



## **Lincoln University Digital Dissertation**

### **Copyright Statement**

The digital copy of this dissertation is protected by the Copyright Act 1994 (New Zealand).

This dissertation may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- you will use the copy only for the purposes of research or private study
- you will recognise the author's right to be identified as the author of the dissertation and due acknowledgement will be made to the author where appropriate
- you will obtain the author's permission before publishing any material from the dissertation.

U N I V E R S I T Y

O F

N E W Z E A L A N D

T H E S I S

P R E S E N T E D F O R T H E D E G R E E O F

M A S T E R O F

A G R I C U L T U R A L S C I E N C E (H O N O U R S)

B Y

JAMES R. BRUCE-SMITH

C A N T E R B U R Y A G R I C U L T U R A L C O L L E G E

1 9 6 2

CONTENTS

INTRODUCTION

PART I: REVIEW OF LITERATURE

CHAPTER I - SULPHUR IN SOILS

Introduction	1
Total Soil Sulphur	2
Fractionation of Total Sulphur	3
(A) The Inorganic Fraction	3

MOVEMENT OF SULPHATE SULPHUR

IN SOILS AS INFLUENCED BY

CERTAIN FERTILISER TREATMENTS



CHAPTER II - SULPHUR IN PLANT TISSUES

Introduction	10
Effects of Sulphur and Assimilation of Sulphur	11
Crop Requirements of Sulphur	12
Sulphur Deficiency in Plants	13
Competition by Plants for Sulphur	14
Use of Sulphur Fertilisers	15
The Sulphur Cycle in Cropland Soils	16



# C O N T E N T S

	PAGE
I N T R O D U C T I O N	1
S E C T I O N I : REVIEW OF LITERATURE	
CHAPTER I - SULPHUR IN SOILS	
Introduction	2
Total Soil Sulphur	3
Fractionation of Total Sulphur	5
(A) The Inorganic Fraction	5
(B) The Organic Fraction	9
Summary	12
CHAPTER II - MINERALIZATION OF ORGANIC SULPHUR	
Introduction	14
Sulphur Content of Organic Matter	15
Mineralization of Simple Organic Sulphur	
Compounds	16
Mineralization of Complex Organic Sulphur	
Compounds	18
Mineralization of Inorganic Sulphur	
Compounds	21
Conclusion	22
CHAPTER III - SULPHUR IN PLANT NUTRITION	
Introduction	24
Uptake of Anions and Accumulation of	
Sulphur	24
Crop Requirements of Sulphur	27
Sulphur Deficiency in Plants	28
Competition by Plants for Sulphur	29
Use of Sulphur Fertilisers	30
The Sulphur Cycle in Grassland Soils	33



	PAGE
CHAPTER IV - PHYSICO-CHEMICAL RETENTION OF SULPHATE BY SOILS	
Anion Adsorption and Exchange	34
Adsorption of Sulphate by Soils	41
Summary	42
S E C T I O N II : EXPERIMENTAL	
CHAPTER V - EXPERIMENTAL PROCEDURES	
Introduction	45
The Soils	46
Field Experimental Procedures	48
Laboratory Experimental Procedure and Methods	50
Extraction of Sulphate	51
Determination of Sulphate	53
Discussion	55
CHAPTER VI - RESULTS AND DISCUSSION	
Soil Analyses	56
(A) X-ray Analyses	56
(B) Chemical Analyses	57
(C) Sulphate Analyses	59
Recovery of Sulphur	63
Criticisms and Conclusions	68
A C K N O W L E D G E M E N T S	70
S U M M A R Y	71
B I B L I O G R A P H Y	72



## I N T R O D U C T I O N

The economic policy of New Zealand must surely be directed towards the maintenance of a continued increasing level of output of primary produce, and to achieve this, more marginal land must be developed. In the South Island there is an area of 12 million acres of tussock grassland - an area of inherent and induced low soil fertility - in fact, marginal land awaiting development.

Field and laboratory studies have revealed that the low soil fertility can often be attributed to certain plant nutrient deficiencies. Generally, nitrogen deficiency is widespread, and because under New Zealand conditions it is too expensive to apply this fertiliser out of the bag, pasture improvement programmes usually incur the introduction of a legume into the sward. However, unless the nutrient requirements of legumes are fully satisfied, they will not fix adequate nitrogen for their companion species. Research undertaken to ascertain these nutrient requirements on many tussock soils has shown an interesting pattern of soil deficiencies of sulphur, phosphorus, and certain trace elements.

Sulphur deficiency has been recorded to be widespread - a reason attributed to the low returns of atmospheric sulphur with the rainfall. Data from field trials containing various sulphur fertiliser treatments has indicated that residual responses often occur. It is the purpose of this thesis to investigate some reactions of the sulphate ion in the soil, and thus explain the residual effects of sulphur fertilisers.



## R E V I E W O F L I T E R A T U R E

CHAPTER ISULPHUR IN SOILSIntroduction

Approximately .06% (Jordan and Ensminger, 1958) of the lithosphere is composed of sulphur. This may occur as the free element in certain volcanic districts, or more commonly, it is found in a combined state in the country rocks. The chief sulphur minerals of igneous rocks are sulphides, e.g., galena, blende, iron pyrites, copper iron pyrites, stibnite, copper glance and cinnabar, and the geochemical considerations of their mineralogy have been outlined by Goldschmidt (1945). While sedimentary rocks may contain sulphides also, (if their genesis involved mainly physical weathering), they more commonly contain sulphur oxidation compounds, e.g., the gypsum, heavy spar and kieserite minerals.

Oxidative weathering of sulphur minerals releases sulphate, which may be leached away in ground waters and sulphate accumulation in sea water averages 2.7 gm per litre. Spray from sea water, geothermal and industrial activity, and certain microbial processes cause atmospheric contamination with sulphur. Thus the sea and atmosphere, as well as rocks, are important sources of sulphur. Because sulphur is essential for biotic processes, the organic matter contains sulphur, and this source is important to the agronomist.

Many soils are formed from the fragmental, rocky material under the interaction of the other four soil-forming processes. In the early stages of development of these soils, sulphur derived from the primary minerals is changed to sulphate, and



while some may be leached, much of this sulphate will be assimilated by plants and converted to the organic form. Thereafter, the atmosphere, the organic matter, and the weathering processes acting upon the primary minerals, supply the soil with sulphur.

To study elements singly, it should not be forgotten that the cycles of other biologically important elements interact continually with one another, and it is necessary to stress the important consideration of the soil's dynamic nature.

#### Total Soil Sulphur

The total sulphur figure given in soil analyses shows wide variation, both between different soils, and between the different horizons of the same soil. Ensminger (1958) gave a range of 140-980 lbs of sulphur per acre as representative for A horizons in U.S.A. Walker and Adams (1959) recorded a considerable range in the percentage total sulphur content of New Zealand soils, as can be seen from the values tabulated below for three soil weathering sequences.

Soil Sequence	A Horizon % Total S	B Horizon % Total S
1. Weakly weathered	.015 - .084	.006 - .024
2. Moderately weathered	.040 - .078	.018 - .042
3. Strongly weathered	.017 - .065	.008 - .026

In an earlier paper (1958a) they recorded a mean weight range in the 0-21 inch depth, of soils formed from different parent materials, of 1200-4000 lbs of total sulphur per acre,



and a decrease in the percentage total sulphur as the soil depth increases is clearly demonstrated.

Now, the soil agronomist is concerned with the prediction of a soil's ability to grow certain crops. He examines soil analytical data with this aim, but Little (1958) has shown that the total sulphur figure alone, is seldom a guide to his cause. Lobb (1954) stated that the sulphur content of plant material was a better indication of the soil sulphur status for plant growth. Other workers have considered carbon: nitrogen: sulphur: phosphorus or organic phosphorus (C: N: S: P or organic P) ratios of soils, and <sup>have</sup> shown that the total sulphur is associated in broad but definite ratio patterns with the organic matter. Thus, Walker and Adams (1958a) recorded a close relationship between total sulphur and nitrogen ( $r = + 0.97$ ) of soils formed from different parent materials, and they (1959a) confirmed the relationship on a weathering sequence of soils derived from the same parent material. Williams and Steinbergs (1958) also recorded a general linear relationship of total sulphur with carbon and nitrogen from a wide range of Australian soils, but they could not find a close relationship with the organic phosphorus. Williams and Donald (1957) gave a C: N: S: organic P mean ratio of 155: 10: 1.4: 0.7 which compared favourably with Williams and Steinbergs' (1958) mean ratio of 150: 10: 1.26: 0.66. Walker and Adams (1958a) recorded a mean topsoil ratio for twenty soils of 130: 10: 1.3: 2.1. Seven of these soils were known to be sulphur responsive and had a mean ratio of 125: 10: 1.4: 2.3. The differences in ratios appear to give

\* The sulphur here is not total sulphur, but non-sulphate sulphur which approximates very closely to it.



little guide, therefore, to the ability of the soil to supply adequate sulphur for plant growth.

#### Fractionation of Total Sulphur

The soil total sulphur may be subdivided into organic and inorganic fractions. Of these, the inorganic fraction is usually very small, and most reports invariably state that most of the soil sulphur is in the organic form. Consideration of the C: N: S: organic P ratios above, substantiates this reasoning.

(A) The Inorganic Fraction: The inorganic fraction is thought to be mainly sulphate, and the amount of this found in soils is an extremely variable quantity, which in part may be ascribed to the chemical methods used for its extraction. Freney (1958a) found that air-drying increased the soluble sulphate, and proposed that the extraction should be carried out as soon as possible on the fresh soil sample after its collection from the field. Accurate measurement of sulphate from the soil-extracted solution is a further difficulty. The turbidimetric methods of Chesnin and Yien (1951), Steinbergs (1955), Hesse (1957) and Bardsley and Lancaster (1960) give slightly different values, and at low concentrations of sulphate, this can lead to significantly different results. The Johnson and Nishita (1952) reduction method is reliable, but it is a more lengthy procedure.

Some extractants are listed below, and the agronomic significance of the corresponding fractions is briefly discussed. Not all workers adhere to a soil : extractant solution ratio of 5 : 1.

Soluble sulphate is usually low, as recorded by Evans



and Rost (1945) - distilled  $H_2O$ , then 1% HCl and distilled  $H_2O$  leachings; Chesnin and Yien (1951) - buffered  $Na\overline{Ac}$ ; Ensminger (1954) -  $Na\overline{Ac}$  and HCl; Mann (1955) - distilled  $H_2O$  and HCl; Kamprath, Nelson and Fitts (1956) -  $H\overline{Ac}$ ; Jordan and Bardsley (1958) - buffered  $Na\overline{Ac}$ ; Little (1958) - HCl; Williams and Steinbergs (1958) - NaCl; McClung, De Freitas and Lott (1959) -  $NH_4\overline{Ac}$ ; Neller (1959) -  $Na\overline{Ac}$ ; and Cairns and Richer (1960) - HCl and  $Na\overline{Ac}$ . Acetate appears to extract more sulphate than chloride, and the amount extracted in all cases is further increased if colloidal material is removed. (Hesse, 1957b; Williams and Steinbergs, 1959; Bardsley and Lancaster, 1960.) Comparisons of various chloride extractants were made by Williams and Steinbergs (1959). However, Ensminger (1954) found that  $KH_2PO_4$  extracted more sulphate than either chloride or acetate from certain heavy soils, and he attributed this phenomenon to the property of certain clays to adsorb sulphate. He presumed that adsorption was an anion exchange reaction, and that not all anions were freely interchangeable. While phosphate would replace sulphate from the clay-sorption-complex, chloride would not, and acetate only partly. Anion exchange is discussed in Chapter IV.

McClung et al (1959) found with pot experiments, that no plants took up more sulphur than was extracted by neutral  $NH_4\overline{Ac}$  from the sulphur-deficient soils studied. Plants showed sulphur-deficiency symptoms when grown in soils where low values of  $NH_4\overline{Ac}$  extractable sulphate were recorded. With soils containing less than 2 p.p.m. extractable sulphate-sulphur, the plants died; with 2-6 p.p.m. plant responses to sulphur were recorded; but if more than 7 p.p.m. of sulphate-sulphur could be extracted from the soil, no plant response to sulphur was apparent. Williams and Steinbergs (1959) extracted sulphate



with 1% NaCl, and treated this solution with  $H_2O_2$  because colloidal material in this soluble extract contained organic sulphate. Even so, their soluble sulphate fraction was small. It did not correlate well with yield of plants, so that it was not considered a suitable measure of sulphur available for plant growth. Metson (1954) earlier had found little distinction between sulphur-responsive and non-responsive New Zealand soils from comparative analyses of their sulphate or total sulphur contents.

Horizon distribution of sulphate was studied by Ensminger (1954) who recorded that the  $KH_2PO_4$  extractable quantity increased with depth, and he associated this with the increased clay content of the lower horizons. Ensminger (1958) declared that although most soils would retain sulphate to some degree, the sub-surface layers would usually contain, and be capable of adsorbing, more sulphate than surface soils. Jordan and Bardsley (1958) confirmed his statement. Neller (1959) recorded only traces of sulphate in topsoils, but found that considerable quantities could be extracted from sub-surface horizons. Further, he associated this increase with not only clay increase, but also with certain clay types. Sulphate extracted from B horizons by McClung et al (1959) was greater than that extracted from most topsoils. In pot experiments with these B horizons, plants were reported to be less responsive to sulphur also. To these workers it seemed probable that while plants growing in topsoils may be responsive to sulphur initially, they may not show the same degree of response once their roots have tapped the lower horizons. Thus, the root system of a crop is an important factor with regard to sulphur deficiency.

The lack of information on the effect that atmospheric



return had on sulphate or total sulphur content of the soil, was pointed out by Walker (1957). Erdman (1922) recorded that sulphur occurred in rainfall chiefly as  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and  $\text{SO}_3$ . Jordan and Ensminger (1958) stated that the amount of sulphur returned from this source varied with the season and the geographical location. MacIntyre, Young, Shaw and Robinson (1952) recorded a mean annual return of 42 lbs sulphur per acre at the University of Tennessee, which had a mean annual rainfall of 51 inches. Mann (1955) recorded that the annual return of sulphur in rainfall was adequate to compensate for crop removal of sulphur in certain English rural areas. Alway, (1940); Thomas, (1943); Fried, (1948); Olsen, (1957) and Harper, (1959) have shown that soils and plants may adsorb some  $\text{SO}_2$  directly from the atmosphere.

Eriksson (quoted by Stephens and Donald, 1958) gave an estimated figure of about 9 lbs per acre as the characteristic sulphur return from unpolluted air. Hutton and Leslie (1958) in Australia recorded at a station 2 miles from the sea coast an annual return of 3 lbs sulphur per acre in a 34 inch rainfall. At another station 40 miles from the coast with a 28 inch rainfall, twice this return of sulphur was recorded. Stations still further inland received as little as 2 lbs sulphur per acre per annum from the rainfall. Walker, Adams and Orchiston (1956) claimed that in certain places in New Zealand, as little as 1 lb per acre, or even less, could possibly be returned in the rainfall, and indeed, an article in the New Zealand Journal of Agriculture\* recently reported a rainfall return of only 0.4 lbs of sulphur per acre at Tara Hills in 1959.

\* N.Z.J.A. 1960 V. 101: p. 328



(B) The Organic Fraction: A brief survey of possible sulphur-containing organic compounds occurring in organic matter is given in Chapter II.

One of the early attempts to fractionate the organic sulphur was carried out by Evans and Rost (1945). After having removed the soluble sulphate by leaching, these workers took the leached soil, oxidised it with  $\text{H}_2\text{O}_2$ , and then measured the sulphur content, which they claimed was a measure of the total organic sulphur. Another portion of the leached soil was peptized with 4%  $\text{NH}_4\text{OH}$  for three days. An aliquot of the supernatant liquid, after removal of suspended material, was then taken to dryness, fused with  $\text{Mg}(\text{NO}_3)_2$  and analysed for sulphur. This fraction, they postulated, was a measure of the organic sulphur in the organic matter considered to be in an advanced stage of mineralization. Evans and Rost called this humus sulphur, and recorded a direct correlation between it, the total organic sulphur, the total nitrogen, and the total carbon in the soils studied.

Mann (1955) used the Evans and Rost technique to show that topsoils, under continuous grain crop in England, became depleted of carbon, nitrogen and organic sulphur to almost the same degree, if organic manures were not employed. However, he recorded that the humus sulphur content of these soils appeared to remain relatively steady. The atmospheric return of sulphur, which he stated was sufficient to maintain the soil sulphur, may in part have accounted for this. Loss of sulphur under cropping had also been reported by Swanson and Latshaw (1922), and McClung et al (1959) report a downward movement of sulphate in cropped soils.

Recently, Williams and Steinbergs (1959) and Bardsley and Lancaster (1960) have criticised the Evans and Rost



technique because of possible losses of volatile sulphur compounds during the  $H_2O_2$  oxidation. The latter workers developed a method for determining "soil sulphur", which, because it did not take into account possible insoluble sulphates, was not analogous with total sulphur. They determined the soil sulphur, then subtracted the value determined for soluble sulphate, and called the fraction left "reserve sulphur". There can be little difference between their "reserve sulphur" and the Williams and Steinbergs (1958) fraction of "non-sulphate sulphur" which was determined by the difference between total sulphur and sulphate sulphur. Both the "reserve sulphur" and the "non-sulphate sulphur" fractions of the respective workers were found to be highly correlated with soil carbon and nitrogen. This has been interpreted as convincing evidence that most of the total sulphur is actually in the organic form.

McClung et al (1959) determined organic sulphur (after removal of sulphate sulphur with  $NH_4\overline{Ac}$ ) by oxidation of the soil with  $H_2O_2$ , followed by a further extraction with  $NH_4\overline{Ac}$ . The extractant solution was taken to dryness, ignited in the presence of  $Mg(NO_3)_2$  and sulphur determined by the Johnson and Nishita (1952) reduction method. A general low level of organic sulphur was recorded. However, they could not find any relationship between this organic sulphur fraction of the soil and the yield of sulphur in plants from pot experiments.

A logical approach to the problem of determining the contribution organic sulphur would make towards plant growth, was made by Williams and Steinbergs (1959). Since most of the sulphur was in the organic form, and since appreciable quantities of soluble organic sulphur could be extracted with the soluble sulphate fraction, (treatment of this extract with



$H_2O_2$  gave a higher sulphate analysis figure) they concluded that part of the organic sulphur could be readily hydrolysed. They found that simple heating of soil released sulphur. Heating the soil with water (1 : 5 ratio) over a boiling water bath until it had evaporated to dryness, followed by heating for an hour in a hot oven, released even more. Other procedures were compared, namely: sulphur in ignited soil, sulphur extracted with NaOH (after Evans and Rost), sulphur extracted after oxidation with  $H_2O_2$  (after Evans and Rost), and sulphur extracted by a soil reduction method. These were called "ignition", "alkali", "organic", and "reducible" sulphur fractions respectively. The results confirmed that organic sulphur comprised the largest fraction of the total sulphur. Alkali, ignition, and reducible sulphur were often quite directly comparable, and always were highly inter-correlated with each other. Up to 50% or more of the total sulphur could be accounted for by these fractions. Examination of the alkali extractable sulphur revealed upon further fractionation, an inorganic and organic component, of which the organic was the larger. Heating of the alkali extract resulted in an increase in the inorganic component, which suggested that part of this was readily hydrolysed to sulphate. They recorded a high correlation of heat-soluble sulphate with water-soluble sulphate, but correlations of these with total, alkali, ignition and reducible sulphur were weak.

In a pot experiment, the yield of plant sulphur was highly correlated with the heat-soluble sulphate content of the soil. Except, however, for the total soluble sulphate, the correlations of other fractions with plant yield were poor. Thus, not only have Williams and Steinbergs achieved a possible useful index of available sulphur, but also, they have revealed



that some of the organic sulphur is composed of organically bound sulphate. Freney (1960) reached a similar conclusion.

Although atmospheric returns of organic sulphur have not been actually recorded, Wilson (1959) recently isolated organic albuminoid nitrogen from New Zealand snow. Since he postulated that this originated from the sea, it seems possible that small amounts of organic sulphur could be derived from that source also.

Finally, it is pertinent to note that McClung et al (1959) and Williams and Steinbergs (1959) recorded a threshold value (2 p.p.m.  $\text{NH}_4\text{Ac}$  extractable - the former; and 8-10 p.p.m. heat-soluble - the latter) of sulphate, below which plants failed to utilise sulphate. Presumably these chemical methods extract some sulphur in a form which is unavailable to plants. Whether this is sorbed sulphate (clay or organic matter sorbed) or readily mineralised organic sulphate, has yet to be ascertained.

### Summary

This section of the review has shown that the total sulphur figure of soils alone has little meaning to the soil agronomist. However, when it is expressed in ratio form with the other major elements, it was found to bear some definite relationship with the soil carbon and nitrogen. From this it is concluded that much of the total sulphur is organic. The subdivision of total sulphur into inorganic and organic fractions was considered, with brief particulars of methods cited. In the discussion an attempt was made to assess the significant features of various fractions in relation to plant yield on sulphur-deficient soils. It was noted that the literature lacked information on the definite effect that atmospheric



returns had on the soil sulphur fractions. Recent work suggests that for plant growth, sulphur can be utilised from the following sources:

- (1) Soluble sulphate in the soil;
- (2) A portion of the soil organic matter (possibly readily hydrolysed organic sulphate);
- (3) Sulphur compounds from the atmosphere.



