LEACHING AND SURFACE RUNOFF LOSSES OF SULPHUR AND

POTASSIUM FROM A TOKOMARU SOIL

A thesis presented in partial fulfilment
of the requirements for the Degree of
Master of Philosophy in Soil Science at
Massey University

Christine M. Smith

1979.

ABSTRACT

Sulphur and potassium surface and subsurface drainage water losses from grazed pastures on a yellow-grey earth soil, the Tokomaru silt loam, were investigated in field experiments. Runoff losses from undrained and drained pastures fertilised in spring or autumn were measured over a six week winter interval in 1976. Losses from undrained pastures were measured throughout the runoff season in 1977. In 1977, S and K leaching losses from pastures fertilised in spring or autumn, were determined by measuring tile drainage water losses and monitoring changes in soil S and K levels. An attempt was also made to relate soil S and K levels to tile drainage water losses.

This field study illustrates that SO_4-S is readily leached in the Tokomaru silt loam. Losses in tile drainage waters occurred from all depths above the mole drains (i.e. 45 cm depth) during individual flow events. On average 7.5 kg dissolved SO_4-S ha^{-1} was lost from the two non-irrigated pastures fertilised in spring. An additional 6.7 kg SO_4-S ha^{-1} was discharged in tile drainage waters from two irrigated pastures fertilised in spring (i.e. total 14.2 kg SO_4-S ha^{-1}). Evidence indicated that SO_4-S may have bypassed the drains in water seeping beyond the fragipan.

An autumn application of fertiliser S (45 kg S ha^{-1}) significantly enhanced the extent of leaching. The equivalent of 10% of the applied S (4.47 ± 1.5 kg SO_4-S ha^{-1}) was leached over a period of 17 weeks from July 1 to September 21. Losses occurred throughout this period. On average, 15.2 kg SO_4-S ha^{-1} was discharged from the two non-irrigated pastures fertilised in autumn. An additional 3.4 kg SO_4S ha^{-1} was lost from the two irrigated pastures.

An appreciable quantity (13.8 kg SO_4-S ha^{-1}) of the fertiliser S applied in autumn but not leached in tile drainage waters, was recovered as water soluble SO_4-S, leached below the 20 cm depth (i.e. below the zone from which pasture species are likely to obtain most

of their S.

Over a period of six weeks in 1976, 0.9 kg SO_4-S ha^{-1} was lost in surface runoff from an undrained pasture fertilised (19 kg S ha^{-1} in superphosphate) in spring. Less SO_4-S was lost from the associated drained plot (0.2 kg SO_4-S ha^{-1}). Undrained and drained plots fertilised in autumn (57 kg S ha^{-1} in superphosphate) lost 8% and 1.8% of the S applied (i.e. 5.5 and 0.9 kg SO_4-S ha^{-1}) respectively. In 1977, on average only 0.8 kg SO_4-S ha^{-1} was transported in surface runoff off two undrained plots fertilised (36 kg S ha^{-1} in superphosphate) in spring. An average of 8.0 kg SO_4-S ha^{-1} was lost from two plots fertilised (55 kg solution S ha^{-1}) in autumn. Hence surface runoff is an important S loss mechanism if undrained plots are fertilised in autum.

Sulphur received in the rainfall over a five month interval in 1977 amounted to 3.1 kg ha^{-1}.

From these results it was concluded that total drainage water losses from non-irrigated, drained pastures were likely to be largely offset by S received in the rain in 1977. A significant net S loss (in relation to annual pasture S requirements) will have occurred from pastures irrigated the preceding summer and/or fertilised in autumn.

Sulphur fertilisation in autumn and winter is not recommended. Under the conditions likely to prevail at this time an appreciable fraction of the applied S may be lost in drainage waters.

Results of this study indicate that leaching is not an important K loss process in the Tokomaru silt loam. Dissolved K leaching losses from pastures fertilised in spring or autumn averaged 4.66 and 4.05 kg K ha^{-1} respectively.

Potassium surface runoff losses are generally of no consequence. In 1976 only 1.1 kg K ha^{-1} was lost from an undrained pasture fertilised (50 kg K ha^{-1}) in spring, whilst 0.3 kg K ha^{-1} was discharged from the associated drained plot. A minimal fraction (3%) of the K applied in autumn (50 kg K ha^{-1}) to an undrained plot was lost in surface runoff. Less than 1% of that applied was discharged from the associated drained plot. Throughout 1977, on average, 1.35 kg K ha^{-1} was discharged from undrained plots fertilised (57 kg K ha^{-1}) in spring. An additional 3.75 kg K ha^{-1} was lost from pastures fertilised (55 kg K ha^{-1}) in autumn.

Rainfall K additions measured over a five month interval in 1977

were low (total 1.4 kg K ha^{-1}). However, because of the trend for K concentrations to vary on a seasonal basis it was concluded that K received in rainfall throughout 1977 was likely to largely offset total drainage water losses from undrained and drained pastures.

The results indicate that K deficiencies in pasture on K retentive yellow-grey earth soils are not attributable to drainage water losses.

Regression analyses showed that SO_4-S concentrations in leachate, but not SO_4-S loadings, were significantly related to water soluble soil SO_4-S levels (0-40 cm), determined at frequent intervals during the drainage season, if the quantity of water percolating through the soil is measured. No relationship was found between measured water soluble or ammonium acetate extractable soil K levels and leachate K concentrations or loadings.

ACKNOWLEDGEMENTS

I wish to express my thanks to Dr P.E.H. Gregg, Department of Soil Science, Massey University, who suggested this study and gave helpful advice, criticism and encouragement during all stages of the project.

Thanks are also extended to Mr R. Tillman of the Soil Science Department, Massey University, for help and advice, and to J. Macintosh for his assistance with the field work.

