net Changes in SO_4-S µg /g Soil				
	Days				
	7	14	21	35	49
St. Bernard	0.0	-1.5	0.0	0.0	17.0
Bearbrook	5.0	0.50	0.50	ND	9.5
Howick	12.5	15.0	40.0	37.5	50.0

ND - not determined

incubation period which converts to 6.75 kg S/ha. This is considered to be a significant contribution for soils which are already relatively high in sulphate sulphur as noted before.

Throughout the incubation period, the Howick soil showed substantially greater net mineralizable sulphate extractable by calcium phosphate (Table 3b) reflecting a greater microbial activity probably due in part to its very narrow C;S ratio (Table 2). However, the C:S ratio of the other soils were still far narrower than the C:S ratio of 200:1 which Singh et al. (1978) found to be associated with net S immobilization.

7. CONCLUSIONS .

1. The total S values ranged from 0.032 to 0.06 per cent and were highly correlated with total N and organic carbon indicating that most of the sulphur was organically bound. Total S values decreased with depth in all three soils.

2. The C:S and N:S ratios were lower than similar ratios reported from other parts of the world but compared well with those reported for other Quebec soils suggesting that narrow C:S and N:S ratio could be á property of most Quebec soils.

3. Extractable sulphate S decreased with depth in contrast to reports from other Eastern Canadian studies which indicated substantial accumulations of sulphate in the subsoils. The values were above critical levels reported for alfalfa and corn indicating that the soils were well supplied with available sulphur.

4. The surface soils showed very weak sulphate adsorption properties suggesting the possibility of losses of S from added sulphur.

5. The mineralizable S analyses indicated that all three soils had some capacity to mineralize sulphur. On average each soil

contributed about 6.75 kg S/ha during the seven-week incubation period which was considered substantial for soils which are already relatively high in sulphate S.

In general, the results obtained in this study show that the three soils had total S values which were well above those reported in S deficient areas. The available sulphate data were generally above critical limits reported for several crops and mineralization resulted in substantial contribution of SO_4-S to the soils. Thus the results indicate that the soils had adequate reserves of sulphur which could meet crop requirements if readily available.

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PREFACE TO CHAPTER 3

The preceding chapter provided information on levels of different forms of sulphur in soils and the potential of the experimental soils to mineralize sulphate. This information alone is not sufficient to predict the need for S fertilization in the area. To be able to draw more reliable conclusions, the next chapter reports results of experiments designed to determine crop response to S application under normal field conditions and to assess contributions of S from rain.

Chapter 3

EFFECTS OF SULPHUR AND PHOSPHORUS FERTILIZATION ON THE YIELD AND QUALITY OF BARLEY (*HORDEUM VULGARE* L.) IN THREE QUEBEC SOILS

9. INTRODUCTION

Concern over the potential of sulphur as a soil fertility problem in the Province of Quebec has already been expressed (Chapter 2). It is based on an apparent trend towards the use of high analysis fertilizers in the province and on findings from studies by Martel and Zizka (1977a,b) which indicated a favourable response to S fertilization by alfalfa and barley. Their findings were based on greenhouse work and presumably did not take into account contributions of S from precipitation, the importance of which has been established in other studies (Eriksson 1960; Jordan and Reisenauer 1957; Johanson 1959; Walker 1955). Furthermore, the effect of S on depressing uptake of P and vice versa has been noted (Caldwell *et al.* 1969; Jones and Ruckman 1972; Nielson *et al.* 1967; Aulakh and Paris-cha 1978). Consequently, the work reported here was undertaken to provide more information on the effects of S fertilization on barley yield and quality under field conditions, to assess any S-P interaction in the field and to assess contributions of S from rain during the growing season.

10. MATERIALS AND METHODS

10.1. Field Experiments

The field experiments were carried out in 1978 and 1979 on three soils. The 1979 plots were located close to the previous year's in order to maximize uniformity in soil conditions. The three soils included a St. Bernard sandy clay loam located at the Macdonald College Seed Farm, a Howick silty clay loam near Riverfield and a Bearbrook clay near Hudson.

Barley (Hordeum vulgare L.) was seeded with a 4-run tractor mounted custom built drill. Each plot of size 1.25 m x 8 m consisted of four rows spaced 20 cm apart. The treatments were arranged in a factorial combination of four levels of S (0, 20, 40 and 60 kg S/ha in 1978 and 0, 10, 20 and 40 kg S/ha in 1979) with three levels of P (0, 75 and 150 kg P_2O_5/ha) added as gypsum and triple superphosphate (1.4% S), respectively. The two fertilizers were placed directly with the seed. Uniform applications of 75 kg N/ha as NH_4NO_3 and 120 kg K_2O/ha as muriate of potash were broadcast immediately after seeding. A randomized complete block design was used with three replicates per site.

The middle six meters portion of each plot was harvested at maturity using a Gravely with a cutting bar attachment.

After harvesting the crop from each plot was weighed, threshed and cleaned. The grain obtained was weighed and the straw weight obtained by difference. Yield results were then adjusted to 0% moisture content after gravimetric determination of the moisture content in the different samples.

10.2. Rain Water Sampling and Analysis

Rain water at each site was collected in two polyethylene tubes 2 m long and 6 cm in diameter, set into the soil and fitted with funnels at the open ends. The water collected in each tube was measured and sampled at the end of each month from May to August. The samples obtained were filtered and analyzed for sulphate-S according to the method of Wurzburger (1970).

10.3. Plant Tissue Analysis

Grain and straw samples were dried at 70° C and ground to less than 2 mm. Plant material was then digested in a 2:1 mixture of HNO_3 and $HClO_4$ for total S and total P determination. Some plant material was also digested using conc. H_2SO_4 and 30% H_2O_2 following the procedure of Miller and Miller (1948) for NH_4-N determination.

Total P was measured using the Vanadomolybdo-phosphoric acid method (Jackson 1958) and NH_4-N was measured following the

alkaline phenol hypochlorite method as described by O'Brien and Fiore (1962). Total S was determined turbidmetrically following the procedure of Tabatabai and Bremner (1970).