## CHAPTER II

### MINERALIZATION OF ORGANIC SULPHUR

#### Introduction

Because sulphate ions are the primary source of the major element sulphur to the plant, it is therefore important to consider how the soil supply of sulphate ions is maintained for plant nutrition. The evidence shows (Chapter I) that the greatest proportion of the total sulphur found in soils occurs in the organic form. Mineralization constitutes the process whereby the sulphate ion is released from these forms, but, unfortunately, the actual pathways of mineralization are far from being completely understood.

Starkey (1950) stated that micro-organisms were responsible for the transformations of organic sulphur, and that many species of fungi, actinomycetes and bacteria were involved. Further, it is certain that different organisms contribute to varying extents, at each stage of what probably is a step-wise breakdown of the compound organic molecules. Factors which influence the activities of the soil microfloral population, e.g., moisture, (Greaves and Carter, 1920); temperature, (Katznelson and Chase, 1944); aeration, pH, substrate availability and competition, and antibiotic toleration and production (Waksman and Hutchings, 1937; Lochhead and Landerkin, 1948 and Brian, 1951) will determine the precise rôle played by the various groups. These aspects are discussed by Eggleton (1938), Russell (1954), and Burges (1958).

Rhizosphere studies have shown that within this zone of the soil there is very intense microbial activity. Its importance must be stressed. Here is a first-hand sphere within the soil for rapid organic matter breakdown, but at the



same time microbial immobilization of nutrients will also take place. The magnitude of these processes is often measured on the basis of nett mineralization or immobilization of a particular nutrient after a given time. Accounts of the rhizosphere are to be found in Russell (1954), Burges (1958), and Rovira (1956<sup>a</sup>, 1959).

#### Sulphur Content of Organic Matter

It is quite apparent that the sulphur content of the soil organic matter will be determined by that of the organic materials added to it, in the form of plant or animal remains. Thomas, Hendricks and Hill (1950) list the sulphur content of a range of plants commonly found in the U.S.A. Organic sulphur compounds associated with plant and animal nutrition have been described by Starkey (1950) and Gilbert (1951). Briefly, these include the amino acids, cystine, cysteine and methionine, the etherial sulphates, thiourea, glucosides, certain alkaloids, the B vitamins, biotin and thiamine, and other volatile compounds such as those found among certain members of the Brassicaceae.

Waksman and Iyer (1937) and Waksman (1952) outlined some aspects of the chemical nature of the soil organic matter and suggested mechanisms relating to its origin, but, as Broadbent (1953, 1955) so clearly emphasised, it is the difficulty of precise characterisation of the organic fractions which retards rapid progress in the elucidation of the actual pathways of organic transformations. Bremner (1955) reviews recent work on the soil organic matter.

Although traces of all the above-mentioned compounds are known to occur in soils, it is considered that protein and humic-protein fractions account for much of the organic sulphur.



Clays adsorb organic molecules (Grim, 1953), and in the clay-sorbed state, Ensminger and Gieseking (1942) demonstrated that proteins were more resistant to proteolytic hydrolysis. It is conceivable that clay-protein-complexes account for a substantial reservoir of organic sulphur. However, recently Williams and Steinbergs (1959) have suggested that part of the organic sulphur fraction is comprised of readily hydrolysed, organically-bound sulphate.

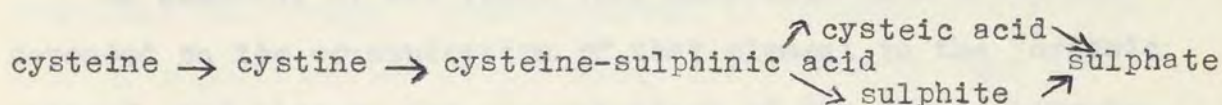
#### Mineralization of Simple Organic Sulphur Compounds

The decomposition of certain organic sulphur compounds was studied by Fredrick, Starkey and Segal (1957). In these compounds the sulphur content varied from 4-42%. It was present in various chemical combinations, but these workers could not associate the rate of breakdown to sulphate with any particular type of sulphur linkage. Some compounds decomposed rapidly, with a consequent soil microbial population increase. Other compounds were found to decompose only slowly. This, they declared, could possibly be explained by toxic decomposition by-products which inhibited the microfloral activities. Thus, cystine, and taurine rapidly released sulphate upon incubation, while thiamine only slowly released it. Methionine decomposition appeared to differ from the decomposition of other compounds, in that volatile compounds (methylthiol and dimethyl disulphide) were end products and not sulphate. Barrow (1959) also recorded this result. By contrast, Hesse (1957) recorded that both methionine and cystine were quantitatively mineralized to sulphate under either incubation or percolation conditions. Quastel and Scholefield (1949) during studies on nitrogen mineralization recorded slow breakdown of methionine. Unfortunately, they did not mention whether



sulphate, volatile sulphur compounds or organic sulphate was formed during these breakdown processes.

The aerobic transformation of cysteine was shown by Freney (1958b, 1960) to follow the pathway:



Although from the intermediate by-product (cysteine-sulphinic acid) many side-branched reactions could probably occur, it was of profound interest that Freney recorded no trace of sulphide. Most generalised accounts of sulphur mineralization, e.g., Starkey (1950), state that sulphide is the intermediate product, and that it is subsequently oxidised to sulphate.

Barrow (1959) initiated his studies on organic matter breakdown by using the simple compounds, sucrose, casein, glycine and cysteine to provide a source of carbon, nitrogen and sulphur. By varying the proportions of these compounds, he altered the C: N: S ratios of this "synthetic organic matter", which was then incubated in a sand medium inoculated with soil micro-organisms. Violent fluctuations in pH values often occurred because of the lack of buffering action of the medium, but he was able to study the effects of respiration and mineralization of carbon, nitrogen and sulphur. Barrow demonstrated that chemical composition had considerable effects on these processes. Further, he concluded that mineralization of nitrogen and sulphur did not necessarily proceed by parallel courses. A low content of either nitrogen or sulphur in the "organic matter" resulted in low mineralization of nitrogen or sulphur respectively, but their respective respiration curve patterns differed. Low sulphur had a marked effect on the



quantity of nitrogen released. He concluded that although adequate sulphur was necessary for nitrogen metabolism, and therefore nitrogen mineralization, the corollary did not apply.

In general, it was found that mineralization of an element depended on the concentration of that element in the "organic matter", and also on the concentration of the other elements. Another trend noted was that reduced supplies of one element caused increased mineralization of other elements within certain limitations. However, he reported that many of these effects would have been of an indirect nature.

#### Mineralization of Complex Organic Sulphur Compounds

After Barrow (1959) had formulated some principles of sulphur mineralization from his synthetic organic matter studies, he then extended his work to the use of plant material as a source of organic matter, in order to ascertain whether the same principles applied. For this work a range of legumes, grasses, native grasses and other species ~~was~~ were used. Some of these plants had been grown on known sulphur-deficient soils.

The results were difficult to interpret. It was shown that the quantity of organic material added for these incubation studies influenced the accuracy of measurement of carbon, nitrogen and sulphur mineralized. Respiration studies indicated a curvilinear relationship between the percentage of nitrogen in the organic material, and the proportion of carbon recovered as  $\text{CO}_2$ . However, no relationship could be found between the botanical nature of the plant sample and the amount of sulphur mineralized. In general, he recorded that incubation of plant samples which had received sulphur fertiliser during their



growth, resulted in increased mineralization of sulphur, as compared with plant samples not so treated. In the latter case, there appeared to be an immobilization of sulphur, as compared with the control soil which was incubated under identical conditions. There appeared to be some interaction between organic matter of the added plant material and the native soil organic matter, which increased the difficulty of interpretation of the results.

As with the previous experiments, it was shown that the nitrogen or sulphur mineralized from material of any given C/N or C/S ratio could vary widely, and this was attributed to the nature of the material, e.g., the lignin content. Lignified material after incubation, was found to have residual organic matter which contained a higher proportion of carbon. It is known (Russell, 1954) that as decomposition proceeds, the residual organic matter becomes less susceptible to microbial attack. Therefore the maturity stage of the plant material must be of importance in such a study. Barrow found that, in general, materials with a C/S ratio of less than 200 mineralized sulphur, while those with a C/S ratio of greater than 420 immobilized it.

Hesse (1957a) reported that appreciable amounts of sulphate were washed from the leaves of forest trees, and he suggested that organic sulphur compounds could be oxidised within the leaves of the forest trees. These leaves had a high methionine and cystine content. Hesse recorded similar trends in mineralization pattern, when freshly ground-up leaves or additions of methionine and cystine were incubated with soil. As mentioned previously, the mineralization to sulphate in these experiments contrasted with other workers' findings. Semi-decomposed litter from the forest floor mineralized less rapidly, while the humus



of the forest topsoil decomposed only very slowly over a six-month period. McClung et al (1959) also found that the rate at which sulphur mineralized from organic matter was very slow.

White (1959) incubated some sulphur-deficient soils and measured the production of sulphate, nitrate and ammonia. Liming increased the soluble sulphate extracted from Cass and Oxford soils after incubation, but did not affect the amount of sulphate mineralized from Kowai and Hurunui soils. He suggested that the HCl extraction used may not have released all the sulphate. However, lime would probably create conditions such that little sulphate would be clay-sorbed under his experimental conditions. The C/S ratio of these four soils was less than 200, and thus from Barrow's (1959) work, organic sulphur could be expected to mineralize, but the incubation period of one month was probably insufficiently long for these processes to occur. Lime increased the total nitrogen mineralized, and because the mineral N/S ratios differed appreciably from the soil N/S ratios, this experiment gave further support to Barrow's suggestion that the mineralization processes of nitrogen and sulphur in the soil are not parallel.

By use of a "balance sheet" technique, Freney and Spencer (1960) showed that the growing plant affected the mineralization of sulphur. They suggested that the rhizosphere was of considerable importance. These workers determined the total sulphur at the beginning and at the end of their experiment, and showed that any sulphate added, which could not be accounted for in terms of plant uptake or extracted as sulphate, must have been immobilized by the soil microflora. With four soils not receiving additions of sulphate, only small amounts of sulphate were mineralized. They failed to relate the quantities mineralized with the C/S or N/S ratios of these soils. On the other



hand, they reported that nett mineralization occurred in these soils during active plant growth. The nett mineralization increased when small additions of sulphate sulphur were applied to the soil, but only up to a certain level, whereafter presumably both mineralization and immobilization of sulphur occurred.

#### Mineralization of Inorganic Sulphur Compounds

It is generally considered that the processes of putrefaction and decay result in sulphur being mineralized to sulphide. Much of the above work appeared to suggest that, in actual fact, many of these mineralization processes might be oxidation processes leading directly to sulphate formation as the end product of mineralization of organic sulphur. However, sulphide can be detected in soil, and an interesting chain of microbial reactions has been demonstrated whereby inorganic sulphur may be cycled in the soil.

The sulphide oxidisers (including the chemosynthetic Beggiatoa, Thiothrix and Achromobacter, and the photoautotrophic Chlorobium, Chromatium, Thiopedia and Thiocapsa) convert sulphide under aerobic (former group) and anaerobic (latter group) to elemental sulphur. Sulphur forms the substrate for the sulphur oxidisers to convert it autotrophically through a series of thionates and polythionates to sulphate as was shown by Gleen and Quastel (1953). The organisms responsible for these processes belong to the Thiobacilli group. Their metabolism has been much studied in connection with the question of the "fundamental unity" of life, by Vogler (1943). Normally, soils contain Thiobacillus thiooxidans, and Th. thioparus, and these are fairly readily isolated, particularly after additions of raw sulphur have been made.



been made to the soil.\* Sulphur oxidation by them leads to the formation of sulphuric acid, and where large quantities of sulphur have been added, the soil reaction may drop to low pH values. Hence the use of sulphur for the reclamation of alkaline soils, as discussed by Rudolfs (1922) and Shedd (1928). The non-biological oxidation of sulphur to sulphate has been discussed by MacIntyre et al (1921) and Quispel, Harmsen and Otzen (1952).

Under water-logged (anaerobic) conditions it is possible for the autotrophic anaerobe Desulphovibrio desulphuricans to reduce the sulphate in soils to sulphide. An informative account of the micro-organisms involved in the inorganic sulphur cycle is given by Postgate (1954).

### Conclusion

Mineralization of organic sulphur from the soil organic matter follows a complex series of reactions about which there is limited understanding at present. It seems probable that both sulphide and sulphate may be end products of the microbial breakdown. Immobilization of sulphur compounds by the soil microflora may occur during the heterotrophic breakdown processes, and the autotrophic inorganic processes.

Because of the inter-relations of soil nitrogen and sulphur, Walker (1957) postulated that for normal soils with N/S ratios of approximately 8 : 1, a probable mineralization rate would be 1½% per annum for each element. Bardsley and Lancaster (1960) give a figure of 2-3% for possible organic sulphur mineralization in humid, temperate soils.

\* The writer was able to isolate Th. thiooxidans from a virgin soil from the Lake Coleridge area.



On the other hand, Barrow (1957, 1960) and Fredrick et al (1957) thought that the processes of nitrogen and sulphur mineralization did not necessarily show parallelism. The breakdown processes depend upon many factors. Barrow (1959) considered that the proportion of the other elements to sulphur in the organic matter was of major importance to sulphur mineralization.



### CHAPTER III

#### SULPHUR IN PLANT NUTRITION

##### Introduction

In the preceeding chapters aspects of soil sulphur fractions and the mineralization of sulphur were discussed. Now it is intended to outline some considerations of the role of sulphur in plant nutrition and plant competition, then briefly discuss crop sulphur requirements, the use of fertiliser sulphur, and finally, the sulphur cycle.

##### Uptake of Anions and the Accumulation of Sulphur

Although plants may absorb some nutrients in the form of compound molecules, e.g., vitamins, it is considered that sulphate ions in the soil solution constitute the major source of the nutrient sulphur. The uptake of ions from this weak solution into the more concentrated plant sap requires the expenditure of energy, which comes from the cytochrome oxidase system according to the "salt respiration" theory (anion respiration) developed by Lundegardh (1939). Theoretical relationships between roots and soils have been discussed by Lundegardh (1942) and Vervelde (1953) also outlined some Donnan principles of ion adsorption. Robertson (1957) introduced the concept of the "apparent free space" in ion accumulation, which displaced the theory of "contact exchange" proposed by Jenny and Overstreet (1939). Bray (1954) described how nutrient mobility would affect plant growth over the growing season, and recently Walker (1960) discussed some considerations of the inter-ionic relationships of the soil-soil solution-plant system.

Kretschmer, Toth and Bear (1953) showed that the uptake of chloride and sulphate ions could vary considerably in



different species. Whereas an increased concentration of chloride in the substrate resulted in a large increase in the chloride concentration of the plant, the corollary for sulphate did not apply to such a marked extent. That is, the plants did not continue to accumulate sulphate. Selective absorption was not demonstrated conclusively, but it was reported that an increase in the chloride content of the plant was counteracted by a reduction in the sulphate content when plants were grown in sodium or potassium salt solutions of these two anions. Stout, Meagher, Pearson and Johnson (1951) recorded that molybdenum uptake was depressed in the presence of sulphate. They gave reasons for believing that the molybdate and sulphate ions actively competed for the same adsorption sites in the plant roots. Tisdale and Bertramson (1949) and Rigg (1954) showed that manganese uptake appeared to be enhanced in the presence of sulphur. This could perhaps be attributed to the low pH values associated with sulphur oxidation causing solubilization of manganese compounds.

That the percentage of sulphur in plants is increased by the addition of sulphur, was recorded by Neidig, McDole and Magnuson (1923), Evans (1931), Sheldon, Blue and Albrecht (1951) and Rendig (1956). The effect of sulphur on plant methionine content has been discussed by Tisdale, Davis, Kingsley and Mertz (1950), Sheldon et al (1951) and Renner, Bentley and McElroy (1953). The former workers reported that the methionine content of lucerne increased as sulphur was applied, but only up to a certain level, because they maintained that the ability of plants to produce amino acids was genetically controlled. Sheldon et al (1951) suggested that methionine increase would occur at the expense of the other amino acids, but, by contrast, Rendig (1956) concluded that lucerne was not



enriched in methionine through sulphur addition.

Anderson and Spencer (1950) demonstrated that sulphur is required by both non-legumes and legumes for protein synthesis, yet they recorded a difference between the two groups of plants in the manner in which they accumulate sulphur. Whereas non-legumes appeared to respond to sulphur only in the presence of adequate nitrogen (Tol<sup>e</sup>man and Stoker, 1941; Conrad, 1950; Cormack, Bentley and Scott, 1951; Sheldon et al, 1951; Renner et al, 1953; Walker and Adams, 1958c; Jordan and Bardsley, 1958; and Rost, Evans and Kramer, 1958) legumes responded to sulphur in its absence if conditions for symbiotic nitrogen fixation were suitable. (Bledsoe and Blazer, 1947; Anderson and Spencer, 1949, 1950; McLachlan, 1955; and Walker and Adams, 1958c.) Spencer (1959) recorded that sulphur nutrition at adequate levels for clovers resulted in increased non-protein, organic sulphur accumulation, but grasses, under reduced nitrogen conditions accumulated sulphate. Walker and Adams (1958c) also showed that sulphate accumulated in grass grown under low nitrogen conditions, and that this was accompanied by a reduction in the percentage of non-protein nitrogen. This was in agreement with the results of Andrew, Kipps and Barford (1952) and Spencer (1959) who found the percentage protein nitrogen increased as a consequence of sulphur addition to grass.

In conclusion, it must be recalled that as well as sulphate ions absorbed through plant roots, sulphur dioxide absorbed through the leaves may also contribute as a source of sulphur in plant nutrition. Olsen (1957) suggested that healthy cotton plants could gain 30% of their sulphur requirements from the atmosphere, and with sulphur-deficient cotton plants, the figure could be up to 50%.



### Crop Requirements of Sulphur

Thomas et al. (1950) gave the sulphur content of 1,000 plants analysed in an extensive survey. Recently, Jordan and Ensminger (1958) have tabulated the quantity of sulphur contained in average production yields of some common crops. Three categories were recorded, into which crops could be subdivided according to their needs of this element:

1. High: Absorb 20-35 lbs of S per acre, e.g., crucifers.
2. Medium: Absorb 12-25 lbs of S per acre, e.g., legumes.
3. Low: Absorb 8-12 lbs of S per acre, e.g., cereals and grasses.

Under New Zealand conditions it is probable that sulphur would be absorbed in higher quantities than these workers have recorded, because crop yields here are generally higher, e.g.,

1. Swede forage crop 40 tons per acre, \* 11.1% D.M. \*\* of 0.5-1% S\*\*\* (on D.M. Basis) represents 50-100 lbs sulphur in the crop.
2. Lucerne under irrigation, 8,000 lbs D.M. (Cousins, pers. comm.) of 0.3-0.4% S\*\*\* represents 24-32 lbs sulphur in the crop.
3. A grass pasture clipping 10,000 lbs D.M. of 0.3-0.4% S\*\*\* represents about 30-40 lbs of sulphur absorbed.

These figures under New Zealand conditions are by no means exceptional.

\* Average yield 1946/47 season. Calder, J.W., 1950  
Canterbury Chamber of Commerce Agriculture Bull. 257.

\*\* Average D.M. figure for swedes. Hadfield, J.W., 1952  
D.S.I.R. Information Series Bull. 5.

\*\*\* Agriculture Department (Pers. comm.) figures for normal healthy plant growth.



### Sulphur Deficiency in Plants

The classical symptoms of sulphur deficiency resemble closely those of nitrogen deficiency, and no doubt this reflects that both these elements are required for protein synthesis. Thus, chlorotic, stunted growth and general unthriftness can be noted in sulphur-deficient plants. Spencer (1959) recorded that, in common with most nutrient deficiencies, the root : top proportion was greater in sulphur-deficient clover, and Hilder and Spencer (1954) found a higher incidence of anthocyanin pigmentation. Nightingale, Schermerhorn and Robbins (1932) associated the thicker cell walls of sulphur-deficient tomato plants with carbohydrate accumulation. Reduced nodulation of sulphur-deficient clovers, according to Anderson and Spencer (1950) is an indirect effect. Rhizobia do not require sulphur in the nitrogen fixation process, but under sulphur-deficient conditions the host plant itself has little demand for nitrogen, and thus nodulation is reduced. In this manner these workers differentiated between the effects of molybdenum and sulphur deficiencies in clover plants.

Differences in biochemical composition resulting from sulphur deficiency have been examined by Nightingale et al. (1932); Thomas et al. (1950); Anderson and Spencer, (1950); Rossiter, (1951, 1952); Ergle and Eaton, (1951); and Rendig, (1956); and Spencer, (1959). Briefly, the recorded main effects were a low protein content (most of the sulphur accounted for as protein sulphur) and reduced proteolysis. If nitrogen was supplied, soluble non-protein nitrogen compounds were noted to accumulate in both legumes and non-legumes. Translocation of protein or organic sulphur does not appear to occur readily. Ergle <sup>(1953 and)</sup> (1954) grew cotton plants



under normal conditions and recorded an accumulation of sulphate in their old leaves. At a later stage, sulphur was shown to be translocated and re-utilised for leaf initiation for a period after the sulphur supply to these plants had been cut off.

In conclusion to this section, it is expedient to note that sulphur deficiency of clovers is often also associated with molybdenum and phosphate deficiencies, or both. McLachlan (1955) stated that under Australian conditions there was a response to molybdenum only after the other deficiencies had been corrected. Walker, Adams and Orchiston (1955) recorded a sulphur and phosphate interaction in the growth of clovers, and Walker and Adams (1958a) have found an association between molybdenum and phosphate responses.

#### Competition by Plants for Sulphur

The existence of competition for sulphur between legumes and grasses has been clearly demonstrated by Walker et al. (1956, 1958c). These workers recorded that under sulphur deficient conditions the grass took up 94% of the sulphate available to a grass-legume sward. However, it is difficult to pinpoint any one condition as being responsible for this greater sulphur uptake by the grass. Competition by plants for nutrients can be resolved into differences in: 1. Growth habit of roots and tops; 2. Response to light; 3. Recovery from grazing or defoliation; 4. Rate of growth; 5. General adaptability of a plant to a wide ecological range; 6. Nutrient availability. If these other factors are temporarily discounted, root growth will be a vital consideration. Grasses have fibrous roots and are probably better able to present a larger surface area to the soil solution than legume roots which



characteristically conform to a taproot pattern. The cation exchange properties displayed by roots could be an important consideration. Some aspects on this topic have been discussed by Lundegardh, (1942); Williams and Coleman, (1950); Mehlick, (1953); Vervelde, (1953); Helmy and Elgabaly, (1959) and Mouat and Walker, (1959). From application of Donnan Equilibria principles it follows that colloids with low cation exchange capacities (C.E.C.) contain greater concentrations\* of monovalent cations, and the lower the C.E.C. of the colloid and the lower the valency of the associated cations, the greater is the concentration of associated anions. Because the Donnan system is reversible, it is possible that low C.E.C. roots will compete successfully for monovalent cations and for cations against high C.E.C. roots. Legume roots in general have about twice the C.E.C. of grass roots. Recently, Butler (1961) has recorded a positive correlation ( $r = 0.8$ ) between the levels of sulphate and phosphate obtained in ryegrass herbage. He also records a strong negative correlation between the root C.E.C. of these plants and the levels of phosphate and nitrate in the herbage, which is in accord with Donnan Equilibria principles. Undoubtedly C.E.C. could be a major factor of plant competition, particularly when a nutrient is in short supply.

#### The Use of Sulphur Fertilisers

Sulphur was used as a fertiliser in England during the 18th and 19th centuries, but after the introduction of superphosphate in 1843, the use of sulphur fertiliser alone almost ceased. Superphosphate contains about 12 lbs of sulphur and

\* At low concentrations the activity of an ion is proportional to its concentration, and thus as long as we keep to very weak solutions it is permissible to use the term concentration in this sense.



10 lbs of phosphate in each hundredweight, so that its widespread usage as a fertiliser to supply phosphate has inadvertently resulted in application of sulphur also. Probably it is because of this that recognition of widespread sulphur deficiency was retarded.

Sulphur has also been much used as a fungicide and as a soil amendment to regulate soil pH values. In this latter respect, sulphur has been widely used for reclamation of alkaline (salty) soils. Erdman (1921) has discussed the effect of the use of gypsum on acid neutral and basic soils. Calcium sulphate is a neutral salt, yet it does affect the soil pH value through calcium exchange for hydrogen on the soil complex. Chee (pers. comm.) carried out a pot experiment studying the effects of calcium and magnesium on clover inoculation, and in one treatment he applied gypsum as a source of calcium. The calcium exchanged for hydrogen on the soil exchange complex to such an extent that the soil reaction fell by one pH unit, and at this level nodulation failed.

The application of sulphur fertilisers in order to rectify the sulphur status of soils is now common practice, and in this review, it will suffice to record that sulphur responses have been obtained in Canada (Cairns and Richer, 1960); in Scotland (Little, 1958); in France (Malavolta, Coury, Galli *et al.* 1955); in Brazil (McClung *et al.* 1959); in the United States (Jordan and Ensminger, 1958); in Australia (Stephens and Donald, 1958); and New Zealand (Lobb, 1959 and Lobb and Bennetts, 1959).

Residual effects from sulphur fertiliser application have been recorded by Walker and Adams (1958b), Jordan and Baker (1959) and Cairns and Richer (1960). Raw elemental sulphur, depending upon granule size, will also give a residual response. Under grazing conditions, animals will return sulphur



by way of the dung and urine excreted, from the herbage ingested. Walker (1957) has likened this to the additional use of fertiliser because much of this sulphur is readily available for plant growth, and the grazing animal must therefore assist the residual effect through its re-cycling of nutrients at an increased rate.

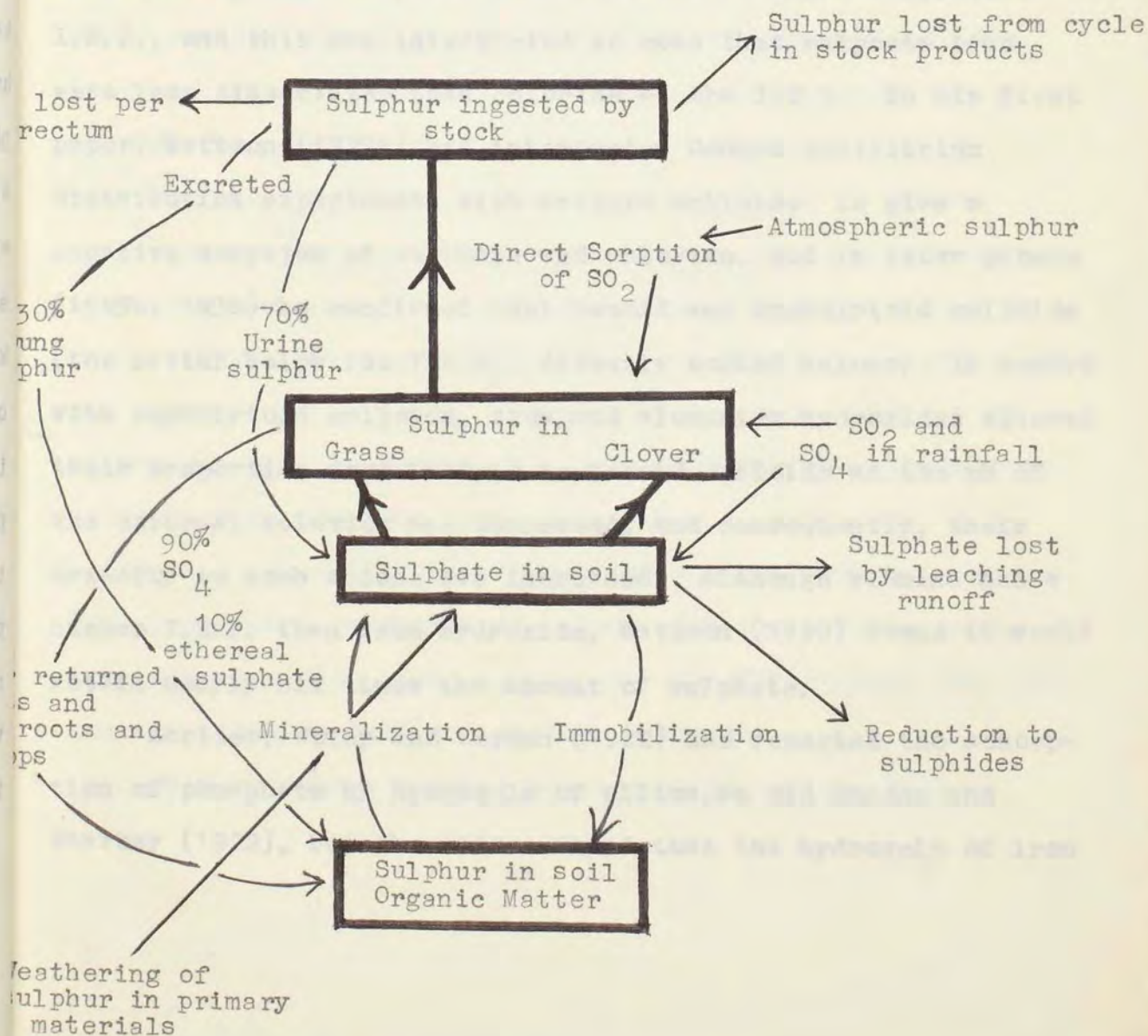
If soils are cropped and the produce removed as grain or animal products, for greater or lesser periods, the soils become depleted in organic matter and reserves of other nutrients. Sears (1953) recorded a rapid deterioration of pasture which was not getting a full return of animal excreta when grazed. The use of superphosphate rectified the losses of sulphur and phosphate and maintained an adequate clover component in the sward. The clover growth supplemented the nitrogen status and stimulated grass growth, with the result that the pasture in that plot produced a similar quantity of dry matter to the plots receiving a full return of excreta. Gilbert (1951) has stated that approximately equal quantities of sulphur and phosphorus are required by crops. Swanson and Latshaw (1922) assessed the loss of sulphur under cropping. Mann (1955) was able to show that the loss in organic sulphur could be compensated for by atmospheric returns from industrial regions. McClung et al. (1959) found a downward movement of sulphur occurred under cropping. The effectiveness of sulphur fertiliser may be reduced when it is applied with phosphorus if phosphate is not deficient, because Ensminger (1954) has shown that sulphate is not retained against leaching by soils in the presence of applied phosphate. Jordan and Baker (1959) used a radio sulphur tracer technique to assess the effectiveness of various sulphur fertilisers commonly used in agricultural practices.



That judicious use of sulphur fertilisers will result in a build-up in organic matter in soils of a deficient sulphur status, has been shown by Williams and Donald (1957) and Hingston (1959). The New Zealand tussock grassland below 3,500 feet altitude undoubtedly has a great potential for improvement if corrected for sulphur and other deficiencies. Current research work has shown that where clover has been established as a result of expedient fertiliser usage, the fertility of the soil can be raised to a level which will encourage the growth of better grass species, thus making a pasture capable of carrying up to 1-2 sheep per acre.

## The Sulphur Cycle of Grassland Soils

This topic has been discussed by Walker (1957) and a diagrammatic Summary is given below:





## CHAPTER IV

### PHYSICO-CHEMICAL RETENTION OF SULPHATE

#### BY SOILS

##### Anion Adsorption and Exchange

On the basis of electrokinetic properties, Sante Mattson (1930) classified colloids into the three categories acidoid, basoid and ampholytoid. Of these, the ampholytoid behaved as a positive colloid (basoid) in acid solution, or as a negative colloid (acidoid) in alkaline solution. In Mattson's second and third papers (1929b, 1930) on the "laws of soil colloidal behaviour", it was recorded that adsorption of anions took place on many colloids when they were at a pH lower than their isoelectric point (I.E.P.). The hydroxides of iron and aluminium retained considerably more sulphate than chloride at their respective I.E.P., and this was interpreted to mean that sulphate ions were less dissociated than chloride at the I.E.P. In his first paper, Mattson (1929a) had interpreted Donnan equilibrium distribution experiments with acidoid colloids to give a negative sorption of sulphate and chloride, and in later papers (1929b, 1930) he confirmed that basoid and ampholytoid colloids (the latter below the I.E.P.) directly sorbed anions. In accord with ampholytoid colloids, iron and aluminium hydroxides altered their properties from acidoid to basoid colloids as the pH of the external solution was decreased, and consequently, their capacity to sorb anions was increased. Although alumina had a higher I.E.P. than iron hydroxide, Mattson (1930) found it would retain nearly six times the amount of sulphate.

Earlier, Wiley and Gordon (1922) had reported the adsorption of phosphate by hydrogels of silica, as did Gordon and Starkey (1922), but the latter found that the hydrogels of iron



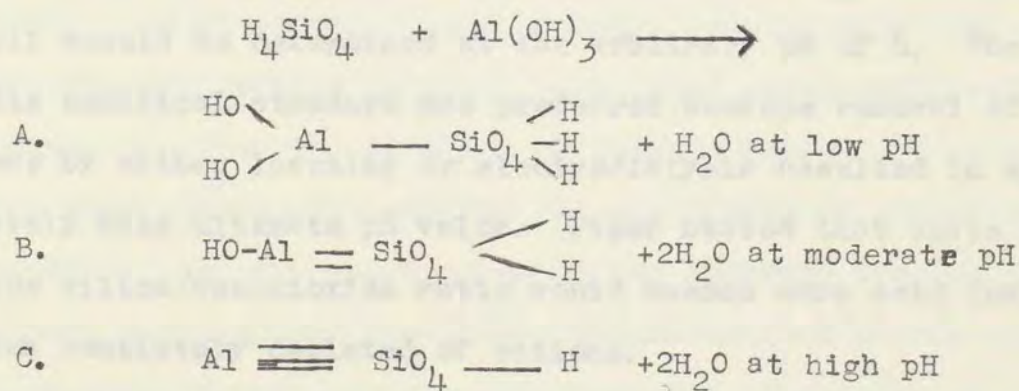
and aluminium exhibited greater adsorption capacities for this anion. Starkey and Gordon (1922) showed that phosphate > sulphate > nitrate was the order of retention of anions by these hydrogels, and that as the pH decreased, so the retention of them became greater. According to Lichtenwalner, Flenner and Gordon (1923) adsorption was specific, although the associated adsorption of cations depended upon the accompanying anion. They reported also that adsorbed nitrate and sulphate on these hydrogels could be leached out by water, but that adsorbed phosphate was only partially leached. When Mattson (1930) examined the adsorption of phosphate, sulphate and chloride from solutions of their respective acids, he found that anion exchange could take place. However, because of the differential retention of these with phosphate > sulphate > chloride, anion exchange, when it occurred, was unidirectional, so that a more strongly sorbed anion only, would replace a more weakly sorbed anion. Phosphate alone, he recorded, could be sorbed by these hydrous oxides in neutral solutions.

Mattson (1930) had stated in a discussion on Donnan equilibrium systems, that all the ions in the system mutually displaced one another according to the adsorption energy of each, and that for each ion there was a limiting potential in the diffuse double layer, above which the ion could not exist in the dissociated state. He considered the adsorption layer to be very complex and prone to change as conditions, e.g., nature and concentration of ions, pH and temperature, changed. Non-dissociated complexes of anions with the hydrous oxides of iron and aluminium could account for the differences recorded between cation and anion exchange behaviour.

With reference to silica/sesquioxide ratios, Mattson



(1930) recorded that silica was electronegative, whilst the sesquioxides were ampholytoid. Since clays were formed by combination of silica and alumina, Mattson suggested that their anion retention capacities would be a function of their silica/sesquioxide ratio, and hence an increase in the sesquioxide content would lead to the formation of non-dissociated complexes with anions. Kelley (1943), while conceding that anion exchange or adsorption was most marked at pH values below the I.E.P., considered that this phenomenon was not wholly explainable in simple terms of acidoid/basoid (i.e., silica/sesquioxide) ratios, because some of the constituents of colloids were amphoteric. Instead, he considered that the nature of the combination between acidoid and basoid was the important factor which influenced the adsorption properties. If anions conformed to Donnan equilibrium principles, then the colloid micelle conceivably could adsorb and/or repel anions at various sites on the crystal edge interface. For example, Kelley considered three hypothetical combinations of one molecule of orthosilicate with one molecule of aluminium hydroxide.



If the OH ion was considered to participate in anion exchange reactions and H<sup>+</sup> ion in cation exchange reactions, then although the silica/sesquioxide ratio remained constant,



the exchange properties of the above compounds could be summarised as follows:

A.	High C.E.C.	and moderate A.E.C.	properties		
B.	Moderate	"	"	low	"
C.	Low	"	"	nil	"

The compound formed would depend on the pH, and thus the anion exchange would depend upon pH, as in fact, laboratory experiments have shown.

Russell (1954) has recorded that some soils and/or clays have, as well as a permanent negative charge, an additional negative charge which develops at high pH values and which is a function of the pH. Buffer curves of soils also indicate that certain soils could have a positive charge developed at low pH. He points out that this phenomenon is probably brought about by the dissociation of aluminium at low pH from the crystal lattice, since, if these soils are treated with Tamm's acid oxalate reagent, the material which gives rise to the positive charge is removed. This reagent extracts active aluminium, as well as iron oxides and a humus fraction. Piper (1950) recommended that the total anion exchange capacity of a soil should be determined at the arbitrary pH of 4. The use of this empirical standard was preferred because removal of cations by either leaching or electrodialysis resulted in approximately this ultimate pH value. Piper stated that soils of a wide silica/sesquioxide ratio would become more acid than pH 4 when completely depleted of cations.

Williams, Scott and McDonald (1958) related phosphate sorption to active aluminium (mainly) and iron (slightly) extracted from soils. They thought that this active fraction was associated more with the organic matter component of the soil than with the clay or silt fraction, because active



aluminium could be closely correlated with organic carbon and loss on ignition values. On the other hand, Coleman (1944) attributed phosphate sorption to the active iron and aluminium associated with the clay fraction. Russell and Low (1954) found that exchangeable aluminium would react with phosphate. When the cation exchange sites on the kaolinite, with which they experimented, were saturated with aluminium, the adsorption of phosphate was increased, but treatments of aluminium-saturated clay with aluminium complexing reagents, resulted in decreased phosphate sorption. Recently, Saunders (1959) has attributed the high phosphate-fixing capacity of soils derived from andesite in New Zealand to their high content of active aluminium.

Dean and Rubins (1947) showed that kaolinite minerals and certain hydrous oxides of iron and aluminium adsorbed phosphate with an accompanying release of hydroxyl ions. This, they concluded, indicated that phosphate sorption was, in reality, an anion exchange process. Dickman and Bray (1941) showed that accessible hydroxyl ions of kaolinite could be replaced by fluoride and phosphate. McAuliffe, Hall, Dean and Hendricks (1947) used deuterium-tagged hydroxyl ions to show that certain clay mineral surface hydroxyl ions could enter anion exchange reactions. From the kinetics of tagged phosphate reactions, they were able to account for two mechanisms of phosphate sorption. One was anion exchange for hydroxyl ions at the crystal surface, and the other, which required a long time to reach equilibrium, was not ascertained.\* McAuliffe *et al.* (1947) measured the occurrence of hydroxylic ions on the

\* Probably it involved lattice substitution reactions.

This phenomenon has since been demonstrated by Schell and Jordan (1959).



surfaces of kaolinite, halloysite, diaspore and gibbsite, and a relationship between this and phosphate adsorption was recorded. Schell and Jordan (1959) further substantiated the relationship between surface chemico-physical properties of clay and anion exchange. Of the clays studied, bentonite, which had the greatest total surface area, was reported to have the greatest A.E.C., and it adsorbed equivalent amounts of both sulphate and phosphate ions. Kaolin, halloysite and pyrophyllite, on the other hand, adsorbed more phosphate than sulphate ions, while chloride ions were adsorbed in traces only. These workers declared that electrodialysis of clays gave a measure of the bonding energy of the anions and showed conclusively that adsorbed phosphate ions on the exchange sites could undergo substitution reactions with aluminium and silica within the crystal lattice.

Fieldes (1958) associated the properties of broken bonds at the edges of the clay allophane with the ability of tetrahedral aluminium to form co-ordinated bonds with oxygen. Not only could water be retained through co-ordination of its oxygen at this broken bond site, but also cation exchange could occur by dissociation of one of the hydrogen ions from the water molecule. However, certain anions which contained oxygen could also be adsorbed at the aluminium tetrahedral site by co-ordination through the oxygen, but Fieldes stated that there would be preferential adsorption for anions whose valency contribution to the oxygen was 1.25 at that tetrahedral site. Molybdate, phosphate, and vanadate anions suited these conditions and were adsorbed. Other anions such as sulphate, nitrate and hydroxyl had a valency discrepancy which prevented their adsorption on steric grounds.

Cook, Cutler, Hill, Wadsworth and Oblad (1953) outlined the thermodynamic principles associated with the aluminium



change-over from tetrahedral to octahedral co-ordination, and proposed that "ion pair" adsorption was one mechanism which could account for cation and anion exchange. With anion adsorption, the non-hydrated anion would be adsorbed on to the colloid site from the compact double layer, and its associated cation would remain in a hydrated state in the diffuse double layer. Judson, Lerew, Dixon and Salley (1953) found that sulphate gegenions could be adsorbed on to anionic agents in multilayer form from sodium sulphate solution. They explained the multilayers as due to polarity of hydrated ions and this approach contrasted sharply with that of Cook *et al.* (1953).

Amphlett (1958) proposed a series of possible reactions of anions with clays which can be summarised as follows:

1. Dissociation of surface hydroxyls could permit anion exchange reactions, but he stipulated that this form of anion exchange would be essentially an "edge and corner" reaction on the clays.
2. Anions of suitable stoichio-chemical properties could be incorporated into the clay crystal by either lattice substitution for, or extension on to, silica tetrahedra.
3. In the case of phosphate, non-exchange reactions could take place to form a heterogeneous series of precipitates with iron, aluminium and calcium.

Recently, Tickhova (1958), and Cairns and Richer (1960) have found that soils with high exchangeable barium could cause the precipitation of sulphate.

Grim (1953) also concluded that anion exchange could take place with the clay minerals by replacement of hydroxyl ions and by lattice substitution and replacement of silica tetrahedra with anions of suitable steric properties. He



discounted Schofield's hypothesis that clays could have both active cation and anion exchange spots on their basal surfaces. Kolthoff (1936) had suggested that counter ions, held in extra-lattice positions at the surface of crystals, owing to unequal distribution of forces in the crystal during cation adsorption, were also exchangeable.