Per cent protein in grain was calculated from the tissue N content by multiplying by 6.25.

11. RESULTS

11.1. Grain and Straw Yields

Added S alone significantly increased grain yields at the 40 kg S/ha rate on the Bearbrook soil in 1978 (Table 4a). However, in 1979 added S resulted in variable grain yield response on this soil (Table 4b) which showed that added S did not have a consistent effect on this soil. The Howick and St. Bernard soils showed non-significant effects to S fertilization (Tables 4a,b and 16a-c). Straw yields were not significantly influenced by added S on all soils (Tables 5a,b).

Added P resulted in significant grain and straw yield increases on the Bearbrook soil in both years of study and on the Howick soil in 1978 (Tables 4a,b and 5a,b). However, there was no significant S x P interaction at the 0.05 probability level observed on either grain or straw yields (Tables 16a-c).

11.2. S Concentration in Grain and Straw

The total S concentration in barley ranged from 0.058 to 0.174 per cent for grain (Tables 6a,b) and 0.061 to 0.209 per cent for straw (Tables 7a,b). Added S increased the S concentration significantly in grain on the St. Bernard and Bearbrook soils in 1979 and in straw on all three soils in 1978 (Tables 16a-c).

Table 4a. S and P effects on yield of barley grain grown on two soils in 1978.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	20	40	60	P Means
		Yield, kg/ha*				
Bearbrook	0	1830c	1840bc	2040b	1860bc	1893b
	75	2420a	2550a	2580a	2440a	2498a
	150	2600a	2550a	2490a	2560a	2550a
	S Means	2283	2313	2370	2287	
Howick	0	1886d	1899d	1975cd	1908d	1917b
	75	2338abc	2034bcd	2213abcd	2199abcd	2196a
	150	2405ab	2267abcd	2325abc	2423a	2355a
	S Means	2210	2067	2171	2177	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 4b. S and P effects on yield of barley grain grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	10	20	40	P Means
		Yield, kg/ha*				
St. Bernard	0	2260ab	2204ab	2475ab	2067b	2252
	75	2057b	2622ab	2096ab	2748a	2381
	150	2455ab	2099ab	2369ab	2526ab	2362
	S Means	2257	2308	2314	2447	
Bearbrook	0	1852cd	1818d	1884bcd	2035abcd	1897b
	75	2119abc	1856cd	2170ab	2221a	2092a
	150	2154ab	2152ab	2307a	2203a	2204a
	S Means	2042ab	1942b	2120a	2153a	
Howick	0	1809	1773	1840	1720	1786
	75	1878	1588	1819	1813	1775
	150	2025	1837	1752	1823	1859
	S Means	1904	1733	1804	1786	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 5a. S and P effects on yield of barley straw grown on three soils in 1978.

Soil Series	Added P, kg P_2O_5/ha	Added S, kg/ha				P Means
		0	20	40	60	
		Yield, kg/ha*				
St. Bernard	0	3160abc	3590ab	3480abc	3750ab	3495
	75	3720ab	3230abc	3190abc	3190abc	3332
	150	3890a	2770c	3110abc	3030bc	3199
	S Means	3591	3199	3256	3323	
Bearbrook	0	1430b	1330b	1480b	1390b	1408b
	75	1970a	1990a	1930a	2080a	1993a
	150	1950a	1860a	2010a	1870a	1923a
	S Means	1783	1727	1807	1780	
Howick	0	1450e	1470e	1510de	1490de	1480b
	75	1760abc	1690abcde	1640cde	1770abc	1715a
	150	1890ab	1720abcd	1650bcde	1910a	1793a
	S Means	1700	1627	1600	1723	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 5b. S and P effects on yield of barley straw grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	10	20	40	P Means
		Yield, kg/ha*				
St. Bernard	0	2118	2338	2258	1777	2123
	75	2165	2498	1987	2474	2281
	150	2145	1946	2119	2229	2109
	S Means	2142	2261	2122	2160	
Bearbrook	0	1171d	1217cd	1293bcd	1213cd	1224b
	75	1414abc	1241bcd	1342bcd	1467ab	1366a
	150	1379abcd	1359abcd	1471ab	1576a	1446a
	S Means	1321ab	1273b	1369ab	1419a	
Howick	0	1118	1057	1321	958	1114
	75	1113	1199	1160	1122	1148
	150	1289	1143	1177	1204	1203
	S Means	1173	1133	1219	1095	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Added P had a significant depressing effect on S concentration in barley grain and straw on the Bearbrook and Howick soils in 1978 (Tables 6a,b and 7a,b) which tended to be more pronounced in the presence of high levels of added S. A significant negative S x P interaction on S concentration in grain was observed only on the Bearbrook soil in 1979 (Tables 6b and 16b).

Although the yields were not significantly influenced by added S, an attempt was made to estimate critical S concentration values in barley grain by plotting grain yields (expressed as % of the control treatment) against their corresponding per cent total S values (Figure 3). The curve obtained for the Bearbrook soil shows that yields decreased at S content values below 0.08% and above 0.11%. No curve could be fitted on the St. Bernard soil data but it is clear from the way the points are spread that S content values above 0.14% were generally associated with higher grain yields. Obviously, accurate critical S values cannot be obtained from the graph; however, roughly they could be within range of 0.08% and 0.14% for the Bearbrook and St. Bernard soils, respectively.