#### Adsorption of Sulphate by Soils

Clay mineralogical data given by Pearson and Ensminger (1948) indicate that sulphate sorption capacities of twelve Alabama soils reported by Ensminger (1954) could be related to the clay components. Subsoil horizons, which contained predominantly 1 : 1 type clay minerals and relatively high iron and/or aluminium hydrous oxide, appeared to have had a greater capacity to adsorb sulphate. A similar relationship was recorded by Kamprath et al. (1956) and Neller (1959). Jordan and Bardsley (1958), Harper (1959) and McClung et al. (1959) found greater quantities of extractable sulphur in clay horizons, but made no attempt to relate it with the clay constituents. MacIntyre et al. (1952) in lysimeter studies recorded that a Cumberland subsoil retained added sulphate.

Laboratory and field experiments by Ensminger (1954) and Kamprath et al. (1956) indicated phosphate would decrease the capacity of soil to adsorb sulphate, and in the above trial of MacIntyre et al., phosphate addition resulted in increased sulphate in the leachings.

Another influential factor accrued to sulphate sorption in soils, is pH. Ensminger (1954) and Kamprath et al. (1956) both recorded greatest sulphate retentions at low pH values. Lime additions made to lysimeter experiments of MacIntyre



et al. (1941) increased the leaching rate of sulphate, and it was postulated by Jordan and Ensminger (1958) that little or none of this ion could be expected to be retained by soils limed to a pH of 6. Probably high pH would be responsible for the trace amounts of sulphate commonly recorded in surface soils.

The effects of cations on sulphate retention by soils have been largely unexplored. However, Cairns and Richer (1960) made a study of the distribution of soluble barium in two soils and reported less sulphate to be extractable from soil horizons containing appreciable quantities of soluble barium. The soil was capable of precipitating sulphate in acid medium. Tickhova (1959) found that the amount of sulphate adsorbed by soils varied according to the cation which occupied the exchange sites. Barium-saturated soil chemically precipitated sulphate, iron-saturated soil sorbed sulphate by physico-chemical reactions and hydrogen-saturated soil also adsorbed sulphate by a means he attributed to the properties of the hydrous oxides. However, the data given for hydrogen-saturated clay would lead one to deduce that adsorption via anion exchange reactions occurred.

### Summary

From the complexity of the data presented by these authors, it is evident that confused interpretation has militated against any simple theory of anion exchange. However, "edge and corner" hydroxyl ions of many clays appear to enter into exchange reactions at suitable pH values, but anions adsorbed at these sites are not completely inter-exchangeable. Usually phosphate replaces other anions, although it is recorded that a bentonite clay adsorbed equiv-



alent amounts of phosphate and sulphate. Under defined conditions, surface hydroxyl ions are replaceable by fluoride or phosphate, which suggests adsorption is an anion exchange reaction.

Steric and stoichiometric-chemical properties are thought by some workers to account for adsorption of certain anions by lattice substitution and extension mechanisms. These considerations provided a reason why cation and anion exchange reactions were not analogous. Formation of complex, heterogeneous physico-chemical compounds of certain anions with the hydrous oxides of iron and aluminium provides a further reason for a difference between these two reactions.

A very marked influence of pH on anion adsorption properties has been shown. Possible effects of low pH values on clay micelles can be summarised as follows:

1. Activation of hydroxyl exchange sites;
2. Alteration of the Donnan distribution of all ions;
3. Displacement of cations from cation exchange sites with possible chemical precipitation reactions;
4. Partial disruption of the crystal lattice edge with a consequent release of active aluminium.

With the hydrous oxides, low pH values appear to activate the hydroxyl exchange sites, or cause the amorphous colloid to adopt a positive charge, after which adsorption of anions can follow by Donnan principles. Unfortunately, Donnan distribution principles have been interpreted differently by the various authors, and it seems that direct or counter-ion adsorption can occur, depending on the hydration state of the ions.

It is evident that sulphate adsorption by soils is associated with the clay horizons and is influenced by lime (pH),



phosphate and certain cations. Therefore, it appears that sulphate adsorption and/or retention phenomena of soils can be explained by:

1. The mechanisms of anion exchange on clay micelles or the hydrous oxides;
2. Ill-defined aspects associated with physico-chemical or straight chemical precipitations with certain hydrous oxides and barium.
3. The specialised interpretation of Donnan principles such as adsorption as counter-ions.

It is possible that all three mechanisms actively contribute.



## E X P E R I M E N T A L

## CHAPTER V

EXPERIMENTAL PROCEDURESIntroduction

The aim of the experiment was to ascertain whether or not the residual responses to sulphur, obtained by Walker and Adams (1958b), could be attributed to the ability of a Kowai soil to adsorb sulphate. Ensminger (1954) reported that phosphate and lime influenced the amount of sulphate retained by certain Alabama soils. Kamprath *et al.* (1956) attributed differences in soil adsorption capacities for sulphate ions to differences in clay mineralogical contents. Two soils (Kowai sandy loam and an Evans steepeland loam) of reportedly contrasting clay mineralogy were used for the purpose of field experiments. Of the two soils, only the Kowai soil was known to be responsive to sulphur.

Field trials were laid down using gypsum as a sulphur source, and the movement of the sulphate ions through the profiles was to be traced. Herbage production cuts were to be made also to determine the plant uptake of sulphur. Rain water collection was undertaken to assess the return of sulphur from the atmosphere.



Profile descriptions of the two soils\* used for the experiment are:

I Rakaia Gorge Site:- (Fig. 1).

Location: Bayfields Estate, Rakaia Gorge: 10 miles northwest of Windwhistle, on high river terrace  $\frac{1}{4}$  mile north of Rakaia River, 70 yds west of Professor Walker's plots.\*\*

Altitude: 1430 ft.

Slope: Slight ( $1^{\circ}$ ) northwesterly general slope.

Topography: Nearly flat tread of high river terrace.

Erosion: Nil on site; liable to severe wind erosion when vegetative cover destroyed.

Vegetation: Original vegetation was fescue tussock association. Area has been ploughed once, but has reverted to fescue tussock and a mixed sward of introduced and native pasture species.

Parent Material: Greywacke loess (6ft thick) overlying greywacke gravels.

Profile:

12 ins Dark greyish brown (10 YR 2/2, moist) fine sandy loam; friable; weak - moderately developed medium nutty structure with 30% moderately developed fine crumbs; abundant roots; many worms and many worm tunnels; indistinct boundary,

12 ins Yellowish brown (10 YR 5/4, moist) silt loam with some grit; slightly sticky; massive; horizon slightly compacted; fragments very hard when dry; few roots; many worm tunnels containing cast granules: indistinct boundary,

ON Weathered loess derived from greywacke.

Classification: Kowai sandy loam.

\* Profile descriptions taken from holes dug inside the plot areas. Profile photographs taken from suitable cuttings within 100 yds radius of the plots.

\*\* Reported by Walker, T.W.; Adams, A.F.R.; and Orchiston, H.D. (1956), Plant and Soil, 7: 290-300.



FIGURE 1

PHOTOGRAPH OF KOWAI SANDY LOAM PROFILE TAKEN WITHIN  
CLOSE PROXIMITY OF RAKAIA GORGE EXPERIMENTAL PLOTS



FIGURE 2

PHOTOGRAPH OF EVANS STEEPLAND LOAM PROFILE TAKEN  
WITHIN CLOSE PROXIMITY OF BANKS PENINSULA EXPERIMENTAL PLOTS





## II Banks Peninsula Site:- (Fig. 2).

Location: Cracroft Wilson Estate, Banks Peninsula:  $\frac{1}{4}$  mile north of Sign of the Kiwi, 70 yds west of Dyer's Pass Road.

Altitude: 900 ft (estimated).

Slope: General slope  $30^{\circ}$  west: site slope approximately  $15^{\circ}$  west.

Topography: Soliflucted slope; small soil-creep terraces approximately 2-3 ft in height. Plot site on a slight bench.

Erosion: Nil.

Vegetation: Dense silver tussock association plus some introduced cocksfoot and white clover.

Parent Material: Loess plus some basaltic colluvium.

### Profile:

6 ins Dark greyish (5 YR 3/1, moist) silt loam with many small partly weathered basaltic fragments (up to 2 ins); strongly developed, medium granular and fine nutty structure; friable; abundant roots; many worm tunnels; diffuse boundary,

10<sup>+</sup>ins Dark yellowish brown (10 YR 3/4, moist) silt loam; sticky; weakly developed fine-medium nutty structure; friable; slightly compacted; many roots; many worm tunnels containing cast granules. Many pebble to boulder-size basaltic fragments with different degrees of weathering and increasing in quantity with depth.

Classification: Evans steepland loam.



### Field Experimental Procedure

Five treatments were used in the field trials. Sulphur (S) was applied in the form of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Phosphate (P) was applied in the form of double superphosphate (21%P) which contained no sulphate. The treatments were as follows:

- A = Control
- B = 40 lbs S
- C = 40 lbs P
- D = 40 lbs S + 40 lbs P
- E = 200 lbs S

Plots of 10 x 10 links in area were used and the five treatments were replicated six times. A plan of the random layout of plots at the respective sites is given in Figures 3 and 4.

The Rakaia Gorge site was chosen with the assistance of Mr A. Adams. The area had previously been ploughed, but had not received fertiliser nor been ploughed for many years. Before the trial was pegged out on 29 September 1959, the vegetative cover was mown to a height of two inches and then raked clean. The materials were mixed with quartz sand and spread by hand. Although a fresh norwesterly wind was blowing at the time, wind drift which occurred during the spreading of the materials was only slight. The plots were oversown with inoculated white clover seed and the trial area was fenced. A gallon plastic flagon and filler were placed inside the fenced area in order to collect rain water samples.

The Banks Peninsula site was chosen with the assistance of Messrs C. Mead, Soil Bureau, Christchurch, and A. Adams. The dense silver tussock cover was scythed off at ground level, and the treatments applied on 30 September 1959. As with the other



FIGURE 3

SKETCH PLAN SHOWING RANDOM LAYOUT OF PLOT TREATMENTS  
OF RAKAIA GORGE FIELD EXPERIMENT

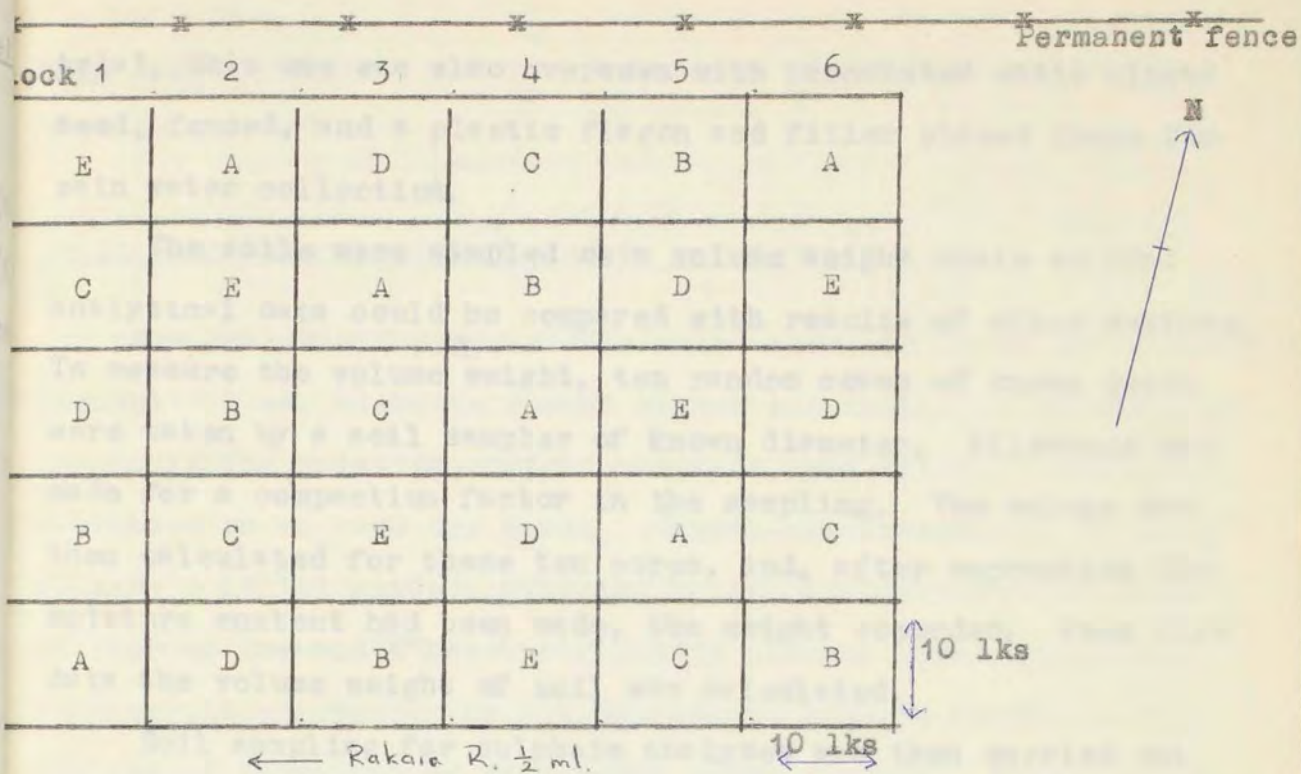
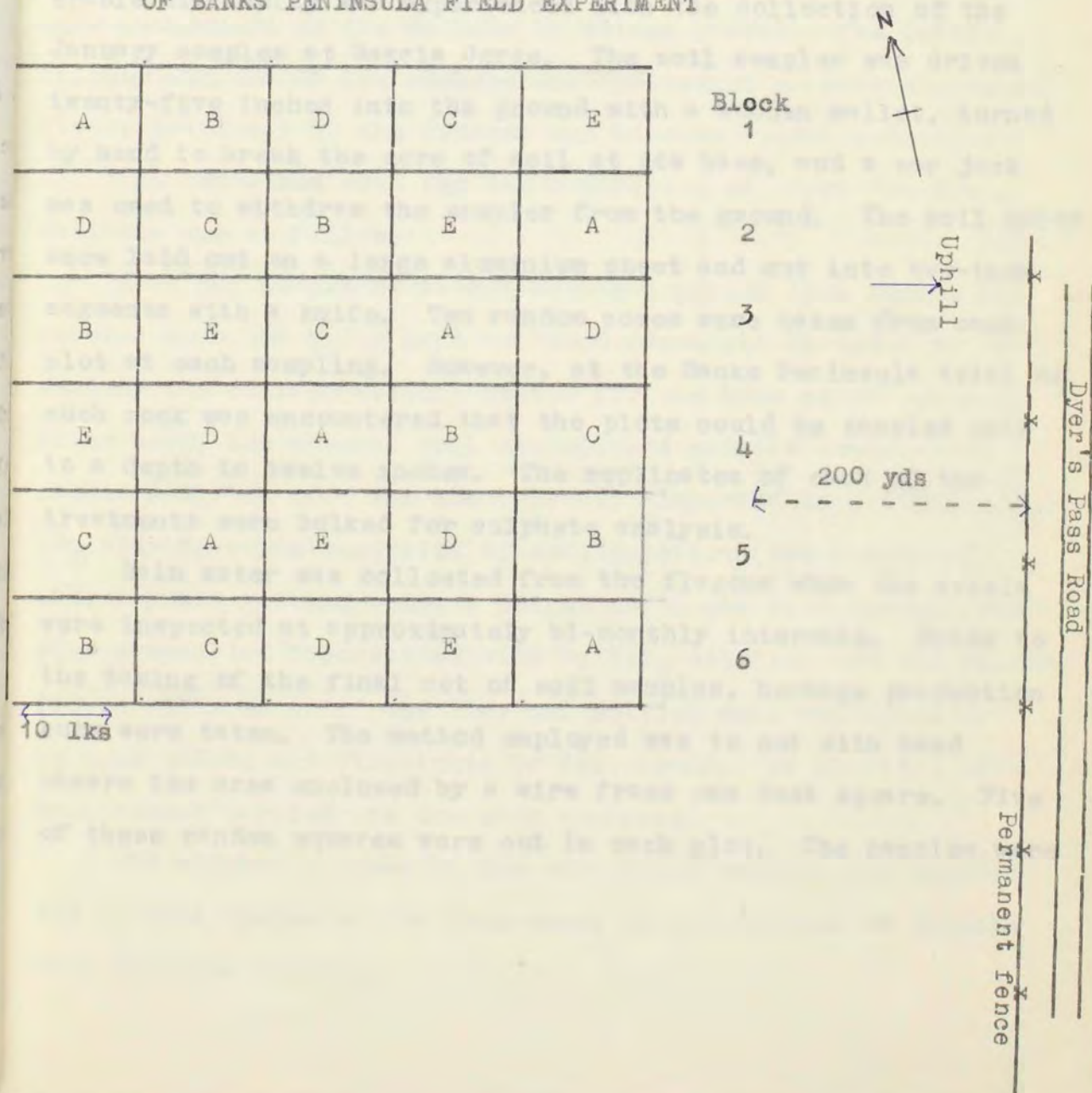


FIGURE 4

SKETCH PLAN SHOWING RANDOM LAYOUT OF PLOT TREATMENTS  
OF BANKS PENINSULA FIELD EXPERIMENT





trial, this one was also oversown with inoculated white clover seed, fenced, and a plastic flagon and filler placed there for rain water collection.

The soils were sampled on a volume weight basis so that analytical data could be compared with results of other workers. To measure the volume weight, ten random cores of known depth were taken by a soil sampler of known diameter. Allowance was made for a compaction factor in the sampling. The volume was then calculated for these ten cores, and, after correction for moisture content had been made, the weight recorded. From this data the volume weight of soil was calculated.

Soil sampling for sulphate analyses was then carried out twice for the Rakaia Gorge trial (29-31 January and 1-2 May 1960), but only once for the Banks Peninsula trial (4 May 1960). Considerable difficulty was experienced with the collection of the January samples at Rakaia Gorge. The soil sampler was driven twenty-five inches into the ground with a wooden mallet, turned by hand to break the core of soil at its base, and a car jack was used to withdraw the sampler from the ground. The soil cores were laid out on a large aluminium sheet and cut into two-inch segments with a knife. Ten random cores were taken from each plot at each sampling. However, at the Banks Peninsula trial so much rock was encountered that the plots could be sampled only to a depth to twelve inches. The replicates of each of the treatments were bulked for sulphate analysis.

Rain water was collected from the flagons when the trials were inspected at approximately bi-monthly intervals. Prior to the taking of the final set of soil samples, herbage production cuts were taken. The method employed was to cut with hand shears the area enclosed by a wire frame one foot square. Five of these random squares were cut in each plot. The samples were



oven dried, weighed, and the dry matter production per acre then calculated.

#### Laboratory Experimental Procedure and Methods

For analytical purposes the soils were air dried and sieved through a 2 mm. sieve to remove stones and roots. Correction of the soils for moisture content was made, and all the results are expressed on an oven dry basis. Carbon was determined by Allison's (1935) method; nitrogen by the Kjeldahl method; total sulphur by Swanson<sup>and</sup> Latshaw's (1922) method; total phosphorus and organic phosphorus by the Walker and Adams's (1958a) modification of Saunders and Williams's (1955) method. PH values were measured by a Radiometer 22 pH meter. Cation exchange capacities, total exchangeable basis (T.E.B.) and the exchangeable cations were determined by the methods of Metson (1956). The total sulphur content of the herbage was determined on bulked samples (after grinding) by the Swanson and Latshaw (1922) method.

The procedure used for the separation of clays for X-ray analysis was as follows:

A 10 gm. sample of sieved soil was placed in a beaker and covered with 30%  $H_2O_2$ ; left to stand overnight in order to destroy the organic matter; heated for one hour at  $90^\circ$  on a water bath; the mineral soil centrifuged and the supernatant liquid decanted off; the mineral soil dispersed in 0.02N.  $Na_2CO_3$ ; the clay fraction separated by sedimentation (the suspended material not settled below a height of 10 cms in 8 hours); the clay suspension flocculated with  $Mg(\overline{Ac})_2$  solution and the excess liquid filtered off. The clay was bottled wet, two drops of toluene added, and dispatched to Wellington. Dr Claridge of Soil Bureau carried out the clay analysis.

The sulphur content of the rain water samples was carried out by Miss Cooper of the Department of Agriculture at Rukuhia Soil Research Station.



### Extraction of Sulphate

The review of literature has shown that phosphate will replace sulphate in anion exchange reaction. It was thought that if sulphate was retained by the soil, the retention mechanism would probably involve an anion exchange reaction which could probably be associated with the clay fraction of the soil. Ensinger (1954) recorded that a solution of  $\text{KH}_2\text{PO}_4$ , containing a concentration of 100 P.P.M. P, extracted more sulphate than did acetate solutions. On the basis of his work, it was therefore decided to use a phosphate solution of the above concentration as the sulphate extractant. However, whether the extractant solution was acetate or phosphate, it was found in preliminary experiments that colloidal material was extracted also. This colloidal material imparted a cloudiness to solutions, even after the solution from extracted soil had been filtered through a No. 42 Whatman paper. Inclusion of active charcoal with the soil during the extraction process clarified the solution obtained after the soil had been filtered off.

Hesse (1957b) reported similar trouble with colloidal matter causing cloudiness in his sulphate extractions. He found that active charcoal clarified the solutions, but reported that it led to erroneous results because of surface adsorption of sulphate on to the active charcoal. He described a method in which the colloidal material was co-precipitated with  $\text{Fe}(\text{OH})_3$  before the analysis for sulphate was carried out. It is interesting to recall that Lichtenwalner *et al.* (1923) found that hydrous oxides of iron would adsorb sulphate at low pH values. Although Hesse used acetate buffered at pH 4.8 for the precipitation medium of this colloidal material, his results showed that good recovery of sulphate was obtained.

Table I shows sulphate recoveries from standard sulphate



solutions were little affected in the presence of the active charcoal source used in this experiment.

TABLE I

SULPHATE RECOVERIES FROM STANDARD SULPHATE  
SOLUTIONS NOT TREATED, OR TREATED WITH  
ACTIVE CHARCOAL

Standard Sulphate Solution S in p.p.m.	<u>Not Charcoal Treated</u>		<u>Charcoal Treated*</u>	
	%T	Sulphate Reading from Graph S in p.p.m.	%T	Sulphate Reading from Graph S in p.p.m.
1	97.8	0.8	97.2	1.2
1	97.4	1.1	97.8	0.8
2	94.8	2.1	95.1	2.0
2	95.0	2.0	95.0	2.0
5	87.6	5.0	87.4	5.1
5	87.5	5.0	87.7	4.9
10	75.0	10.0	74.8	9.9
10	75.2	10.1	75.0	10.0
15	62.4	14.9	62.4	14.9
15	62.4	14.9	62.4	14.9

\* 100 ml of standard sulphate solution duplicates were shaken for half an hour with 2 gm of active charcoal, filtered through No. 42 Whatman filter paper and 20 ml aliquots of this used for the sulphate determination.



### Determination of Sulphate

Much difficulty was experienced in finding a method for sulphate determination which would be both accurate and rapid. Preliminary investigations were carried out using the Ashgar, Qayyum and Rana (1956) and the Sporek (1958) methods. These methods were found to be insufficiently sensitive at the low concentrations of sulphate in the soil-extracted solutions. Turbidimetric determinations of sulphate precipitated as barium sulphate were then experimented with. Steinberg's (1955) "seed suspension" method was considered to be unsatisfactory because the standard curve when plotted was slightly sigmoid, with the curve flattening out at very low concentrations of sulphate. The Chesnin and Yien (1951) method was finally adopted as the most suitable procedure. In this method the barium sulphate is precipitated under controlled conditions and gum acacia is used to stabilise the precipitate. Calibration of the standard graph from standard sulphate solutions showed that the points when plotted lay on a straight line.

### Method for Determination of Extractable Sulphate:

#### Reagents;

Phosphate solutions; 100 p.p.m. P; dissolve 5.02 gm of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , A.R., in distilled water and make up to 10 litres.

0.25% gum acacia solution; dissolve 2.5 gm of gum acacia in hot distilled water and make up to 1 litre. Filter the solution and filter periodically to keep it clear.

Active charcoal; B.D.H. reagent.

Barium chloride crystals;  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , A.R., crystals were ground in a ball-mill and screened between 60-40 B.S.S. sieves.

Standard sulphate solution, containing 50 p.p.m. S; dissolve 0.271 gm  $\text{K}_2\text{SO}_4$ , A.R., in the standard phosphate solution and make up to 1 litre.



### Procedure

Duplicates of 20 gm of soil + 2 gm of active charcoal were weighed into 250 ml Erlenmeyer flasks and 100 ml of the 100 p.p.m. P solution added. The flasks were stoppered tightly with cork bungs and shaken for half an hour on an end-over-end shaker. The flask contents were filtered through a dry No. 42 Whatman filter. 20 ml aliquots of the filtrate were pipetted into 25 ml volumetric flasks. To each, 1 gm of  $\text{BaCl}_2$  crystals was added and the flask stoppered tightly and the contents shaken thoroughly for one minute. 1 ml of gum acacia solution was run in to the volumetric flask from a burette graduated in 0.1 ml divisions, the flask again stoppered tightly and shaken for one minute. Then the flask was made up to volume with distilled water, shaken again for one minute, and allowed to stand for five minutes. The percentage transmission (%T) was read in a Coleman Universal Model 14 electrophotometer 5-30 minutes later. A complete blank (without soil) was carried out and this was used as the standard (set to 100% T) against which the %T reading of the samples was taken. The sulphur content was read from a standard graph.

### Preparation of the Standard Graph

Standards containing 0, 1, 2.5, 5, 10, 15 and 20 p.p.m. S were made up from the stock 50 p.p.m. S standard sulphate solution. Triplicates containing 20 ml aliquots of these standards were pipetted into 25 ml volumetric flasks. 1 gm of  $\text{BaCl}_2$  crystals, 1 ml of the gum acacia was added, and the flask made up to volume following the procedure described above. The %T was read for each standard and the average of the triplicates used to plot the graph which is shown in Fig. 5.

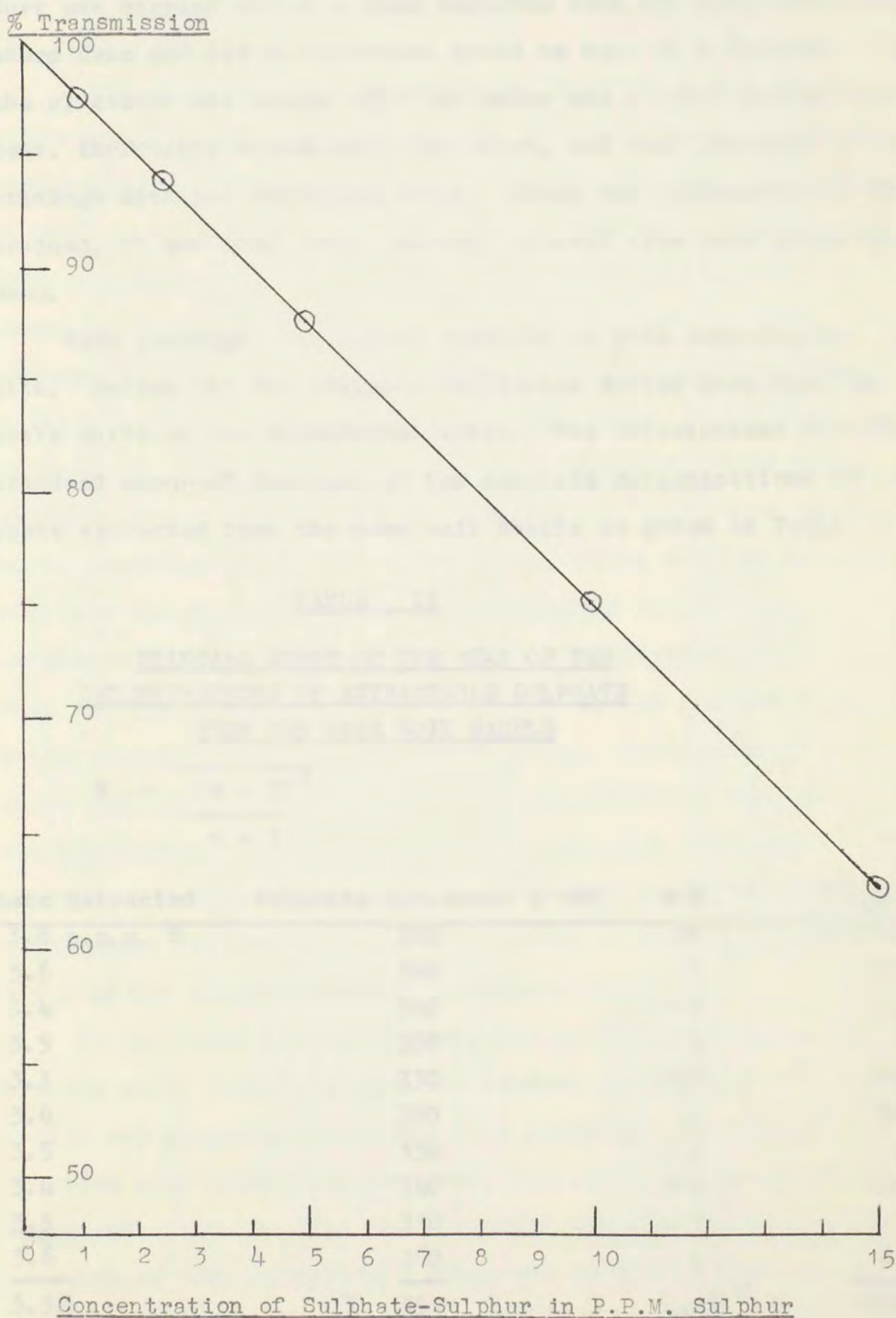
The wavelength setting used for the electrophotometer was  $525\mu$  and a blue filter (range  $633-667\mu$ ) was inserted also.



FIGURE 5

STANDARD GRAPH

% Transmission at 525 $\mu$  Plotted  
Against Sulphate-Sulphur Concentration





### Discussion

When chemical analyses involve the determination of trace amounts of a substance, special care has to be taken to avoid contamination of the glassware. In this experiment the analytical work was carried out in a room isolated from the main laboratory where dust and air disturbances could be kept to a minimum. All the glassware was washed with hot water and a sulphur-free detergent, thoroughly rinsed with hot water, and this followed by three rinsings with hot distilled water. After the glassware had drip drained, it was oven dried and kept covered from dust until next used.

With practice, the method appeared to give reproducible results. Seldom did the complete duplicates differ more than two scale units on the electrophotometer. The calculations for the standard error of the mean of ten separate determinations of sulphate extracted from the same soil sample is given in Table II.

TABLE II

STANDARD ERROR OF THE MEAN OF TEN  
DETERMINATIONS OF EXTRACTABLE SULPHATE  
FROM THE SAME SOIL SAMPLE

$$S = \frac{(x - \bar{x})^2}{n - 1}$$

phate Extracted	Sulphate Extracted x 100	$x - \bar{x}$	$(x - \bar{x})^2$
3.8 p.p.m. S	380	28	784
3.6	360	8	64
3.4	340	-12	144
3.5	350	- 2	4
3.3	330	-22	484
3.6	360	8	64
3.5	350	- 2	4
3.4	340	-12	144
3.5	350	- 2	4
3.6	360	8	64
<u>3.52</u>	<u><math>\bar{x}</math> 352</u>	$(x - \bar{x})^2$	<u>1760</u>

$$S^2 = \frac{1760}{9} = 195.5$$

S 14 Divide this by 100

Standard error of the mean is 0.14



## CHAPTER VI

### RESULTS AND DISCUSSION

#### Soil Analyses

##### (A) X-ray Analyses

X-ray analyses carried out by Dr Claridge showed that there was little difference between the clay components of the horizons of the Kowai sandy loam profile. The mineralogy clearly reflected the loessial derivation of the soil, because the clay fraction was largely composed of unexpanded micas, with about equal quantities of chlorite and vermiculite. The chlorite did not collapse on heating to 500°C, and the vermiculite did not collapse on potassium saturation, but did collapse on heating. Data given by Fieldes and Swindale (1954) would indicate that these clays have formed under conditions of moderate leaching at low base saturation levels, and the Kowai soil has the features of a weakly-weathered stage in clay development. The blue-grey colour of the micaceous clays in this profile was pointed out by Dr Claridge as another characteristic property of weakly-weathered soils. Consideration of the above features, together with the sandy nature of the soil, and the immaturity of the profile development, (as evidenced by the indistinct horizon boundaries) confirm that the Kowai soil development pattern is being modified by a continual accumulation of the parent material, greywacke loess.

In the Evans steepland loam, the chief clay mineral was hydrous mica, variously expanded between 10-14<sup>0</sup>A, but a little kaolin and montmorillonite was also present. The coarse clay fraction gave indefinite patterns, similar to those of the Kowai soil, but the clay had a reddish colouration due to the presence of some haematite. Since the fine clay fraction had



TABLE III

## GENERAL SOIL ANALYSES

Kowai sandy loam

Depth	C	N	C/N	S	Total P	Org. P	Org. P of Total P	pH	C.E.C.	T.E.B.	B.S	Ca	K	Mg
Ins	%	%	Ratio	%	%	%	%		me. %	me. %	%	me. %	me. %	me. %
0-6	2.6	.16	16.2	.031	.066	.038	57.6	5.7	12.1	6.1	51	3.0	1.5	2.0
6-12	2.0	.14	14.3	.027	.057	.031	54.5	5.6	10.7	3.2	30	2.9	0.8	0.4
12-18	1.4	.08	17.5	.019	.058	.034	58.5	5.5	8.1	3.0	37	1.9	0.5	0.4
18-24	0.8	.05	16.0	.015	.057	.033	58.0	5.8	7.0	3.5	50	2.9	0.5	0.5

Evans steepland loam

0-6	3.9	.27	14.4	.045	.073	.042	57.5	5.9	20.0	14.8	74	9.2	1.2	4.2
6-12	1.9	.11	17.2	.024	.051	.023	45.0	6.0	15.2	11.2	75	7.0	1.0	3.1



TABLE IV

ACRE WEIGHTS OF C, N, S, TOTAL P AND ORGANIC P IN THE SOIL HORIZONSKowai sandy loam

Depth	Volume Weight	C	N	S	Total P	Organic P
Ins	lbs per acre x 10 <sup>6</sup>	lbs	lbs	lbs	lbs	lbs
0- 6	1.51	39,300	2,420	468	1,000	574
6-12	1.67	33,400	2,340	452	952	517
12-18	1.85	25,900	1,480	352	1,070	630
18-24	2.00	16,000	1,000	300	1,140	660

Evans steeppland loam

0- 6	1.37	53,400	3,700	616	1,000	575
6-12	1.89	35,900	2,080	454	965	435



TABLE V

## ORGANIC COMPONENTS OF THE SOIL HORIZONS EXPRESSED AS RATIOS

Kowai sandy loam

Depth in Ins	C/N	C/S	C/Org. P	N/S	N/Org. P	S/Org. P	C	N	S	Org. P
0- 6	16.2	84	69	5.2	4.2	.8	163	: 10	: 1.9	: 2.4
6-12	14.3	74	65	5.2	4.5	.9	143	: 10	: 1.9	: 2.2
12-18	17.5	74	41	4.2	2.4	.6	175	: 10	: 2.4	: 4.3
18-24	16.0	53	24	3.3	1.5	.5	160	: 10	: 3.0	: 6.6

Evans steepland loam

0- 6	14.4	86	93	6.0	6.4	1.1	144	: 10	: 1.7	: 1.6
6-12	17.2	79	79	4.6	4.8	1.0	172	: 10	: 2.2	: 2.1



the same blue-grey colour as that of the Kowai soil, Dr Claridge considered that the Evans soil appeared to have its clay derived largely from loess, which was older than that of the Kowai soil, because most of the micas had hydrated. Thus, chlorite and vermiculite as present in the Kowai soil, had largely disappeared in the Evans soil. However, he thought that some of the clay was derived from, or under the influence of weathering of, the underlying basalt, namely, the haematite of the coarse clay fraction and the montmorillonite and kaolin of the fine clay fraction. Fieldes and Swindale (1954) have described montmorillonite development under conditions of restricted leaching at moderate to high pH values and high base saturation levels. Presumably weathering of the basic plagioclase feldspar components of the basalt would ensure the above conditions. The kaolin would probably be derived from the coalescence of hydrous oxides. No estimate of the quantities of kaolin or montmorillonite was made, but it was considered that they were quite low. Similarly, although the amorphous oxide content was not measured, Dr Claridge considered that its quantity would be low because the clay mineralogy was developed largely from loessial components of the parent material. In the Kowai soil, he thought that the amorphous oxide content would be very low. Mechanical analyses carried out on these two soils showed that the Kowai soil contained 10% and 18% clay in the A and B horizons, while the figures for the Evans soil were 21% and 29% for these respective horizons.

#### (B) Chemical Analyses

The general soil analyses of the Kowai and Evans soils are shown in Table III, and the acre weights of the major organic constituents are given in Table IV. It can be seen that the



C.E.C. values reflect the mineralogical pattern outlined by Dr Claridge, while the low base saturation levels of the Kowai soil indicate that it is moderately leached. Although in the Kowai soil the percentage of carbon, nitrogen and sulphur decreases considerably as depth down the profile increases, this decrease is less pronounced when these elements are considered on a horizon acre weight basis, because the density of the soil increases with depth. The total phosphorus and organic phosphorus, in contrast to the other organic constituents, remain relatively constant throughout the profile. In Table V, because the percentage of nitrogen is low, the C/N ratios tend to be wide, but on the other hand, the N/S ratios are narrower than Walker and Adams (1958c) recorded for a Kowai soil. The usual trend is for N/S ratios to widen with increasing profile depth. With the Evans soil, the organic constituents are similar in amount to those described by Walker and Adams (1958c) for Takahe soils which are of loessial derivation, and this ties in well with the mineralogical data presented above.

For both soils, the percentage of organic phosphorus of the total phosphorus values are similar to those recorded by the above workers for similar soils. As they have shown, this would indicate that plant available phosphorus would not be expected to be a critical factor limiting plant growth on these soils, because the clay minerals derived from weathering micas, lack phosphate-fixing components. However, even though the Evans soil is considered to be mainly of loessial derivation, the low Truog phosphorus values (2-3mg% - quoted by Soil Bureau) indicate that the traces of kaolin and hydrous oxides present have imparted some phosphate-fixing properties to the soil. A slight response by clovers to phosphate would be expected on the basis of these low Truog values.



The total sulphur analyses from the Kowai soil are low. Undoubtedly the low atmospheric return of sulphur accounts for this. Rain-water analyses confirmed that the concentration of sulphur was only 0.27 p.p.m., whether the rain-bearing wind was the north-westerly, (typical of the summer period) or the southerly, (typical of the winter period). The annual rainfall of this Rakai Gorge area may vary from about 30-50 inches, which represents a return of 1.8-3.1 lbs of atmospheric sulphur per acre annually.

By comparison, due to its closer proximity to the sea, the total sulphur content of the Evans soil is higher in the topsoil, but similar in the next horizon to that of the Kowai soil. The sulphur content of rain-water collected at the Banks Peninsula trial site was 1.15 p.p.m., and, with a mean rainfall of 35 inches, this represents an annual atmospheric return of approximately 9.1 lbs of sulphur per acre. However, it is probable that this is a conservative figure, since no rain-water was collected over the winter period, when it would be expected that the sulphur content would be considerably higher because of the proximity of the site to Christchurch City (which is infamous for its winter smog).