Ward et al. (1973) reported a critical value of 0.15% S for barley and wheat which is in fair agreement with the value obtained for the St. Bernard soil. However, the fact that the two critical levels estimated in this study are not identical

Table 6a. S and P effects on per cent total S in barley grain grown on three soils in 1978.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	20	40	60	P Means
		S, %*				
St. Bernard	0	0.137	0.132	0.166	0.156	0.148
	75	0.134	0.149	0.149	0.133	0.141
	150	0.163	0.152	0.162	0.155	0.158
	S Means	0.145	0.144	0.159	0.148	
Bearbrook	0	0.085ab	0.072ab	0.077ab	0.083ab	0.079a
	75	0.086ab	0.085ab	0.096a	0.095a	0.091a
	150	0.071ab	0.073ab	0.062b	0.058b	0.066b
	S Means	0.080	0.077	0.079	0.079	
Howick	0	0.142ab	0.174a	0.148ab	0.113b	0.144a
	75	0.154ab	0.123ab	0.114b	0.125ab	0.129ab
	150	0.121ab	0.118b	0.128ab	0.104b	0.118b
	S Means	0.139	0.138	0.130	0.114	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 6b. S and P effects on per cent total S in barley grain grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	10	20	40	P Means
		S, %*				
St. Bernard	0	0.130ab	0.169a	0.145ab	0.137ab	0.145
	75	0.142ab	0.154a	0.136ab	0.150a	0.146
	150	0.111b	0.139ab	0.162a	0.166a	0.145
	S Means	0.128b	0.154a	0.147a	0.151a	
Bearbrook	0	0.058d	0.130a	0.116ab	0.116ab	0.105
	75	0.089bcd	0.067cd	0.109ab	0.105abc	0.092
	150	0.087bcd	0.118ab	0.101abc	0.098bc	0.101
	S Means	0.078b	0.105a	0.109a	0.106a	
Howick	0	0.128	0.128	0.115	0.112	0.120
	75	0.114	0.096	0.137	0.148	0.124
	150	0.141	0.128	0.140	0.109	0.129
	S Means	0.127	0.118	0.131	0.122	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 7a. S and P effects on per cent total S in barley straw grown on three soils in 1978.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	20	40	60	P Means
		S, %*				
St. Bernard	0	0.101c	0.149abc	0.175abc	0.161abc	0.146
	75	0.125bc	0.133abc	0.171abc	0.139abc	0.142
	150	0.125bc	0.179ab	0.209a	0.154abc	0.167
	S Means	0.117b	0.154ab	0.185a	0.151ab	
Bearbrook	0	0.115bcd	0.157ab	0.169a	0.165a	0.152a
	75	0.081de	0.061e	0.071de	0.145abc	0.089b
	150	0.103cde	0.097de	0.090de	0.078de	0.092b
	S Means	0.099b	0.104ab	0.110ab	0.129a	
Howick	0	0.150b	0.173ab	0.173ab	0.190a	0.172a
	75	0.149b	0.164ab	0.164ab	0.173ab	0.163ab
	150	0.149b	0.149b	0.157b	0.159b	0.154b
	S Means	0.149b	0.162ab	0.165ab	0.174a	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 7b. S and P effects on per cent total S in barley straw grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	10	20	40	P Means
		S, %*				
St. Bernard	0	0.203	0.222	0.219	0.217	0.215
	75	0.199	0.231	0.201	0.217	0.212
	150	0.212	0.202	0.208	0.204	0.207
	S Means	0.205	0.218	0.209	0.213	
Bearbrook	0	0.152a	0.154a	0.133ab	0.158a	0.149a
	75	0.111ab	0.110ab	0.108ab	0.147a	0.119b
	150	0.138ab	0.149a	0.086b	0.145a	0.130ab
	S Means	0.133ab	0.138ab	0.109b	0.150a	
Howick	0	0.110	0.118	0.130	0.133	0.123
	75	0.112	0.119	0.129	0.124	0.121
	150	0.123	0.119	0.129	0.124	0.124
	S Means	0.115	0.119	0.129	0.127	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

suggests that critical values may vary from soil to soil and in this case reflects differences on the availability of S from the two soils.

11.3. S Uptake by Barley Grain and Straw

Sulphur uptake by barley grain (Tables 8a,b) was only increased significantly by added S on Bearbrook soil in 1979 (Table 16b). The largest increase was obtained by application of 10 kg S/ha. Added P significantly increased S uptake on the Bearbrook soil in 1978 at its low rate of application (75 kg P_2O_5/ha) but had no effect at its high rate (Tables 8a and 16b). The increase was a consequence of P addition increasing per cent S in the grain and also grain yield (Tables 4a and 6a).

Addition of S and P had no effect on the uptake of S by barley straw (Tables 9a,b and 16a-c).

11.4. Per Cent Protein in Grain

The per cent protein in grain ranged from 8.4 to 16.3% (Tables 10a,b). Generally the values for both years compared well on the Bearbrook and St. Bernard soils but showed marked differences on the Howick soil. Added S alone significantly increased per cent protein in grain only on the Bearbrook soil in 1978 (Table 10a) but a positive trend was also observed in 1979 (Table 10b). These results suggest that added S enhanced