#### (C) Sulphate Analyses

The results of the horizon distribution of sulphate-sulphur are shown for the Banks Peninsula experiment in Table VII. Replicates of each treatment were bulked for analysis because the trial was considered to be experimentally unsound - the scything of the silver tussock at ground level had led to the exposure of much bare ground. After the treatments had been applied, there was no rain for about three weeks, and then came a heavy down-pour. On the unavoidable steep slope of the trial site, with so



Horizon	Reps of Treatment A							Reps of Treatment B							Reps of Treatment C							Reps of Treatment D							Reps of Treatment E						
Depth Ins	1	2	3	4	5	6	Mean	1	2	3	4	5	6	Mean	1	2	3	4	5	6	Mean	1	2	3	4	5	6	Mean	1	2	3	4	5	6	Mean
0- 2	2.2	1.7	1.7	1.7	1.6	1.7	1.8	2.6	3.2	2.9	2.6	2.4	2.6	2.7	2.2	1.8	1.6	2.6	2.4	1.8	2.1	1.4	2.4	3.0	2.0	3.1	2.0	2.3	10.1	9.0	7.8	4.4	5.1	5.3	6.9
2- 4	2.2	2.0	2.0	1.2	2.0	1.4	1.8	2.1	2.9	0.2	2.7	1.6	2.9	2.4	1.0	2.0	1.6	1.6	2.4	1.6	1.7	2.0	2.4	2.2	2.4	2.0	2.4	2.2	11.6	9.7	11.9	-	6.8	8.3	9.7
4- 6	2.6	2.0	2.2	1.6	2.2	1.7	2.0	2.1	3.5	0.2	2.9	1.6	2.0	2.4	1.0	1.8	1.6	1.6	1.6	1.6	1.5	1.6	2.6	2.2	2.4	3.1	3.9	2.6	15.7	15.6	16.1	19.3	11.2	11.8	14.9
6- 8	1.8	1.7	1.6	1.4	1.6	1.6	1.6	2.9	3.1	1.4	2.6	2.4	2.7	2.7	1.2	1.6	1.6	1.6	1.6	1.6	1.5	1.6	2.4	2.0	2.5	2.0	3.2	2.3	14.1	13.5	13.6	18.9	9.8	12.3	13.7
8-10	2.4	1.6	1.7	1.2	2.0	1.1	1.8	3.1	2.8	1.4	2.2	2.2	2.4	2.5	1.4	1.6	1.6	1.6	1.6	1.6	1.6	2.0	2.0	3.2	2.0	2.0	2.8	2.3	10.2	11.8	10.4	16.2	10.6	8.2	11.2
10-12	1.6	1.7	2.2	1.2	1.0	1.7	1.6	2.7	3.3	Trace	2.5	2.2	2.6	2.7	1.4	1.6	2.0	2.0	1.6	1.6	1.7	1.6	2.0	2.8	1.7	2.0	2.6	2.1	8.2	8.3	7.1	15.6	9.0	6.6	9.1
12-14	1.6	1.4	1.6	1.6	1.7	1.6	1.6	1.8	2.2	Trace	2.0	1.8	2.0	2.0	1.4	1.6	2.0	1.6	1.6	1.8	1.7	1.2	1.6	2.8	2.4	2.4	2.2	2.1	4.5	7.5	5.3	5.7	9.0	6.3	6.4
14-16	1.7	1.6	1.7	1.2	1.6	1.2	1.5	1.9	2.0	Trace	2.2	1.3	1.8	1.8	1.2	1.8	1.6	1.6	1.8	1.6	1.6	1.6	1.6	3.3	2.0	1.6	2.5	2.1	2.0	6.7	4.7	4.1	7.1	4.5	4.9
16-18	1.4	1.4	1.2	1.2	1.6	1.2	1.3	1.6	1.4	0.8	1.6	1.2	1.4	1.4	1.4	1.6	1.2	1.2	1.6	1.6	1.4	0.8	1.2	2.0	0.8	1.2	2.0	1.3	1.8	4.3	4.5	2.0	4.3	4.5	3.6
18-20	1.6	1.4	1.6	1.2	1.0	1.2	1.3	1.2	1.2	2.0	1.3	1.1	1.3	1.2	1.0	1.2	1.2	1.2	1.4	1.6	1.3	2.4	2.0	1.6	3.0	3.9	2.1	2.5	1.5	3.7	3.9	-	3.7	3.9	3.4
20-22	1.4	1.6	1.7	1.0	1.4	1.4	1.4	0.8	1.2	Trace	1.1	1.0	1.0	1.0	1.0	1.4	1.2	2.4	1.4	1.6	1.5	0.4	0.2	1.4	0.8	1.6	2.6	1.2	1.2	4.4	-	1.0	3.5	2.4	2.5
22-24	1.2	1.6	1.3	0.9	1.3	1.2	1.2	1.0	1.0	Trace	1.2	1.0	0.8	1.0	1.0	2.0	1.4	1.2	1.2	1.6	1.4	0.8	0.8	1.8	1.0	1.2	2.0	1.3	1.1	4.4	2.0	-	2.4	3.9	2.8

Horizon	Reps of Treatment A							Reps of Treatment B							MAY SAMPLING Reps of Treatment C							Reps of Treatment D							Reps of Treatment E						
Depth Ins	1	2	3	4	5	6	Mean	1	2	3	4	5	6	Mean	1	2	3	4	5	6	Mean	1	2	3	4	5	6	Mean	1	2	3	4	5	6	Mean
0- 2	1.9	1.9	1.6	1.7	1.4	1.7	1.7	2.4	2.4	2.8	2.2	2.6	2.0	2.4	1.8	1.8	1.8	1.8	1.7	1.8	1.8	1.6	2.2	1.8	1.9	1.8	2.0	1.9	6.8	5.3	4.2	3.7	4.6	4.8	4.9
2- 4	2.0	1.6	1.8	2.1	1.9	1.5	1.8	3.1	2.8	2.6	3.0	1.8	2.9	2.7	2.2	1.8	1.9	1.9	2.1	2.0	2.0	1.8	2.4	1.9	2.1	1.8	2.2	2.0	9.5	7.7	9.7	10.3	6.8	7.4	8.5
4- 6	2.2	1.8	2.1	1.9	1.7	1.8	1.9	3.0	2.8	2.8	2.6	3.0	2.8	2.8	1.6	2.0	2.4	2.0	1.7	1.8	1.9	2.8	3.1	2.7	3.2	2.4	2.8	2.8	12.6	12.8	13.9	15.1	11.3	10.4	12.7
6- 8	2.6	1.6	2.2	2.2	1.8	1.7	2.0	2.9	3.1	2.9	2.7	2.9	3.0	2.9	1.0	1.8	1.7	1.7	1.4	1.6	1.5	3.2	3.0	2.9	3.0	2.8	3.1	3.0	13.2	11.3	10.5	16.5	10.4	11.7	12.3
8-10	1.9	2.0	1.6	1.8	1.4	1.5	1.7	2.6	2.9	3.0	2.6	2.8	2.8	2.7	1.5	1.7	1.8	1.6	1.4	1.6	1.6	2.4	3.0	2.6	2.9	2.5	2.6	2.7	10.1	10.8	9.7	14.3	9.6	9.1	10.6
10-12	1.4	2.1	1.7	2.2	2.0	1.6	1.8	2.5	2.8	2.8	2.4	2.8	2.5	2.6	1.4	1.6	1.6	1.6	1.6	1.6	1.6	1.8	2.8	2.4	2.2	2.6	2.6	2.4	11.4	12.7	9.9	15.4	10.3	9.9	11.6
12-14	1.7	1.1	1.8	2.0	1.7	2.0	1.9	2.6	2.2	2.7	2.5	2.4	2.2	2.4	1.6	1.6	1.6	1.4	1.8	2.0	1.7	2.7	2.7	2.3	-	2.5	2.2	2.5	9.1	10.4	8.9	11.0	8.7	11.1	9.9
14-16	-	1.5	1.8	1.8	1.8	1.6	1.7	1.8	1.8	2.6	2.6	2.2	2.0	2.2	1.4	1.7	1.6	1.5	1.5	1.6	1.6	2.2	2.5	2.2	2.4	2.2	2.2	2.3	8.7	8.8	8.1	7.8	9.5	8.4	8.6
16-18	1.2	1.4	1.8	1.8	1.5	1.4	1.5	2.0	1.8	2.5	2.3	2.0	1.8	2.1	1.3	1.6	1.7	1.6	1.6	1.6	1.6	2.1	2.6	1.9	2.2	2.2	2.4	2.2	-	7.5	6.7	7.1	7.9	8.5	7.5
18-20	1.4	1.2	2.0	1.3	1.6	1.2	1.4	1.6	2.0	2.4	2.4	2.0	1.9	2.1	1.1	1.4	1.4	1.3	1.6	1.2	1.3	1.2	2.6	2.1	2.3	2.0	2.2	2.1	6.8	5.7	6.3	5.0	6.2	5.8	6.0
20-22	0.8	1.4	1.1	1.4	1.2	1.0	1.1	1.6	1.8	2.4	2.2	2.0	1.6	1.9	1.2	1.3	1.0	2.0	1.8	1.2	1.4	1.0	2.4	1.8	2.0	1.6	1.4	1.7	4.9	5.2	4.7	4.3	5.6	4.4	4.9
22-24	1.1	1.0	0.8	1.2	1.2	1.4	1.3	1.2	1.6	1.8	2.0	1.7	1.5	1.6	1.0	1.2	1.6	1.4	1.0	1.2	1.2	1.1	2.1	1.6	1.8	1.4	1.4	1.6	3.1	4.0	3.6	3.4	4.2	2.8	3.5

\* Treatment B3 of January sampling was omitted when calculating the mean. Water instead of phosphate solution was accidentally used for the sulphate extraction.

TABLE VI.  
P.P.M. OF SULPHATE SULPHUR IN TWO INCH  
HORIZONS FROM RAKAIA GORGE EXPERIMENT.



TABLE VII

HORIZON DISTRIBUTION OF SULPHATE SULPHUR FROM BANKS PENINSULA EXPERIMENT:  
BULKED REPLICATES OF TREATMENTS EXPRESSED IN P.P.M. AND POUNDS PER ACRE  
OF SULPHUR

Horizon Depth Ins	Vol. Wt lbs/acre $\times 10^5$	Treatment A		Treatment B		Treatment C		Treatment D		Treatment E	
		S: ppm	S: lbs/acre	S: ppm	S: lbs/acre	S: ppm	S: lbs/acre	S: ppm	S: lbs/acre	S: ppm	S: lbs/acre
0- 2	3.90	5.5	2.14	4.5	1.75	6.3	2.46	6.5	2.53	7.9	3.08
2- 4	4.50	4.6	2.07	4.4	1.98	5.0	2.25	4.1	1.85	5.9	2.68
4- 6	5.32	3.8	2.02	4.6	2.45	3.7	1.97	4.4	2.34	5.5	2.92
6- 8	5.86	4.0	2.34	4.3	2.52	3.4	1.99	4.3	2.52	5.0	2.93
8-10	6.35	3.5	2.22	3.3	2.10	3.4	2.16	3.3	2.10	6.3	4.00
10-12	6.72	4.0	2.69	3.3	2.22	3.4	2.29	3.8	2.56	5.0	3.36
Totals			13.48		13.02		13.12		13.90		18.97



much bare ground exposed, the surface runoff from this rain caused the treatments to run together. Lateral movement of sulphur fertilisers has been recorded by Barrow and Spencer (1959) on a  $3^{\circ}$  slope from plot trials on a sandy loam soil. They did not preclude possible surface runoff as a cause of this movement, but suggested that it was chiefly caused by lateral movement of percolating water through the soil horizons. With the Banks Peninsula trial, contamination of the plots would have been minimised had the treatments been lightly watered into the ground after their application. Yet, a downhill movement of treatments on this steep slope would probably have been unavoidable whenever excessive moisture was percolating through the soil.

Because there is little difference between the treatments recorded in Table VII, it clearly demonstrates that a mixing of the materials has taken place. From the quantities of sulphur applied, it is possible to assume that approximately a 56 lbs per acre rate of sulphate-sulphur would have been distributed over all the plots if complete mixing of all the treatments had occurred. Of this sulphur, approximately 20 lbs per acre has been recovered by the herbage (Table IX) or 30 lbs per acre by the plants, (assuming a root/top ratio of  $1/2$ ) and an average of about  $13\frac{1}{2}$  lbs per acre of sulphate-sulphur from the soil (to a 12 inch depth). That makes a total of 43 lbs of sulphur accounted for from the assumed 56 lbs per acre applied, but of course this does not take into account sulphate already in the soil, which, due to mineralization processes associated with the decay of the dead silver tussock roots, could amount to a considerable fraction of the  $13\frac{1}{2}$  lbs per acre rate of sulphur extracted from the soil. Never-the-less, because the sulphur recovery is incomplete, it is suggested that either



some sulphate has moved down below the 12 inch depth, that sulphate adsorption by kaolin and hydrous oxides has occurred, or that microbial immobilization has taken place. Although the mineralogical data of the previous section indicated that these two clay fractions were present only in small quantities, the low Truog phosphorus values have indicated that the Evans soil could have anion retention properties, but the reviewed literature would be interpreted to imply that phosphate rather than sulphate would occupy the exchange sites under the experimental conditions here prevailing.

The results of the distribution of sulphate-sulphur for the Rakais Gorge experiment are given in Table VI. A summary of the mean distributions for the various treatments is given in Table VIII, and the changes in these distributions means over three months are plotted in Fig. 6. The rainfall from the date of laying down the plots until the first sampling was 13.99 inches, and until the second sampling was 23.36 inches, which represents an atmospheric return over these periods of 0.8 lbs and 1.4 lbs per acre of sulphur respectively. Since this sulphur return was the same over all the plots, it has been neglected when assessing the total recovery of the sulphur applied, which is made in Table X.

It can be seen that the mean sulphate content of the control plots (A) and the 50 lbs of phosphorus plots (C) is very low. The mean distribution of it remains relatively constant down through the profile horizons and over the time period. With the 40 lbs of sulphur treatment (B), the sulphate appears to be concentrated in the top 14 inches at the first sampling. Below 14 inches, the distribution pattern follows that of the no sulphur treatment. At the May sampling, some three months later, the intervening 9.37 inches of rain had caused the sulphate-sulphur to be leached down through the profile. This is



TABLE VIII

HORIZON DISTRIBUTION OF SULPHATE SULPHUR FROM RAKAIA GORGE EXPERIMENT:  
TREATMENT MEANS EXPRESSED IN P.P.M. AND POUNDS PER ACRE OF SULPHUR

Horizon Depth Ins	Vol. Wt lbs/acre $\times 10^2$	Treatment A				Treatment B				Treatment C				Treatment D				Treatment E			
		S: ppm		S: lbs/acre		S: ppm		S: lbs/acre		S: ppm		S: lbs/acre		S: ppm		S: lbs/acre		S: ppm		S: lbs/acre	
		Jan.	May	Jan.	May	Jan.	May	Jan.	May	Jan.	May	Jan.	May	Jan.	May	Jan.	May	Jan.	May	Jan.	May
0- 2	4.73	1.8	1.7	.85	.80	2.7	2.4	1.28	1.13	2.1	1.8	1.00	.85	2.3	1.9	1.09	.90	6.9	4.9	3.26	2.32
2- 4	4.97	1.8	1.8	.90	.89	2.4	2.7	1.19	1.34	1.7	2.0	.85	.99	2.2	2.0	1.09	.99	9.7	8.5	4.82	4.22
4- 6	5.36	2.0	1.9	1.07	1.02	2.4	2.8	1.29	1.50	1.5	1.9	.80	1.02	2.6	2.8	1.40	1.50	14.9	12.7	8.00	6.81
6- 8	5.50	1.6	2.0	.88	1.10	2.7	2.9	1.48	1.60	1.5	1.5	.83	.83	2.3	3.0	1.26	1.65	13.7	12.3	7.55	6.76
8-10	5.57	1.8	1.7	1.00	.95	2.5	2.7	1.39	1.50	1.6	1.6	.89	.89	2.3	2.7	1.28	1.50	11.2	10.6	6.24	5.90
10-12	5.67	1.6	1.8	.91	1.02	2.7	2.6	1.54	1.47	1.7	1.6	.97	.91	2.1	2.4	1.19	1.36	9.1	11.6	5.16	6.57
12-14	5.92	1.6	1.9	.95	1.12	2.0	2.4	1.18	1.42	1.7	1.7	1.00	1.00	2.1	2.5	1.24	1.48	6.4	9.9	3.80	5.86
14-16	6.13	1.5	1.7	.92	1.04	1.8	2.2	1.10	1.35	1.6	1.6	.98	.98	2.1	2.3	1.29	1.39	4.9	8.6	3.00	5.27
16-18	6.44	1.3	1.5	.84	.97	1.4	2.1	.90	1.35	1.4	1.6	.90	1.03	1.3	2.2	.84	1.41	3.6	7.5	2.32	4.84
18-20	6.52	1.3	1.4	.85	.91	1.2	2.1	.79	1.37	1.3	1.3	.85	.85	2.5	2.1	1.63	1.37	3.4	6.0	2.22	3.91
20-22	6.59	1.4	1.1	.93	.72	1.0	1.9	.66	1.25	1.5	1.4	.99	.92	1.2	1.7	.79	1.12	2.5	4.9	1.65	3.23
22-24	6.88	1.2	1.3	.83	.90	1.0	1.6	.69	1.10	1.4	1.2	.96	.83	1.3	1.6	.90	1.10	2.8	3.5	1.93	2.41
Totals		18.8	19.8	10.92	11.44	23.8	28.4	13.49	16.38	19.0	19.2	11.02	11.10	24.3	27.2	14.00	15.77	89.1	101.0	49.95	58.10



(TABLE 3)

evidenced by the increased mean concentration of it down to the 22 inch depth. Of the 40 lbs of sulphur applied, only 5 lbs has been accounted for as additional extractable sulphate-sulphur from these <sup>0</sup>plants as compared with the control plots seven months after applications of it were made.

The 40 lbs of sulphur plus 40 lbs of phosphorus treatment (D) means show a similar distribution pattern as was described for treatment B. MacIntyre et al. (1952) recorded that phosphate additions to lysimeter trials caused sulphate to be leached more rapidly from the soil, and Ensminger (1954) reported that phosphate reduced the capacity of soils to adsorb sulphate. However, in this Rakai Gorge experiment, within the variability of the data, there appears to be no significant difference between the 40 lbs of sulphur alone and the 40 lbs of sulphur plus 40 lbs of phosphorus treatments. The recovery of soil extractable sulphate-sulphur from treatment D is only 4.4 lbs greater than that of the control treatment.

The 200 lbs of sulphur treatment (E) shows more clearly that sulphate is moving down through the soil profile. At the January sampling (four months after the treatments were applied) the extractable sulphate figures show that sulphate has moved all the way down the profile through the depth sampled, but it appears to be mainly concentrated in the top 16 inches of the soil, with a peak concentration (Fig. 6) about the 6 inch depth.

In May the distribution pattern has changed, so that the sulphate is relatively concentrated to about the 20 inch depth, but compared with the other treatments, it is obvious that the downward movement has proceeded below the actual sampled depth. The distribution at this stage is more evenly spaced throughout the upper A-B transition horizon.

The extractable sulphate-sulphur data <sup>of</sup> ~~presented in~~ Table VI (converted to pounds of sulphur per acre per two inch horizon)



## (Table XI)

was statistically analysed by Mr N. Mountier, Senior Scientific Officer, Department of Agriculture, Wellington. Mr Mountier reported that from a comparison of all five treatments sampled in January, treatment E differed significantly at the 1% level from the other four treatments. This means that the effect of the heavy dressing had reached down the profile to the 22-24 inch depth by January (see Fig. 6) and in May also, treatment E was still highly significantly different from the other four treatments (see Fig. 6).

Because the significant differences needed to compare treatment A-D were greatly inflated by the inclusion of treatment E, this latter treatment was omitted in order to compare the main effects of sulphur and phosphorus in these four treatments (Table XI). Table XI and Fig. 6 show that the effect of 40 lbs of sulphur goes down to the 12-14 inch horizon at least. The 18-20 inch horizon gives odd results: there is the only significant phosphorus effect, and also the effect of the 40 lbs of sulphur turns up again. This is caused by the high figures recorded for treatment D in Table VI which cannot be satisfactorily explained. The statistical analyses of the May samples in Table XI shows that at this time the effect of 40 lbs of sulphur is significant at the 22-24 inch horizon (see Fig. 6), but that there is no effect from the phosphorus.

Recovery of Sulphur

Table IX presents the dry matter production, the percentage total sulphur and the calculated yield in the herbage as influenced by the various treatments at both trial sites. At the time of cutting, the whole of the Banks Peninsula trial had a relatively even and balanced sward of both grasses and clovers, which suggests that there was no apparent deficiency of either



TABLE IX

TOTAL DRY MATTER PRODUCTION, % SULPHUR AND YIELD OF SULPHUR IN THE HERBAGERakaia Gorge Experiment\*

Treatment	Total D.M. lbs/acre	% Sulphur in Herbage	Yield of Sulphur in Herbage lbs/acre	Amended Yield of Sulphur** lbs/acre
A	3,420	0.179	6.1	6.1
B	4,410	0.220	9.7	13.8
C	4,000	0.182	7.3	7.3
D	6,250	0.220	13.8	13.8
E	4,640	0.275	12.7	17.2

\* These plots were grazed by cattle which broke down the fence prior to taking the production plots.

Banks Peninsula Experiment

\*\* Amended yield calculated for Treatments B and E, by assuming a D.M. production similar to Treatment D (6,250 lbs/acre).

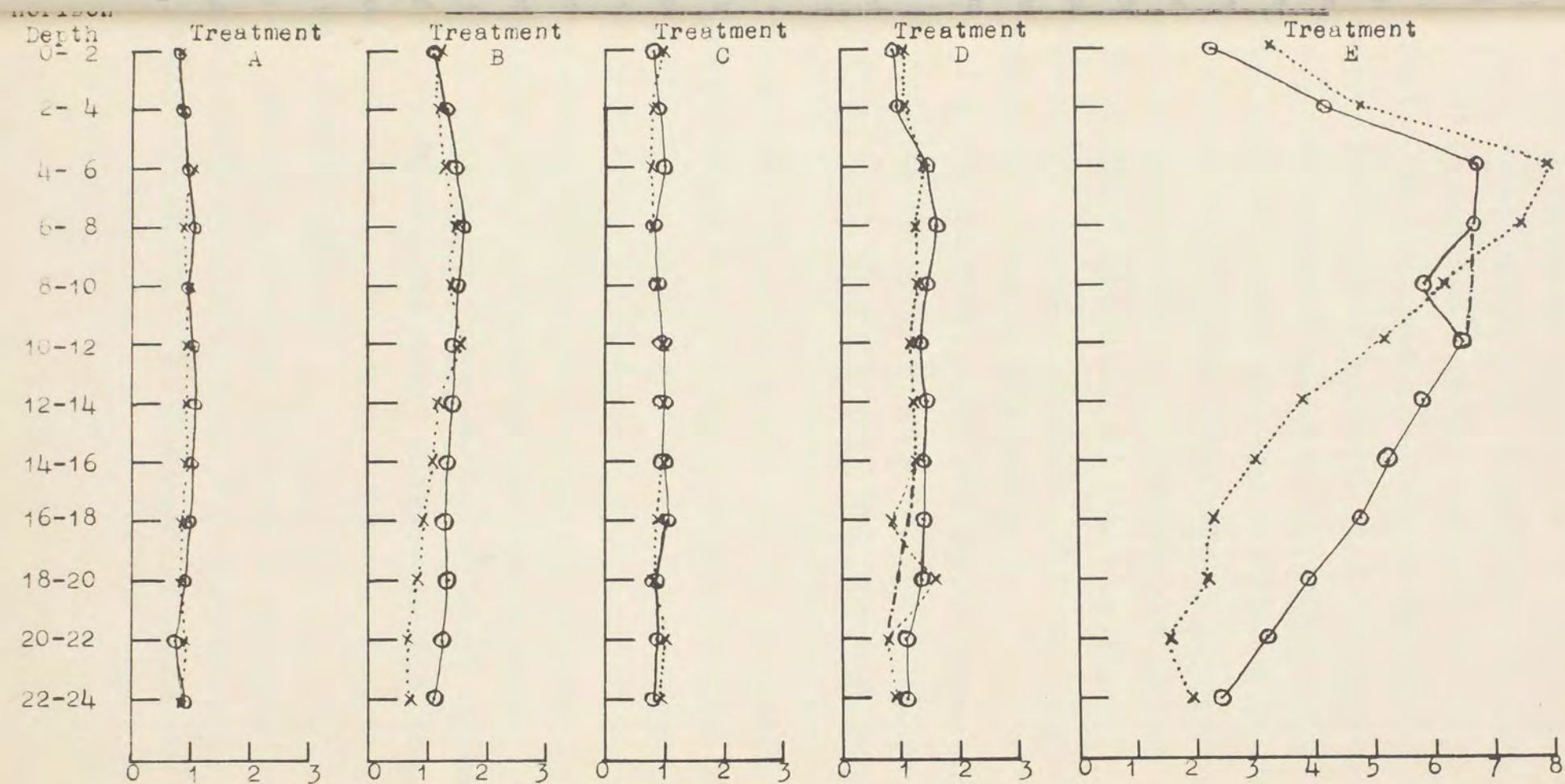
A	3,520	0.508	17.9
B	3,840	0.522	20.0
C	3,640	0.536	19.5
D	3,640	0.508	18.6
E	4,070	0.577	23.5



phosphorus or sulphur at this trial. Not only does this confirm that the treatments became thoroughly mixed, but also it suggests that the soil lacks a marked phosphate-fixing ability. Under thorough mixing of the treatments, about 16 lbs of phosphate per acre would have been applied to the trial area; i.e., approximately equivalent to a  $1\frac{1}{2}$  cwt of superphosphate per acre topdressing rate. Good clover growth at this fertiliser level implies that the soil is not markedly responsive to phosphate. Also, the high percentage of total sulphur, regardless of the treatment, in the Banks Peninsula herbage, further confirms that the applied treatments became well mixed. McNaught and Chrisstoffels (1961) record that applications of sulphur nearly always result in increased total sulphur concentrations in the herbage, and they also record that heavy applications of superphosphate made to certain soils may result in total sulphur concentrations in excess of 0.6% in the herbage, particularly in grasses. Their work indicates that levels of total sulphur are influenced by the nitrogen status. In this Banks Peninsula trial, scything the silver tussock foliage at ground level killed the plants and presumably this made sufficient nitrogen available (through the decay and mineralization of the silver tussock roots) to account for the high sulphur content in the grass component of the herbage, but to this end, possible underground transference of nitrogen from the clovers also, can not be discounted.