Table 8a. S and P effects on S uptake by barley grain grown on two soils in 1978.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	20	40	60	P Means
		S, kg/ha*				
Bearbrook	0	1.56bc	1.35c	1.55bc	1.56bc	1.51b
	75	2.03abc	2.17ab	2.49a	2.33a	2.25a
	150	1.86abc	1.87abc	1.56bc	1.48bc	1.69b
	S Means	1.82	1.80	1.87	1.79	
Howick	0	2.70	3.26	3.01	2.41	2.84
	75	2.92	2.49	2.50	2.92	2.87
	150	3.57	2.67	2.99	2.50	2.77
	S Means	3.06	2.80	2.83	2.61	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 8b. S and P effects on S uptake by barley grain grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	10	20	40	P Means
		S, kg/ha*				
St. Bernard	0	2.99	3.76	3.56	2.80	3.28
	75	3.14	4.00	2.79	4.13	3.40
	150	2.77	2.93	3.68	4.22	3.51
	S Means	2.97	3.56	3.34	3.72	
Bearbrook	0	1.12b	2.36a	2.20a	2.34a	2.01
	75	1.78ab	1.24b	2.38a	2.35a	1.94
	150	1.92ab	2.67a	2.34a	2.16a	2.27
	S Means	1.61	2.09	2.31	2.28	
Howick	0	2.32	2.31	2.16	2.06	2.21
	75	2.14	1.69	2.60	2.72	2.28
	150	2.85	2.36	2.15	1.93	2.32
	S Means	2.44	2.12	2.31	2.24	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 9a. S and P effects on S uptake by barley straw grown on three soils in 1978.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	20	40	60	P Means
		S, kg/ha*				
St. Bernard	0	3.06b	5.44ab	6.13a	6.02a	5.16
	75	4.61ab	4.30ab	5.39ab	4.50ab	4.70
	150	4.85ab	4.91ab	6.51a	4.79ab	5.26
	S Means	4.17b	4.88ab	5.10ab	6.00a	
Bearbrook	0	1.65bcd	2.08abcd	2.49ab	2.30abc	2.13
	75	1.57bcd	1.23d	1.38cd	3.02a	1.80
	150	1.99bcd	1.84bcd	1.81bcd	1.46cd	1.78
	S Means	1.74	1.72	1.90	2.26	
Howick	0	2.85b	3.32ab	3.39ab	3.63ab	3.30
	75	3.50ab	3.35ab	3.67ab	3.78ab	3.58
	150	3.60ab	3.20ab	3.64ab	3.86a	3.58
	S Means	3.32	3.29	3.57	3.76	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 9b. S and P effects on S uptake by barley straw grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha				P Means
		0	10	20	40	
		S, kg/ha*				
St. Bernard	0	4.33ab	5.36ab	4.96ab	3.84b	4.62
	75	4.33ab	5.85a	4.00b	5.38ab	4.89
	150	4.59ab	3.98b	4.46ab	4.58ab	4.40
	S Means	4.42	5.06	4.47	4.60	
Bearbrook	0	2.12ab	1.88ab	1.73ab	1.94ab	1.92
	75	1.59ab	1.39ab	1.47ab	2.14ab	1.65
	150	1.84ab	2.14ab	1.26ab	2.28a	1.88
	S Means	1.85ab	1.80ab	1.49b	2.12a	
Howick	0	1.21	1.23	1.75	1.26	1.36
	75	1.25	1.51	1.64	1.39	1.45
	150	1.58	1.35	1.47	1.50	1.48
	S Means	1.35	1.36	1.62	1.38	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 10a. S and P effects on per cent protein in barley grain grown on three soils in 1978.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	20	40	60	P Means
		Protein, %*				
St. Bernard	0	13.4	12.1	12.7	14.9	13.3
	75	13.0	13.1	16.3	15.7	14.0
	150	13.2	15.7	16.2	10.6	13.9
	S Means	13.2	13.6	15.1	13.0	
Bearbrook	0	12.7e	14.1abc	14.1abc	14.3abc	13.8
	75	14.5abc	13.3bc	13.6abc	15.7a	14.3
	150	15.4ab	13.5abc	14.0abc	15.3ab	14.5
	S Means	14.2ab	13.6b	13.9ab	15.1a	
Howick	0	9.1	9.6	9.1	9.4	9.3
	75	8.7	9.6	8.6	8.9	8.9
	150	8.4	9.4	9.1	8.9	8.9
	S Means	8.7	9.5	8.9	9.0	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 10b. S and P effects on crude protein in barley grain grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	10	20	40	P Means
		Protein, %*				
St. Bernard	0	14.5ab	14.7ab	14.8ab	14.1b	14.5
	75	14.8ab	14.8ab	14.7ab	14.7ab	14.8
	150	14.1b	15.8a	14.9ab	14.6ab	14.8
	S Means	14.5	15.1	14.8	14.4	
Bearbrook	0	12.5	12.6	12.8	13.2	12.8
	75	12.4	12.6	12.9	12.9	12.6
	150	12.4	12.6	12.8	12.4	12.6
	S Means	12.4	12.6	12.8	12.9	
Howick	0	15.8ab	14.2c	15.6ab	15.7ab	15.3
	75	15.7ab	14.6bc	15.1abc	15.5ab	15.2
	150	15.1abc	14.9bc	16.0a	15.1abc	15.3
	S Means	15.5a	14.6b	15.6a	15.4a	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

uptake and utilization of nitrogen on this soil for protein synthesis. The positive effect of added S on protein content has also been reported on other crops by Jordan (1967) and Aulakh and Parischa (1978). Added P had no effect on per cent protein in barley grain (Tables 16a-c).

11.5. N:S Ratios in Barley Grain

The N:S ratios in grain calculated in this study are presented in Table 11. The average N:S ratios in the absence of added S were 18.1, 36.2 and 19.7 for the St. Bernard, Bearbrook and Howick soils respectively. These values were all above the critical limit of 16:1 proposed by Dijkshoorn and Van Wijk (1967) suggesting that the crops were inadequately supplied with S. Application of S significantly narrowed the ratios on the St. Bernard and Bearbrook soils (Tables 11 and 16a,b). Addition of 10 kg S/ha alone decreased the N:S ratio in grain from 18.1 to 14.2 and 36.2 to 15.5 on the St. Bernard and Bearbrook soils respectively, indicating an adequate supply of S at this rate of S fertilization.

An attempt was made to relate N:S ratios in grain with grain yields as done for S concentration. The relationship obtained (Figure 4) was less defined compared to the one obtained with S concentration (Figure 3). However, it is evident that for the St. Bernard soil, grain yields tended to decrease

Table 11. S and P effects on N:S ratios in barley grain grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	10	20	40	P Means
		N:S*				
St. Bernard	0	18.1ab	14.2c	16.7abc	16.5abc	16.4
	75	16.7abc	15.9bc	18.1abc	15.7bc	16.6
	150	20.3a	18.2ab	15.3bc	14.5bc	17.1
	S Means	18.4a	16.7ab	16.1b	15.5b	
Bearbrook	0	36.2a	15.5c	17.5c	18.4c	21.9
	75	23.7bc	29.8ab	17.6c	19.8c	22.7
	150	22.5bc	19.6c	21.7c	20.4c	21.1
	S Means	27.5a	21.6b	18.9b	19.5b	
Howick	0	19.7	17.9	22.2	28.5	22.1
	75	23.4	26.4	23.9	17.1	22.7
	150	17.2	18.9	20.7	22.5	19.9
	S Means	20.1	21.1	22.3	22.7	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

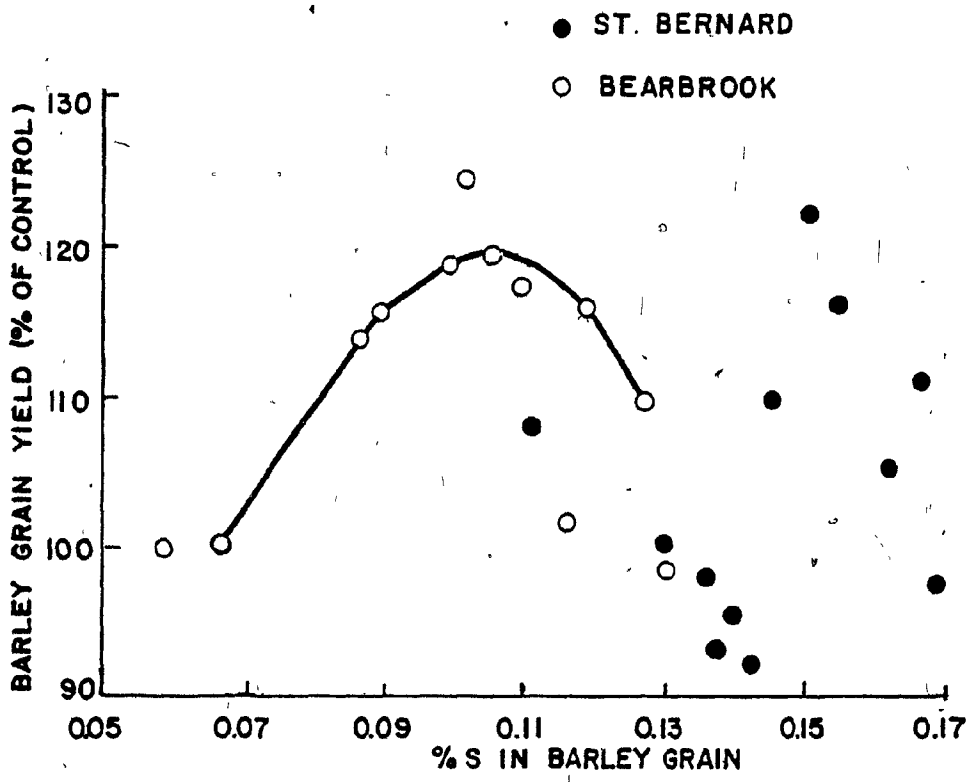

Figure 3. Barley grain yield as related to per cent total S in grain.

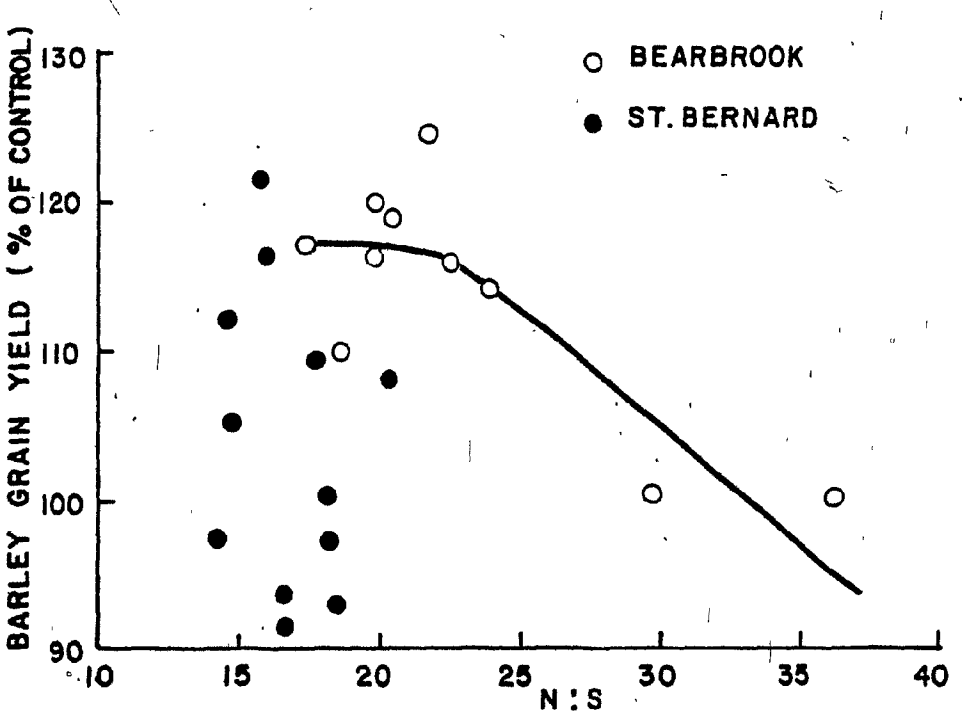

Figure 4. Barley grain yield as related to N:S ratios in the grain.

at N-S ratios above 15:1 and on the Bearbrook soil higher yields were generally associated with N-S ratios below 24:1. These two values would appear to be the approximate critical N-S ratios in barley grain grown on the two soils. The two estimates are not identical which may again reflect differences on the availability of N and S on the two soils and caution against generalizing one value for all soil types.

11.6. P Concentration in Grain and Straw

The total P concentration in barley ranged from 0.036 to 0.185 per cent for straw (Tables 13a,b) and 0.323 to 0.577 per cent for grain (Tables 12a,b). The P concentration was comparatively higher in grain than in straw at all levels of added S and P combinations. Added S increased P concentration in grain only on the Howick soil in 1978 (Tables 12a and 16a-c). In straw, added S significantly increased P concentration on the Bearbrook and Howick soils in 1978 and 1979 respectively (Tables 13a,b and 16b,c). Generally applications of 10 or 20 kg S/ha depending on soil and year resulted in relatively large increases in P concentration while smaller increases or decreases were recorded with subsequent S additions.