With the Rakaia Gorge trial, the plots not treated with sulphur were grass dominant, and those treated with sulphur were clover dominant. In contrast to the other trial, the levels of total sulphur in the herbage cut from this trial are much lower. With the no sulphur treatments, less than 0.2% sulphur is present, which, on the basis of the "critical levels" suggested by





Pounds per Acre of Sulphur

x.....x.....x Mean of January sampled analyses

o-----o-----o Mean of May sampled analyses

FIGURE 6.



McNaught and Chrisstoffels, implies that the herbage is sulphur deficient. However, even the herbage cut from the treatments containing applications of 40 lbs of sulphur, has a lower percentage of total sulphur than the "critical level" (0.26%) given by these workers for white clover at grazing height. The percentage total sulphur recorded in herbage from treatments B and D is comparable with that recorded by Walker and Adams (1958a) for clover in their  $N_6, S_2$  treatment at this same area, but is less than that recorded by them for first year plant analyses when higher rates of gypsum were used in another trial (1958b). These workers had earlier suggested 0.2% as a tentative "critical level" for white clover. The high rate of sulphur applied did not result in a luxury consumption of sulphur by this herbage.

It was unfortunate that this Rakasia Gorge trial was grazed, because this has meant that the total dry matter production and the yield of sulphur figures given for this trial in Table IX are therefore not absolute values. Even so, the recovery of sulphur by the herbage for treatments B and D is higher than that obtained by Walker and Adams (1958b) from an application of 42 lbs of sulphur in the first year. No estimate of the extent of grazing can be made, but the sulphur treatments which had better growth and produced more palatable herbage, would have been the more heavily grazed. The highest total yield of dry matter recorded by Walker and Adams (1958a) at this locality was 6,700 lbs for their  $N_6, S_2$  treatment in a wet season, and this level of production was approached during this 1959/60 season.

Although the sulphur recovered by the plants is not absolute, an amended value has been included in Table X to assess the recovery of sulphur from the rate applied with each



TABLE X

TOTAL RECOVERIES OF SULPHUR CALCULATED IN POUNDS PER ACRE FOR THE RAKAIA GORGE EXPERIMENT

Treatment	Sulphate-S Applied	S Recovered in Plant Tops*	Total S Recovered by Plants**	Sulphate-S in Profile to 24 Inch Depth***	Total S Accounted for	S Recovered in Excess of Control
A	-	6.1	9.2	11.4	20.6	-
B	40	13.8	20.7	16.4	37.1	16.5
C	-	7.3	11.0	11.1	22.1	-
D	40	13.8	20.7	15.8	36.5	15.9
E	200	17.2	25.6	58.1	83.7	63.1

\* Amended values (see Table IX).

\*\* Calculated from a hypothetical root/top ratio of  $1/2$ , i.e., Sulphur recovered by plant tops  $\times 3/2$ .

\*\*\* May samples (see Table VIII).



treatment. The amended value has been derived by considering that the dry matter of 6,250 lbs obtained for treatment D would also have been obtained for treatments B and E (Table IX). This is a reasonable assumption because the Kowai soil is not known from Walker and Adams' work to be phosphate responsive. Table X indicates that the recovery has been very poor indeed for all three sulphur treatments. From 40 lbs of sulphur applied in treatments B and D, only 16.5 lbs and 15.9 lbs of it respectively, can be accounted for as "plant sulphur" or soil extractable sulphate, while from treatment E only 63.1 lbs of sulphur can similarly be accounted for from the 200 lbs applied. The seemingly unaccountable discrepancies amount to approximately 23.5 lbs, 24 lbs and 137 lbs of sulphur respectively from these treatments.

Soils exhibiting Yellow Grey Earth characteristics have associated with their B horizon development, gammadet or macroprismatic structure. Separating the macroprismatic units are fractures or macropores, through which drainage of excess moisture takes place. However, when the whole soil profile becomes wetted, these macroprismatic units expand in a lateral plane and the macropores become sealed. Drainage is then retarded, for it is then confined to the micropore system. Conversely, when the soil dries again, the macroprismatic units shrink and the macropores reopen. Under conditions of intermittent wetting and drying of the soil, such as occurs when the rainfall comes in the form of infrequent heavy showers, e.g., at Rakaiia Gorge in the summer period, two drainage pathways are operative. With dry soil conditions, rainfall would rapidly percolate through the sandy topsoil dissolving soluble salts, and then rapidly drain through the macropore system, but, during prolonged rainfall, and thus, prolonged moist soil cond-



COMPARISON OF TREATMENTS A, B, C AND D WITHOUT E  
DATA EXPRESSED IN POUNDS PER ACRE PER TWO INCH HORIZON DEPTH

JANUARY SAMPLES

Treatments	HORIZON DEPTH IN INCHES											
	0-2	2-4	4-6	6-8	8-10	10-12	12-14	14-16	16-18	18-20	20-22	22-24
No S (A+C)	.90	.87	.98	.88	.90	.93	.96	.95	.89	.84	.96	.91
S (B+D)	1.18	1.15	1.37	1.38	1.36	1.35	1.20	1.20	.89	1.21	.72	.78
Difference	.28*	.28*	.39**	.50**	.46**	.42**	.24*	.25	0	.37*	-.24	-.13
No P (A+B)	1.05	1.05	1.22	1.20	1.17	1.20	1.05	1.02	.89	.83	.80	.78
P (C+D)	1.04	.97	1.14	1.07	1.09	1.08	1.11	1.13	.89	1.23	.88	.92
Difference	-.01	-.08	-.08	-.13	-.08	-.12	.06	.11	0	.40*	.08	.14

MAY SAMPLES

No S (A+C)	.82	.94	1.03	.98	.92	.96	1.00	.98	.99	.90	.84	.81
S (B+D)	1.01	1.17	1.52	1.63	1.52	1.43	1.45	1.35	1.38	1.34	1.19	1.10
Difference	.19**	.23**	.49**	.65**	.60**	.47**	.45**	.37**	.39**	.44**	.35*	.29*
No P (A+B)	.97	1.12	1.27	1.36	1.25	1.27	1.23	1.15	1.15	1.14	1.01	.95
P (C+D)	.87	.99	1.27	1.25	1.19	1.12	1.23	1.17	1.22	1.11	1.03	.96
Difference	-.10*	-.13	0	-.11	-.06	-.15	0	.02	.07	-.03	.02	.01

\* Significant at 5% level; \*\* Significant at 1% level.

TABLE XI.



itions, drainage would be via the micropore system, again carrying soluble salts with it. Although unsupported, it is proposed that much of the sulphate-sulphur applied to the plots would be leached through the macropore system and accumulate in the compacted loessial zone underlying the B horizon, which was not reached with the 24 inch depth soil samples taken. It is thought that the analytical data presented in Table VI records the soil extractable sulphate which has leached via the micropore system.

Walker et al. (1956) calculated that 1 acre inch of rain could dissolve 500 lbs of gypsum, i.e., approximately equivalent to 100 lbs of sulphur, so that less than  $1\frac{1}{2}$  inches of rain could dissolve sufficient sulphur to account for the discrepancy of 137 lbs with treatment E if this solution drained through the soil profile via the macropore system. The rainfall from the laying down of the trial until the final sampling was 23.36 inches.

Other factors contributing to a greater or lesser extent to the discrepancy of sulphur recovered from the treatments cannot be precluded. Of these, conversion of some sulphate to organic sulphur by the soil microflora would surely occur. Possibly, under wet soil conditions, some sulphate would be reduced to hydrogen sulphide and lost through volatilisation. It is also possible that the sulphate extraction agent (100 p.p.m. P, phosphate solution) used, and the method of sulphate determination, were unsatisfactory, even though good agreement was obtained for all the duplicate samples analysed.

The work of Ensminger (1954), Kamprath et al. (1956), Jordan and Bardsley (1958), Harper (1959), McClung et al. (1959) and Neller (1959) has shown that sulphate retention is associated with the clay horizons of soils. In Chapter IV the discussion



suggested that the clay minerals involved in anion retention would be chiefly the 1 : 1 lattice type and the amorphous hydrous oxides. Because the literature failed to demonstrate conclusively that anion retention and exchange occurred extensively with the 2 : 1 lattice type minerals, it seems probable that the weakly-weathered micaceous clays described in this Kowai soil would not retain sulphate. Further, the anion retention properties of clays were found from the literature to be associated with low pH values, and the pH values of the Kowai soil do not fit these conditions. Therefore, it seems probable that the Kowai soil would retain little sulphate against leaching, and the sulphate level changes recorded in the experiment appear to be in accord with an expected percolation rate of moisture through the micropore system as outlined above.

#### Criticisms and Conclusions

The results and lack of results described in this thesis illustrate the need for extreme care when planning experimental work. The fact that the clay mineralogical data from the two soils used in the experiments would show such close affinities, was not foreseen. The Kowai sandy loam was chosen because it was expected to have low A.E.C. properties because of its sandy texture and its probable weakly-weathered micaceous clay mineralogy. The Evans steep-land loam was chosen because it was considered that it would have moderate A.E.C. properties because of the underlying basalt being expected to constitute its parent material. This soil was recommended by Soil Bureau, who also gave assurance of its phosphate-fixing power on the basis of the low Truog phosphate values. (A horizon, 3 mg% P, and B horizon 2 mg% P). Although the experiment on this soil was most unsatisfactory, it did appear that this soil lacked a high phosphate-fixing ability, and this was contrary to expectations.



That the Banks Peninsula trial was located on a steep, uneven slope was unavoidable since the Evans soil represents a steep-land phase, but the possibility of reducing the extent of mixing, which occurred to the treatments applied, could have been achieved if appropriate measures had been taken.

When the sampling depth was chosen, it was thought that most of the sulphur would have been recovered within this depth, which included the effective rooting zone of the plants grown. However, it would have been more suitable to have sampled the soil at 6 inch horizons down to a depth of 48 inches. Because this was not done, the hypothesis proposed to account for the low recovery of sulphur from the applied treatment rates in the Rakai Gorge experiment can only be speculative. A radio tracer technique was used to assess the soil sulphate adsorption capacities of the individual treatment horizons sampled in January, but the results of this work were inconclusive and are not presented.

It would be unwise to draw definite conclusions from the experiments here described. Although pasture improvement on a Kowai soil can be brought about by oversowing the virgin tussock with clovers and grasses used in conjunction with a sulphur fertiliser, it is suggested that heavy applications of gypsum would be wasteful since it appears that sulphate will leach fairly rapidly through the soil. Improved pasture production will best be maintained by frequent light topdressings of sulphur fertilisers. However, the slower movement rate of sulphate-sulphur through the micropore drainage system indicates that some sulphate will remain within the rooting zone of plants for an appreciable period, and this would in part account for the residual effects of sulphur fertilisers used for pasture improvement on the Kowai soil.



## A C K N O W L E D G E M E N T S

I wish to express my sincere appreciation for the advice and assistance of my tutor, Mr A. F. R. Adams, and to Professor T. W. Walker. Also, I thank Mr C. J. Cran, Manager of "Bayfields Estate", and Mr J. F. Wilson of "Cracroft Wilson Estate", for permission to locate experimental plots on their respective farms.

I express my gratitude to the following persons for assistance given:-

Dr G. G. Claridge, Soil Bureau, Wellington

Mr C. B. Mead, Soil Bureau, Christchurch

Miss M. Cooper, Department of Agriculture, Galloway  
Laboratory, Hamilton

Mr N. S. Mountier, Department of Agriculture, Biometrics  
Division, Wellington

Mr H. Horn, Lincoln College

Finally, I wish to thank the Shell Oil Company of New Zealand Limited for their generous £100 Scholarship.



## S U M M A R Y

In this thesis literature is reviewed on aspects of soil sulphur. Factors concerning the availability of sulphur for plant growth are discussed, and some mechanisms of anion exchange phenomena are considered with particular reference to possible clay adsorption of sulphate ions by soils.

Experiments were conducted on two soils, namely, a Kowai sandy loam from Rakai Gorge, and an Evans steep land loam from Banks Peninsula. To determine the movement of sulphate-sulphur in these two soils, certain fertiliser treatments were applied to field plots, from which soil samples were analysed for sulphate content by a modified Chesnin and Yien technique.

The low quantities of sulphate-sulphur extracted from within the 24 inch sampled depth of the Kowai soil, indicate that it has little capacity to retain sulphate against leaching. Not only has this soil a low clay content, but also the 2 : 1 type clay minerals contained in it are shown from the reviewed literature to lack anion exchange properties. The occurrence of drainage via the macropore system has been hypothesised as a major factor causing rapid leaching of sulphate, but it is considered that the less rapid movement of dissolved salts via the micropores would ensure sufficient sulphate to be retained within the effective rooting zone of plants to account for residual responses to sulphur fertiliser on the Kowai soil.

With the Evans steep land loam, the unsuitable location of experimental plots permitted lateral movement of fertiliser treatments, which nullified results. The clay of this soil is derived mainly from weathered greywacke loess and not basalt as was supposed. Because its major clay constituents are also of the 2 : 1 type, the Evans soil would not be expected to adsorb sulphate ions.



## B I B L I O G R A P H Y

- ALLISON, L.E., 1935: Organic Carbon by Reduction of Chromic Acid. Soil Sci., 40: 311-320.
- ALWAY, F.J., 1940: A Nutrient Element Slighted in Agricultural Research. J. Amer. Soc. Agron., 32: 913-921.
- AMPHLETT, C.B., 1958: Ion Exchange in Clay Minerals. Endeavour, 17: No. 67.
- ANDERSON, A.J., and SPENCER, D., 1949: Molybdenum and Sulphur in Symbiotic Nitrogen Fixation. Nature, 164: 273-274.
- ANDERSON, A.J., and SPENCER, D., 1950: Sulphur in Nitrogen Metabolism of Legumes and Non-legumes. Aust. J. Sci. Res., 3: 431-449.
- ANDREW, C.S., KIPPS, E.H., and BARFORD, H., 1952: Plant Responses to Nitrogen and Sulphur on a Heavy Clay Soil from the Darling Downs, South-east Queensland. Aust. J. Agric. Res., 3: 111-127.
- ASGHAR, A.G., QAYYUM, M.A., and RANA, G.M., 1956: A Method for the Volumetric Estimation of Sulphates in Soils and Irrigation Water. Soil Sci., 83: 239-241.
- BARDSLEY, C.E., and LANCASTER, J.D., 1960: Determination of the Reserve Sulphur and Soluble Sulphate in Soils. Soil Sci. Soc. Amer. Proc., 24: 265-268.
- BARROW, N.J., 1957: Renovation of Phalaris Pastures with Special Reference to Nitrogen and Sulphur Relationships. Aust. J. Agric. Res., 8: 617-633.
- BARROW, N.J., 1959: Studies of the Recomposition of Organic Matter with Special References to Production of Sulphate. Ph.D. Thesis, lodged with the University of New England.
- BARROW, N.J., and SPENCER, K., 1959: Lateral Movement of Fertiliser Sulphur. J. Aust. Inst. Agric. Sci., 25: 208-209.



- BARROW, N.J., 1960: The Effect of Varying the Nitrogen Sulphur and Phosphorus Content of Organic Matter on its Decomposition. Aust. J. Agric. Res., 11: 317-330.
- BLEDSE, R.W., and BLAZER, R.E., 1947: The Influence of Sulphur on Yield and Composition of Clovers Fertilised with Different Sources of Phosphate. Agron. J., 39: 146-152.
- BRAY, R.H., 1954: A Nutrient Mobility Concept of Soil-Plant Relationships. Soil Sci., 78: 9-22.
- BREMNER, J.M., 1954: A Review of Recent Work on Soil Organic Matter II. J. Soil Sci., 5: 214-232.
- BRIAN, P.W., 1951: Antibiotics Produced by Fungi. Bot. Rev., 17.
- BROADBENT, F.E., 1953: The Soil Organic Fraction. Advances in Agronomy, 5: 153-183.
- BROADBENT, F.E., 1955: Basic Problems in Organic Matter Transformations. Soil Sci., 79: 107-114.
- BUTLER, G.W., 1961: Some Aspects of Chemical Composition in Relation to Animal Health. Proc. Lin. Coll. Farmers' Conference, 11: 96-104.
- BURGES, A., 1958: Micro-organisms in the Soil. Hutchinson University Library, London.
- CAIRNS, R.R., and RICHER, A.C., 1960: A Comparative Study of a Sulphur Responsive and Non-responsive Grey-Wooded Soil. Canadian J. Soil Sci., 40: 246-254.
- CHESNIN, L., and YIEN, C.H., 1951: Turbidimetric Determination of Available Sulphates. Soil Sci. Soc. Amer. Proc., 15: 149-151.
- COLEMAN, R., 1944: Phosphorus Fixation by the Coarse and Fine Clay Fractions of Kaolin and Montmorillonite Clays. Soil Sci., 58: 71-77.
- CONRAD, J.P., 1950: Sulphur Fertilisation in California and Some Related Factors. Soil Sci., 70: 43-54.



- COOK, M.A., CUTLER, I.B., HILL, G.R., WADSWORTH, M.E., and OBLAD, A.G., 1953: A Mechanism of Cation and Anion Exchange Capacity. J. Phys. Chem., 57: 1-6.
- CORMACK, D.V., BENTLEY, C.F., and SCOTT, D.B., 1951: Fertiliser Studies with Radioactive Sulphur. Sci. Agric., 31: 41-51.
- DEAN, L.A., and RUBINS, E.J., 1947: Anion Exchange in Soils, 1. Soil Sci., 63: 377-406.
- DICKMAN, S.R., and BRAY, R.H., 1941: Replacement of Adsorbed Phosphate from Kaolinite by Fluoride. Soil Sci., 52: 263-275.
- EGGLETON, W.G., 1938: The Influence of Environmental Factors on Numbers of Soil Micro-organisms. Soil Sci., 46: 351-363
- ENSMINGER, L.E., 1954: Some Factors Affecting the Adsorption of Sulphate by Alabama Soils. Soil Sci. Soc. Amer. Proc., 18: 259-264.
- ENSMINGER, L.E., 1958: Sulphur in Relation to Soil Fertility. Ag. Expt. Stn of the Alabama Polytechnic Institute, Bull. 312.
- ERDMAN, L.W., 1921: The Effect of Gypsum on Soil Reaction. Soil Sci., 12: 433-448
- ERDMAN, L.W., 1922: The Sulphur Content of Rainfall. Soil Sci., 14: 363-367
- ERGLE, D.R., and EATON, F.M., 1951: Sulphur Nutrition of Cotton. Plant Physiol., 26: 639-654.
- ERGLE, D.R., 1953: Effect of Low Nitrogen and Sulphur Supply on their Accumulation in the Cotton Plant. Bot. Gaz., 114: 417-426.
- ERGLE, D.R., 1954: Utilisation of Storage Sulphur by Cotton and the Effect on Growth and Chloroplast Pigments. Bot. Gaz., 115: 417-426.
- EVANS, R.E., 1931: Studies of Sulphur of Pasture Grass; 1. The Cystine Content of Pasture Grass. J.A.S., 21: 806-821.