Added P resulted in increases in P concentration in barley grain on the Bearbrook soil in both years (Tables 12a,b) and in straw on the Bearbrook and Howick soils in 1979 (Tables

Table 12a. S and P effects on per cent total P in barley grain grown on three soils in 1978.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	20	40	60	P Means
		P, %*				
St. Bernard	0	0.430	0.442	0.440	0.435	0.437
	75	0.437	0.447	0.430	0.437	0.438
	150	0.432	0.448	0.438	0.420	0.435
	S Means	0.433	0.446	0.436	0.431	
Bearbrook	0	0.337cde	0.348abcde	0.323e	0.352abcde	0.340b
	75	0.350abcde	0.340bcde	0.365abc	0.372a	0.357a
	150	0.368ab	0.328de	0.357abcd	0.345abcde	0.350ab
	S Means	0.352ab	0.339b	0.348ab	0.356a	
Howick	0	0.549bc	0.565ab	0.556bc	0.564ab	0.559
	75	0.546bc	0.577a	0.554abc	0.530c	0.552
	150	0.540bc	0.558ab	0.562ab	0.545bc	0.551
	S Means	0.545b	0.567a	0.557ab	0.546b	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 12b. S and P effects on per cent total P in barley grain grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	10	20	40	P Means
		P, %*				
St. Bernard	0	0.460ab	0.449ab	0.460ab	0.492a	0.465
	75	0.457ab	0.468ab	0.430ab	0.480ab	0.459
	150	0.417b	0.487a	0.491a	0.456ab	0.463
	S Means	0.444	0.468	0.461	0.476	
Bearbrook	0	0.350c	0.367bc	0.373bc	0.350c	0.360c
	75	0.368bc	0.372bc	0.377abc	0.385ab	0.375b
	150	0.406a	0.382abc	0.389ab	0.383ab	0.390a
	S Means	0.374	0.374	0.380	0.373	
Howick	0	0.404	0.380	0.404	0.409	0.399
	75	0.390	0.379	0.388	0.405	0.391
	150	0.390	0.391	0.397	0.383	0.390
	S Means	0.394	0.383	0.396	0.399	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 13a. S and P effects on per cent total P in barley straw grown on three soils in 1978.

Soil Series	Added P, kg P_2O_5/ha	Added S, kg/ha				P Means
		0	20	40	60	
		P, %*				
St. Bernard	0	0.147	0.152	0.165	0.163	0.157
	75	0.185	0.169	0.145	0.150	0.162
	150	0.160	0.259	0.207	0.179	0.201
	S Means	0.164	0.193	0.172	0.164	
Bearbrook	0	0.048bcd	0.065ab	0.058bc	0.074a	0.062a
	75	0.049bcd	0.055bc	0.062ab	0.041cd	0.052b
	150	0.036d	0.050bcd	0.062ab	0.053bcd	0.050b
	S Means	0.044b	0.057a	0.061a	0.056a	
Howick	0	0.055bc	0.045c	0.043c	0.056bc	0.049
	75	0.052bc	0.071a	0.045c	0.049bc	0.054
	150	0.062ab	0.051bc	0.053bc	0.057bc	0.056
	S Means	0.056a	0.055a	0.047b	0.054ab	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 13b. S and P effects on per cent total P in barley straw grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	10	20	40	P Means
		P, %*				
St. Bernard	0	0.167ab	0.172ab	0.163ab	0.170ab	0.168a
	75	0.175a	0.169ab	0.147ab	0.143ab	0.159ab
	150	0.139ab	0.153ab	0.163ab	0.132b	0.147b
	S Means	0.161	0.165	0.158	0.149	
Bearbrook	0	0.089b	0.093ab	0.106ab	0.083b	0.093b
	75	0.089b	0.093ab	0.103ab	0.106ab	0.098ab
	150	0.118a	0.109ab	0.096ab	0.097ab	0.105a
	S Means	0.099	0.098	0.102	0.095	
Howick	0	0.070d	0.077cd	0.080cd	0.088abc	0.079b
	75	0.080cd	0.089abc	0.097a	0.088abc	0.089a
	150	0.077cd	0.094ab	0.094ab	0.096a	0.090a
	S Means	0.076b	0.087a	0.090a	0.091a	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

13a,b and 16b,c).

11.7. P Uptake by Grain and Straw

Added S had no effect on P uptake by grain on all soils (Tables 14a,b) but led to significant increase in P uptake by straw on the Bearbrook soil in 1978 (Tables 15a and 16a-c).

Added P increased P uptake significantly in barley straw and grain on the Bearbrook soil in both years of study and on the Howick soil in 1978 (Tables 14a,b and 15a,b). A positive S x P interaction was observed on the Bearbrook soil in 1978 (Tables 15a and 16b) in that P uptake was increased at all combinations of S and P.

11.8. Contributions of S from Rain

There were only minor variations in the amount of S collected on the Seed Farm site but there were appreciable differences on the amounts collected at the Hudson and Riverfield sites (Table 17). The variability could be related to sources whose contribution was dependent on the direction of prevailing winds. However, it is evident from the data that the contributions were substantial and if the trend is maintained throughout the year, the contributions could be in excess of 10 kg S/ha/year.