- EVANS, C.A., and ROST, C.O., 1945: The Total Organic Sulphur and Humus Sulphur of Minnesota Soils. Soil Sci., 59: 125-126.
- FIELDER, M., and SWINDALE, L.B., 1954: Chemical Weathering of Silicates in Soil Formation. N.Z. J. Sci. Tech., 36B: 140-154.
- FIELDER, M., 1958: Soil Science and Extension Work: The Role of Clays in Soil Fertility. D.S.I.R. Soil Bureau Publ. No. 167.
- FREDRICK, L.R., STARKEY, R.L., and SEGAL, W., 1957: Decomposability of Some Organic Sulphur Compounds in Soil. Soil Sci. Soc. Amer. Proc., 21: 287-292.
- FRENEY, J.R., 1958a: Determination of Water Soluble Sulphate in Soils. Soil Sci., 86: 241-244.
- FRENEY, J.R., 1958b: Aerobic Transformation of Cysteine to Sulphate in Soil. Nature, 182: 1318-1319.
- FRENEY, J.R., 1960: Oxidation of Cysteine to Sulphate in Soil. Aust. J. Biol. Sci., 13: 387-392.
- FRENEY, J.R., and SPENCER, K., 1960: Soil Sulphate Changes in the Presence and Absence of Growing Plants. Aust. J. Agric. Res., 11: 339-345.
- FRIED, M., 1948: The Absorption of Sulphur Dioxide by Plants as Shown by the Use of Radioactive Sulphur. Soil Sci. Soc. Amer. Proc., 13: 135-138.
- GILBERT, F.A., 1951: The Place of Sulphur in Plant Nutrition. Bot. Rev., 17: 671-691.
- GLEEN, H., and QUASTEL, J.H., 1953: Sulphur Metabolism in the Soil. Appl. Microbiol., 1: 70-77.
- GREAVES, J.E., and CARTER, E.G., 1920: Influence of Moisture on the Bacterial Activities of the Soil. Soil Sci., 10: 361-387.
- GRIM, R.E., 1953: "Clay Mineralogy". McGraw-Hill Book Company, Inc., New York.



- GOLDSCHMIDT, V.M., 1945: The Geochemical Background of Minor Element Distribution. Soil Sci., 60: 1-9.
- GORDON, N.E., and STARKEY, E.B., 1922: Influence of Soil Colloids on Available Salts. Soil Sci., 14: 1-7.
- HARPER, H.J., 1959: Sulphur Content of Oklahoma Soils, Rainfall and Atmosphere. Oklahoma State University Bull. B-536.
- HELMY, A.K., and ELGABALY, M.M., 1959: Exchange Capacity of Plant Roots II. Some Factors Affecting the C.E.C. Plant and Soil, 10: 93-100.
- HESSE, P.R., 1957a: Sulphur and Nitrogen Changes in Forest Soils of East Africa. Plant and Soil, 9: 86-96.
- HESSE, P.R., 1957b: The Effect of Colloidal Organic Matter on the Precipitation of Barium Sulphate and a Modified Method for Determining Soluble Sulphate in Soils. Analyst, 82: 710-712.
- HILDER, E.J., and SPENCER, K., 1954: Influence of Sulphur on a Natural Medicago Pasture. J. Aust. Inst. Agric. Sci., 20: 171-176.
- HINGSTON, F.J., 1959: The Loss of Applied Phosphorus and Sulphur from Soils under Pasture in Western Australia. J. Aust. Inst. Agric. Sci., 25: 209-213.
- HUTTON, J.T., and LESLIE, T.I., 1958: Accession of Non Nitrogenous Ions Dissolved in Rainwater to Soils in Victoria. Aust. J. Agric. Res., 9: 492-507.
- JENNY, H., and OVERSTREET, R., 1939: Contact Exchange Between Plant Roots and Soil Colloids. Soil Sci., 47: 257-272.
- JOHNSON, C.M., and NISHITA, H., 1952: Microestimation of Sulphur in Plant Materials and Irrigation Waters. Analyt. Chem., 24: 736-742.
- JORDAN, H.V., and BARDSLEY, C.E., 1958: Response of Crops to Sulphur on Southeastern Soils. Soil Sci. Soc. Amer. Proc., 22: 254-256



- JORDAN, H.V., and ENSMINGER, L.E., 1958: Role of Sulphur in Soil Fertility. Advances in Agronomy, 10: 408-432.
- JORDAN, J.V., and BAKER, G.O., 1959: Sulphur Studies in North Idaho Soils, Using Radio Sulphur. Soil Sci., 88: 1-6.
- JUDSON, C.M., LEREW, A.A., DIXON, J.K., and SALLEY, D.J., 1953: Radio-tracer Study of Sulphate Ion Adsorption at the Air/solution Interface in Solutions of Surface-active Agents. J. Phys. Chem., 57: 916-923.
- KAMPRATH, E.J., NELSON, W.L., and FITTS, J.W., 1956: The Effect of pH, Sulphate and Phosphate Concentrations on the Adsorption of Sulphate by Soils. Soil Sci. Soc. Amer. Proc., 20: 463-466.
- KATZNELSON, H., and CHASE, F., 1944: Qualitative Studies of Soil Micro-organisms: Influence of Season and Treatment on Incidence of Nutritional Groups of Bacteria. Soil Sci., 58: 473-479.
- KELLEY, W.P., 1943: On Mattson's Papers on "Laws of Soil Colloidal Behaviour". Soil Sci., 56: 433.
- KOLTHOFF, 1936: Adsorption on Ionic Lattices. J. Phys. Chem., 40: 1027-1039.
- KRETSCHMER, A.E., TOTH, S.J., and BEAR, F.E., 1953: Effect of Chloride Versus Sulphate Ions on Nutrient-Ion Absorption by Plants. Soil Sci., 76: 193-199.
- LICHTENWALNER, D.C., FLENNERS, A.L., and GORDON, N.E., 1923: Adsorption and Replacement of Plant Food in Colloidal Oxides of Iron and Aluminium. Soil Sci., 15: 157-165.
- LITTLE, R.C., 1958: Sulphur in Soils III - A Study of the Readily Soluble Sulphate Content and of the Total Sulphur Content of Soil. J. Sci. Food Agric., 9: 273-281.
- LOBB, W.R., 1954: Sulphur Investigations in North Otago. N.Z. J. Agric., 89: 434-439.
- LOBB, W.R., 1959: Fertility Problems of Marginal Areas of the South Island. N.Z. J. Agric., 99: 207-221.



- LOBB, W.R., and BENNETS, R.L., 1959: Fertiliser Responses on the Plains Soils of Canterbury. N.Z. J.A., 99: 317-325.
- LOCHHEAD, A.G., and LANDERKIN, G.B., 1948: Aspects of Antagonisms Between Micro-organisms in the Soil. Plant and Soil, 1: 271-276.
- LUNDEGARDH, H., 1939: An Electro-chemical Theory of Salt Absorption and Respiration. Nature, 143: 203-204.
- LUNDEGARDH, H., 1942: Electro-chemical Relations Between Root System and the Soil. Soil Sci., 54: 177-189.
- McAULIFFE, C.D., HALL, M.S., DEAN, L.A., and HENDRICKS, S.B., 1947: Exchange Reactions Between Phosphates and Soils. Soil Sci. Soc. Amer. Proc., 12: 119-123.
- MacINTYRE, W.M., GRAY, F.J., and SHAW, W.M., 1921: Soil Sci., 11: 249-254.
- MacINTIRE, W.H., SHAW, W.M., and ROBINS, B., 1941: Influence of Limestone and Dolomite upon Sulphate Retention from Annual Additions of Potassium Sulphate. Soil Sci., 51: 73-84.
- MacINTIRE, W.H., YOUNG, J.B., SHAW, W.M., and ROBINSON, B., 1952: Nitrogen Recoveries from Applications of Ammonium Chloride, Phosphate and Sulphate, and Outgo of Complementary Ions in Rainwater Leachings Through a Six-foot Soil-subsoil Column. Soil Sci. Soc. Amer. Proc., 16: 301-306.
- McLACHLAN, K.D., 1955: Phosphorus, Sulphur and Molybdenum Deficiency of Eastern Australia in Relation to Nutrient Supply and Some Characteristics of Soil and Climate. Aust. J. Agric. Res., 6: 673-684.
- McCLUNG, A.C., De FREITAS, L.M.M., and LOTT, W.L., 1959: Analysis of Several Brazilian Soils in Relation to Plant Response to Sulphur. Soil Sci. Soc. Amer. Proc., 23: 221-224.



- McNAUGHT, K.J., and CHRISSTOFFELS, P.J.E., 1961: Effect of Sulphur Deficiency on Sulphur and Nitrogen Levels in Pastures and Lucerne. N.Z. J. Agric. Res., 4: 177-196.
- MALAVOLTA, E., COURY, T., GALLI, F., et al., 1955: Effects of Sulphur, Boron and Inoculation on Lucerne. Soils and Ferts, 18: (No. 415),
- MANN, H.H., 1955: Variation of Sulphur in Soils under Continuous Grain Crop. J. Soil Sci., 6: 241-247.
- MATTSON, S., 1929a: Laws of Soil Colloid Behaviour: I Cataphoresis, Soil Sci., 28: 179-220.
- MATTSON, S., 1929b: Laws of Soil Colloid Behaviour: II Flacculation and Dispersion. Soil Sci., 28: 373-409.
- MATTSON, S., 1930: Laws of Soil Colloid Behaviour: III Isoelectric Precipitates. Soil Sci., 30: 459-495.
- MEHLICK, A., 1953: Factors Affecting Adsorption of Cations by Plant Roots. Soil Sci. Soc. Amer. Proc., 17: 231-234.
- METSON, A.J., 1954: Sulphur in Soils. N.Z. Soil News: No. 4.
- METSON, A.J., 1956: Methods of Chemical Analysis for Soil Survey Samples. N.Z. Soil Bureau Bull. No. 12.
- MOUAT, M.C.H., and WALKER, T.W., 1959: Competition for Nutrients Between Grasses and White Clover. Plant and Soil, 11: 30-51.
- NEIDIG, R.E., McDOLLE, G.R., and MAGNUSON, H.P., 1923: The Effect of Sulphur, Calcium and Phosphorus on Alfalfa. Soil Sci., 16: 127-136.
- NELLER, J.R., 1959: Extractable Sulphate-Sulphur in Soils of Florida in Relation to the Amount of Clay in the Profile. Soil Sci. Soc. Amer. Proc., 23: 346-348.
- NIGHTINGALE, G.T., SCHERMERHORN, L.G., and ROBBINS, W.R., 1932: Effects of Sulphur Deficiency on Metabolism in Tomato Plants. Plant Physiol., 18: 334-344.
- OLSEN, R.A., 1957: Absorption of Sulphur Dioxide from the Atmosphere by Cotton Plants. Soil Sci., 84: 107-111.



- PEARSON, R.W., and ENSMINGER, L.E., 1948: Types of Clay Minerals in Alabama Soils. Soil Sci. Soc. Amer. Proc., 13: 153-
- PIPER, C.S., 1950: Soil and Plant Analysis. Interscience Publishers Inc., New York.
- POSTGATE, J., 1954: The Sulphur Bacteria. New Biology, (Penguin Books Ltd, Great Britain). 17: 58-76.
- QUASTEL, J.H., and SCHOLEFIELD, P.G., 1949: Influence of Organic Nitrogen Compounds on Nitrification in Soil. Nature, 164: 1068-1072.
- QUISPEL, A., <sup>GW</sup>HARMSSEN, and OTZEN, D., 1952: Contribution to the Chemical and Biological Oxidation of Pyrite in Soil. Plant and Soil, 4: 43-55.
- RENDIG, V.V., 1956: Sulphur and Nitrogen Composition of Fertilised and Unfertilised Alfalfa Grown on a Sulphur Deficient Soil. Soil Sci. Soc. Amer. Proc., 20: 237-240.
- RENNER, R., BENTLEY, C.F., and McELROY, L.W., 1953: Nine Essential Amino Acids in the Protein of Wheat and Barley Grown on Sulphur Deficient Soil. Soil Sci. Soc. Amer. Proc., 17: 270-273.
- RIGG, T., 1954: Note on the Use of Sulphur in Tobacco Growing. N.Z. Soil News, No. 4.
- ROBERTSON, R.N., 1957: Electrolytes in Plant Tissue. Endeavour, 16: 193-198.
- ROSSITER, R.C., 1951: Studies on Nutrition of Pasture Plants in the Southwest of Western Australia: II. Visual Symptoms of Mineral Deficiencies on the Dwalganup Strain of Trifolium Subterranean. Aust. J. Agric. Res., 2: 14-23.
- ROSSITER, R.C., 1952: Studies on Nutrition of Pasture Plants in the Southwest of Western Australia: IV. The Effect of Sulphur on the Growth of Subterranean Clover. Aust. J. Agric. Res., 3: 7-15.



- ROST, C.O., EVANS, C.A., and KRAMER, W.H., 1958: Sulphur Fertilisation of Oats in North Central Minnesota. University of Minnesota Agric. Expt. Bull. No. 444.
- ROVIRA, A.D., 1956a: A Study of the Development of Root Surface Microflora During the Initial Stages of Plant Growth. J. Appl. Bact., 19: 72-79.
- ROVIRA, A.D., 1956b: Root Excretions in Relation to the Rhizosphere Effect, I, II & III. Plant and Soil, 7: 178-217.
- ROVIRA, A.D., 1959: Root Excretions in Relation to the Rhizosphere Effect, IV. Plant and Soil, 11: 53-64.
- RUDOLFS, W.R., 1922: Sulphur Oxidation in Black-Alkali Soils. Soil Sci., 13: 215-229.
- RUSSELL, Sir John E., 1954: Soil Conditions and Plant Growth. 8th edition. Longmans, Green & Co., London.
- RUSSELL, G.C., and LOW, P.F., 1954: Reaction of Phosphate with Kaolinite in Dilute Solution. Soil Sci. Soc. Amer. Proc., 18: 22-25.
- SAUNDERS, W.M.H., and WILLIAMS, E.G., 1955: Observations on the Determination of Total Organic Phosphorus in Soils. J. Soil Sci., 6: 254-267.
- SAUNDERS, W.M.H., 1959: Effect of Phosphate Topdressing on a Soil from Andesitic Volcanic Ash: 1, 2, and 3. N.Z. J. Agric. Res., 2: 427-462 and 659-665.
- SCHELL, W.R., and JORDAN, J.V., 1959: Anion Exchange Studies of Pure Clays. Plant and Soil, 10: 303-318.
- SEARS, P.O., 1953: Pasture Growth and Soil Fertility: I. The Influence of Red and White Clovers, Superphosphate, Lime, and Sheep Grazing on Pasture Yield and Botanical Composition. N.Z. J. Sci. Tech., 35A: (Suppl. 1) 1-29.
- SHEDD, O.M., 1928: Oxidation of Sulphur in Limed and Unlimed Soils. Soil Sci., 26: 93-105.



- SHELDON, V.L., BLUE, W.G., ALBRECHT, W.A., 1951: 1. Biosynthesis of Amino Acids According to Soil Fertility: 2. Methionine Content of Plants and the Sulphur Applied. Plant and Soil, 3: 361-365.
- SPENCER, K., 1959: Growth and Chemical Composition of White Clover as Affected by Sulphur Supply. Aust. J. Agric. Res., 10: 500-517.
- SPOREK, K.F., 1958: Complexometric Determination of Sulphate. Analytical Chem., 30: 1032-1035.
- STARKEY, E.B., and GORDON, N.E., 1922: Influence of Hydrogen-Ion Concentration on the Adsorption of Plant Food by Soil Colloids. Soil Sci., 14: 449-457.
- STARKEY, R.L., 1950: Relations of Micro-organisms to Transformations of Sulphur in Soils. Soil Sci., 70: 55-65.
- STEINBERGS, A., 1955: A Method for the Determination of Total Sulphur in Soils. Analyst, 80: 457-461.
- STEPHENS, C.G., and DONALD, C.M., 1958: Australian Soils and their Responses to Fertilisers. Advances in Agronomy, 10: 167-256.
- STOUT, P.R., MEAGHER, W.R., PEARSON, G.A., and JOHNSON, C.M., 1951: Molybdenum Nutrition of Crop Plants. Plant and Soil, 3: 51-86.
- SWANSON, C.O., and LATSHAW, W.L., 1922: Sulphur as an Important Fertility Element. Soil Sci., 14: 421-430.
- THOMAS, M.D., 1943: Sulphur Nutrition of Alfalfa. Plant Phys., 18: 345-
- THOMAS, M.D., HENDRICKS, R.H., and HILL, G.R., 1950a: Sulphur Content of Vegetation. Soil Sci., 70: 9-18.
- \* TICKHOVA, E.P., 1958: The Importance of Exchangeable Cations in the Adsorption of  $\text{SO}_4$  by Soils. Soviet Soil Science (English Transl.) Oct. 1959. 165-168.
- TISDALE, S.L., and BERTRAMSON, B.R., 1949: Elemental Sulphur and its Relationship to Manganese Availability. Soil Sci. Soc. Amer. Proc., 14: 131-137.
- \* THOMAS, M.D., HENDRICKS, R.H., and HILL, G.R., 1950b: Sulphur Metabolism in Alfalfa. Soil Sci., 70: 19-26.



- TISDALE, S.L., DAVIS, R.L., KINGSLEY, A.F., and MERTZ, E.T., 1950: Methionine and Cystine Content of Two Strains of Alfalfa as Influenced by Different Concentrations of the Sulphate Ion. Agron. J., 42: 221-225.
- TOLEMAN, B., and STOKER, G.L., 1941: Sulphur and Nitrogen Deficiency Relationships in Sugar Beets Grown for Seed in Oregon. Amer. Soc. Agron., 33: 1072-1079.
- VERVELDE, G.J., 1953: The Donnan Principle in the Ionic Relations of Plant Roots. Plant and Soil, 4: 309-322.
- VOGLER, K.G., 1943: Studies on the Metabolism of Autotrophic Bacteria I, II and III. J. Gen. Physiol., 26: 89, 103 and 157.
- WALKER, T.W., ADAMS, A.F.R., and ORCHISTON, H.D., 1955: The Effects and Interactions of Sulphur, Phosphorus and Molybdenum on the Growth and Composition of Clovers. N.Z. J. Sci. Tech., 36A: 470-482.
- WALKER, T.W., ADAMS, A.F.R., and ORCHISTON, H.D., 1956: The Effects of Levels of Calcium Sulphate on the Yield and Composition of a Grass and Clover Pasture. Plant and Soil, 7: 290-300.
- WALKER, T.W., 1957: The Sulphur Cycle in Grassland Soils. J. Brit. Grassland Soc., 12: 10-18.
- WALKER, T.W., and ADAMS, A.F.R., 1958a: Studies on Soil Organic Matter: 1. Influence of Phosphorus Content of Parent Materials on Accumulations of Carbon, Nitrogen, Sulphur and Organic Phosphorus in Grassland Soils. Soil Sci., 85: 307-318.
- WALKER, T.W., and ADAMS, A.F.R., 1958b: Residual Effects of Calcium Sulphate on the Yield and Composition of a Grass-Clover Association. Plant and Soil, 10: 176-182.
- WALKER, T.W., and ADAMS, A.F.R., 1958c: Competition for Sulphur in a Grass-Clover Association. Plant and Soil, 9: 353-366.



- WALKER, T.W., and ADAMS, A.F.R., 1959: Studies on Soil Organic Matter. 2. Soil Sci., 87: 1-10.
- WALKER, T.W., 1960: Uptake of Ions by Plants Growing in Soil. Soil Sci., 89: 328-332.
- WAKSMAN, S.A., and IYER, K.R.N., 1932: The Chemical Nature and Origin of Humus. Soil Sci., 34: 43-69.
- WAKSMAN, S.A., and HUTCHINGS, 1937: Associations and Antagonistic Effects of Micro-organisms. III. Soil Sci., 43: 89-77-92.
- WAKSMAN, S.A., 1952: "Soil microbiology." John Wiley & Sons.
- WHITE, J.G., 1959: Mineralization of Nitrogen and Sulphur in Sulphur Deficient Soils. N.Z. J. Agric. Res., 2: 255-258.
- \* WILLIAMS, D.E., and COLEMAN, N.T., 1950: Cation Exchange Properties of Plant Root Surfaces. Plant and Soil, 2: 243-256.
- WILLIAMS, C.H., and DONALD, C.M., 1957: Changes in Organic Matter and pH in Australian Podzolic Soils as Influenced by Subterranean Clover and Superphosphate. Aust. J. Agric. Res., 8: 179-189.
- WILLIAMS, C.H., and STEINBERGS, A., 1958: Sulphur and Phosphorus in Some Eastern Australian Soils. Aust. J. Agric. Res., 9: 483-491.
- WILLIAMS, C.H., and STEINBERGS, A., 1959: Soil Sulphur Fractions as Chemical Indices of Available Sulphur in Some Australian Soils. Aust. J. Agric. Res., 10: 340-352.
- WILLIAMS, E.G., SCOTT, N.M., and McDONALD, M.J., 1958: Soil Properties and Phosphate Sorption. J. Sci. Food Agric., 9: 551-559.
- WILEY, R.C., and GORDON, N.E., 1922: Adsorption of Plant Food by Colloidal Silica. Soil Sci., 14: 441-448.
- WILSON, A.T., 1959: Organic Nitrogen in New Zealand Snows. Nature, 183: 318-319.