Table 14a. S and P effects on P uptake by barley grain grown on two soils in 1978.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/he				P Means
		0	20	40	60	
		P, kg/ha*				
Bearbrook	0	6.15c	6.40c	6.58c	6.54c	6.42b
	75	8.47b	8.69ab	9.40ab	9.09ab	8.91a
	150	9.56a	8.52ab	8.86ab	8.81ab	8.94a
	S Means	8.06	7.87	8.28	8.15	
Howick	0	10.34c	10.70bc	10.99abc	10.73bc	10.69b
	75	12.77ab	11.72abc	12.22abc	11.65abc	12.09a
	150	13.00ab	12.63abc	13.07ab	13.19a	12.97a
	S Means	12.04	11.68	12.09	11.86	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 14b. S and P effects on P uptake by barley grain grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha				P Means
		0	10	20	40	
		P, kg/ha*				
St. Bernard	0	10.61ab	9.82ab	11.43ab	10.15ab	10.50
	75	9.38ab	12.27ab	9.10b	13.23a	10.99
	150	10.38ab	10.28ab	11.70ab	11.58ab	10.98
	S Means	10.12	10.79	10.74	11.65	
Bearbrook	0	6.48d	6.72cd	7.03bcd	7.12bcd	6.84c
	75	7.83abc	6.91cd	8.21ab	8.56a	7.88b
	150	8.76a	8.21ab	8.98a	8.49a	8.61a
	S Means	7.69ab	7.28b	8.08a	8.06a	
Howick	0	7.37	6.74	7.43	6.98	7.13
	75	7.32	5.85	7.06	7.31	6.89
	150	7.89	7.20	6.83	6.91	7.21
	S Means	7.53	6.60	7.11	7.07	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 15a. S and P effects on P uptake by barley straw grain on three soils in 1978.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	20	40	60	P Means
		P, kg/ha*				
St. Bernard	0	4.62	5.44	5.78	6.12	5.49
	75	6.88	5.45	4.74	4.72	5.45
	150	6.32	7.00	6.30	5.37	6.25
	S Means	5.93	5.97	5.61	5.40	
Bearbrook	0	0.68e	0.85cde	0.86cde	1.04abc	0.86b
	75	0.96abcde	1.08abc	1.20ab	0.86cde	1.03a
	150	0.70de	0.93b-e	1.24a	0.98abcd	0.96a
	S Means	0.78b	0.95a	1.10a	0.96a	
Howick	0	0.79bc	0.66c	0.64c	0.84bc	0.73b
	75	0.91bc	1.18a	0.73bc	0.85bc	0.92a
	150	1.16a	0.87bc	0.88bc	1.07ab	0.99a
	S Means	0.95a	0.90a	0.75b	0.92a	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 15b. S and P effects on P uptake by barley straw grown on three soils in 1979.

Soil Series	Added P kg P_2O_5/ha	Added S, kg/ha 0	10	20	40	P Means
		P, kg/ha*				
St. Bernard	0	3.58	4.27	3.69	3.02	3.64
	75	3.75	4.33	3.91	3.55	3.64
	150	3.03	3.02	3.49	2.92	3.11
	S Means	3.45	3.88	3.70	3.16	
Bearbrook	0	1.04de	1.14cde	1.38a-d	0.99e	1.14b
	75	1.30b-e	1.16cde	1.40a-d	1.56a	1.36a
	150	1.61a	1.47abc	1.43abc	1.54ab	1.51a
	S Means	1.32	1.26	1.40	1.37	
Howick	0	0.76b	0.82ab	1.05ab	0.84ab	0.87b
	75	0.89ab	1.06ab	1.13a	0.98ab	1.01ab
	150	0.99ab	1.08ab	1.07ab	1.16a	1.07a
	S Means	0.88	0.98	1.09	0.99	

*Means in the body of the table, S means or P means, within each soil series, having a common letter or none at all are not significantly different (P = 0.05) according to the new Duncan Multiple Range (DMR) test.

Table 16a. Probabilities associated with F-statistics for different sources on the St. Bernard soil.

Source	Probability of Greater Value of F						
	Yield	Total S	S Uptake	Total P	P Uptake	Protein	N:S
Grain				1978			
S	nd	0.323	nd	0.497	nd	0.442	0.870
P	nd	0.116	nd	0.947	nd	0.815	0.473
S x P	nd	0.497	nd	0.940	nd	0.263	0.290
				1979			
S	0.680	0.046*	0.218	0.240	0.445	0.181	0.035*
P	0.610	0.991	0.755	0.889	0.786	0.465	0.705
S x P	0.082+	0.092+	0.116	0.113	0.190	0.396	0.050*
Straw				1978			
S	0.199	0.012*	0.099+	0.696	0.916		
P	0.217	0.265	0.614	0.160	0.545		
S x P	0.052	0.878	0.537	0.640	0.698		
				1979			
S	0.857	0.420	0.428	0.400	0.331		
P	0.458	0.446	0.424	0.055+	0.215		
S x P	0.257	0.390	0.123	0.350	0.516		

nd = not determined.

+,*,** Significant at the 0.1, 0.05 and 0.01 probability levels, respectively.

Table 16b. Probabilities associated with F statistics for different sources on the Bearbrook soil.

Source	Probability of Greater Value of F						
	Yield	Total S	S Uptake	Total P	P Uptake	Protein	N:S
Grain				1978			
S	0.380	0.973	0.969	0.136	0.476	0.076+	0.963
P	0.0001**	0.003**	0.0002**	0.045*	0.0001**	0.378	0.030*
S x P	0.214	0.523	0.488	0.020*	0.223	0.955	0.539
				1979			
S	0.034*	0.014*	0.017*	0.800	0.055+	0.189	0.006**
P	0.0002**	0.301	0.211	0.0009**	0.0001**	0.628	0.724
S x P	0.489	0.021*	0.032*	0.202	0.457	0.621	0.004**
Straw				1978			
S	0.621	0.110	0.136	0.005**	0.002**		
P	0.0001**	0.0001**	0.208	0.010**	0.037*		
S x P	0.523	0.010**	0.010**	0.018*	0.040*		
				1979			
S	0.102	0.050*	0.095+	0.766	0.459		
P	0.0008**	0.055+	0.376	0.107	0.0006**		
S x P	0.444	0.590	0.556	0.090+	0.115		

+,*,**Significant at the 0.1, 0.05 and 0.01 probability levels, respectively.

Table 16c. Probabilities associated with F statistics for different sources on the Howick soil.

Source	Probability of greater value of F						
	Yield	Total S	S Uptake	Total P	P Uptake	Protein	N:S
Grain				1978			
S	0.461	0.238	0.551	0.008**	0.889	0.105	0.488
P	0.001**	0.088+	0.927	0.381	0.0005**	0.378	0.355
S x P	0.856	0.357	0.343	0.128	0.930	0.955	0.590
				1979			
S	0.706	0.908	0.969	0.516	0.484	0.010**	0.878
P	0.775	0.864	0.935	0.568	0.804	0.915	0.625
S x P	0.948	0.648	0.739	0.821	0.881	0.262	0.435
Straw				1978			
S	0.168	0.031*	0.107	0.056+	0.166		
P	0.0001**	0.038*	0.164	0.143	0.025*		
S x P	0.505	0.816	0.797	0.006**	0.116		
				1979			
S	0.658	0.292	0.477	0.001**	0.261		
P	0.604	0.909	0.795	0.003**	0.068+		
S x P	0.697	0.976	0.831	0.484	0.892		

+,*,** Significant at the 0.1, 0.05, and 0.01 probability levels, respectively.

Table 17. Sulphur added to the soil from precipitation during the growing season (May to August).

Soil Series (Location)	Average Amount of S Collected (kg S/ha) 1978	1979	Average
St. Bernard (Seed Farm)	7.4	6.8	7.1
Bearbrook (Hudson)	8.6	3.9	6.3
Howick (Riverfield)	7.9	3.0	5.5

12. DISCUSSION

The yield results showed that added S increased grain yield only on the Bearbrook soil in 1978 but had no effect on this soil in 1979, and on the St. Bernard and Howick soils in both years of study. The general lack of significant response to added S could partly be explained by the fact that the soils tested were high in available S as discussed in Chapter 2. It could also be attributed to substantial contributions of SO_4-S from rain estimated to be in excess of 10 kg S/ha at all three sites. Yield responses in Nebraska (U.S.A.) (Fox et al. 1964) and other places (Johanson 1959, Walker 1955) were generally obtained in areas receiving less than 6.7 kg S/ha/year from rain. In this study, S inputs from rain during the growing season alone were roughly equivalent to S removals by the barley crop which averaged 8.0, 3.9 and 6.9 kg S/ha for the St. Bernard, Bearbrook and Howick soils respectively, indicating that S in rain alone could supply the total requirement of the barley crop. Thus the effect of the decrease in S added to soil due to the growing use of concentrated fertilizers with little or no S has not been felt due to S additions from rain.

Added P increased barley yields on the Bearbrook and Howick soils but had no effect on the St. Bernard soil. The

greater yield response to added P observed on the Bearbrook soil was related to lower soil test P on this soil compared to the other soils (Table 1) and was clearly reflected in the significant increases in P concentration and uptake. The lack of P effect on the St. Bernard soil could be explained by the fact that this soil tested high in available P.

Sulphur concentration in grain and straw was depressed by added P on the Bearbrook and Howick soils in 1978. Similar results have been reported in other studies (Jones et al. 1972; Nielson et al. 1967; Aulakh and Parischa 1978) and this effect has generally been attributed to phosphate ions being more competitive than sulphate ions on the root absorption sites or for uptake pathways within the root or stem cells. In this study it could also be partly due to a dilution effect since added P increased grain yields significantly on the two soils.

The consistent increase in P concentration in barley grain and straw observed on the Bearbrook soil was to be expected because as noted before this soil tested lower in available P than the other soils. However, the increase in P concentration with added S observed on the Howick soil for barley straw and grain was in contrast to results from other studies (Caldwell et al. 1969; Jones et al. 1972; Aulakh and Parischa 1978) in which the P content in plant tissue was decreased when S was applied to the soil.

The relationships between per cent total S and N-S ratios in grain with grain yields indicated that both parameters could serve as good indices of S adequacy in plants. However, per cent total S would be preferable because getting N-S ratios involves two separate time consuming chemical determinations. The results also indicated that the range and critical levels of the two parameters may vary markedly from soil to soil, so before any one of them can be adopted for evaluating S status of crops in the area more studies are needed to establish the critical levels more accurately and their variability from soil to soil.

13. CONCLUSIONS

The results of this study showed that:

1. Changes in barley yields due to S fertilization were only significant on the Bearbrook soil in 1978. The general lack of significant responses on the other soils was attributed to substantial additions of S from rain and high soil S status of the soils.

2. Added S increased S concentration in grain and straw. Critical S concentrations in grain were estimated to be 0.08% and 0.14% for the Bearbrook and St. Bernard soils respectively.

3. Protein content of grain was significantly increased by increments of added S on the Bearbrook soil in 1978 indicating that added S enhanced uptake and utilization of N for protein synthesis.

4. The average N:S ratios in grain in the absence of added S were 18.1, 36.2 and 19.7 for the St. Bernard, Bearbrook and Howick soils respectively. Sulphur fertilization significantly narrowed the ratios on the St. Bernard and Bearbrook soils and critical N:S ratios were estimated to be within the range of 15:1 and 24:1 for the two soils respectively.

5. Phosphorus concentration in grain was increased significantly by added S on the Howick soil in 1978 and in straw on

the Bearbrook soil in 1978. These results were in contrast to findings from other studies which have indicated a depressing effect of added S on P content.

6. Added P significantly increased yield, P concentration and uptake on the Bearbrook and Howick soils. Relatively larger increases were obtained on the Bearbrook soil because this soil tested low in available P.

In general the results of the two years field study on the three soils showed that S fertilization did not improve barley yield output significantly to warrant recommending S fertilizers. The increasing use of concentrated fertilizers with little or no S has not resulted in significant yield decreases probably due to substantial S additions from rain. Thus if additions from rain should drop substantially, the possibility of S deficiencies cannot be ruled out in future. The negative S x P interaction effect with respect to yields reported in other studies was not observed in this study.

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CONCLUSIONS

The status of sulphur and the effect of added sulphur and phosphorus on growth of barley (Hordeum vulgare L.) was studied on three Quebec soils. The results indicated that the soils had adequate reserves of total and available sulphur and that mineralization resulted in a substantial contribution to the available SO_4 pool. All surface soils showed considerable negative sulphate adsorption.

The results of the field study showed that added sulphur increased barley grain yield significantly on the Bearbrook soil in 1978 only. The general lack of significant response was attributed to substantial contributions of S from rain and the fact that the available S levels of the soils were also high. Added phosphorus influenced yield significantly on the Bearbrook and Howick soils. A negative S x P interaction on S concentration in grain was observed on the Bearbrook soil. However, no significant S x P interaction was observed with respect to yields.