My sister, Julie's assistance with the figures, and my mother's support throughout, are much appreciated.

Finally, my sincere thanks to Mrs E. Hartstone who so ably typed the manuscript.

TABLE OF CONTENTS

LIST OF PLATES

LIST OF FIGURES

LIST OF TABLES

CHAPTER I INTRODUCTION

In grazed pastures, nutrient ions move continuously from the soil to the plant and back into the soil, either directly in plant residues or indirectly via the grazing animal. Nutrient ions exist in a variety of soil, plant and animal pools within this cycle. Additions to and losses from the cycle occur by a variety of processes.

Within this cycle, the size of a particular plant available soil nutrient pool at any one time (assuming the other nutrient levels are adequate), controls and may limit plant growth and hence animal production.

Factors which influence the size of the plant available pool, aside from the rate of plant nutrient uptake, include:

(i) the rate at which the nutrient ion is recycled into the plant available soil pool, and

(ii) the balance between non-cyclic additions to and losses from the plant available soil nutrient pool.

If the relative importance of those factors affecting the pool size can be defined, the principal factors responsible for inducing pasture nutrient deficiencies can be determined and reasoned improvements made in management practices.

The most widespread nutrient deficiency in New Zealand pastures is phosphate-phosphorus. The P-cycle in grazed pastures, and the importance of various loss mechanisms in inducing P deficiencies have, however, been studied in some detail.

Pasture production is also frequently limited by sulphur and potassium deficiencies.

Sulphur deficiencies generally follow a cessation in S fertiliser applications, but deficiencies do also occur in areas receiving regular S applications at rates sufficient to meet pasture requirements. In some instances, the S cycle turnover rate may limit productivity. Net S immobilisation may also account for the occurrence of S deficiencies. Frequently, however, pasture S deficiencies in New Zealand have been attributed to significant plant available soil SO_4-S losses in surface and, in particular subsurface drainage waters. At the time this study was commenced, S drainage water losses in New Zealand had not been measured in the field.

In New Zealand pasture potassium deficiencies are endemic on certain soils. In other areas, K deficiencies have arisen following the correction of other nutrient deficiencies and subsequent increases in the general level of productivity. The K cycle turnover rate is unlikely to limit productivity as K, existing only in ionic combination, may move rapidly through the cycle. Potassium losses from the cycling pool must exceed additions to the cycle. Potassium losses associated with grazing animals may be important. Controversy exists, regarding the importance of K drainage water losses in promoting K deficiencies. Drainage water K losses have not been investigated in the field in New Zealand.

The principal aim of this study was to measure plant available sulphate-sulphur and potassium surface and subsurface drainage water losses, from a New Zealand soil in the field.

CHAPTER II REVIEW OF LITERATURE

II.1 SULPHUR REVIEW

II.1.1 THE SULPHUR CYCLE IN GRAZED PASTURES

Sulphur occurs in both organic and inorganic combinations in the soil-plant-animal cycle. Pasture S deficiencies may be induced by a slow S cycle turnover rate and/or the addition of insufficient S to the cycling pool to offset the losses occurring from this pool. The relative importance of these factors in inducing S deficiencies (especially under New Zealand conditions) is considered in this review. Included is a discussion on the nature of the various S pools in the soil-plant-animal cycle, the S turnover rate, and the processes whereby S is added to or lost from the cycle.

II.1.1.1 Soil sulphur

In intensively used pastoral soils S occurs in several important pools, viz:

(i) the readily plant available inorganic SO_4-S pool,

(ii) the organic S pools.

II.1.1.1.1 The readily plant available soil SO_4-S pool

Water soluble and adsorbed sulphate-sulphur comprise the readily plant available sulphur pool (e.g. Freney *et al.*, 1962). In most well drained soils of the humid-temperate regions SO_4-S in this pool comprises less than 10% of the total S in the topsoil (Ensminger, 1954; Freney, 1961; Metson, 1969).

Water soluble sulphate is immediately plant available. Several parts per million water soluble sulphate-sulphur is typical in New Zealand soils (Blakemore *et al.*, 1968). The level may vary on a seasonal basis however (Williams, 1968; Barrow, 1974), attributable to the influence of climatic conditions on S mineralisation, leaching, and plant uptake rates. Water soluble sulphate is in a rapid exchange equilibrium with adsorbed sulphate.

Adsorbed sulphate-sulphur levels are generally low (i.e. $\lesssim$ 4 mg/100 gm soil) in New Zealand topsoils (Blakemore *et al.*, 1968). Levels increase with depth in some New Zealand soils in association with increasing 1:1 clay mineral, allophane, and/or Al and Fe hydrous oxide content (Metson, 1969) which favour SO_4-adsorption (e.g. Ensminger, 1954; Chao *et al.*, 1962a, b). Adsorbed SO_4-S is less readily available in soils with a high, rather than a low, sulphate adsorption capacity (Barrow, 1969).

The depth of plant S uptake is important in assessing the size of the readily plant available S pool. Pasture S responses occurred on a yellow-brown loam, despite the presence of considerable SO_4-S (i.e. 70-80 ppm S) in the 30-40 cm depth. During (1972) concluded, therefore, that this subsoil S was not plant available. Till and May (1970a) also concluded that grasses and clovers obtained S only from the topsoil (i.e. 0-7.5 cm) as, in a field trial with labelled S, the specific activities of herbage and topsoil S were approximately the same but considerably higher than the specific activity of subsoil S. This is not, however, conclusive evidence. A limited amount of subsoil S may have been taken up by the pasture.

In contrast, Gregg *et al.* (1977) reported uptake of subsoil S. In a sandy soil and silt loam, plants obtained 24% and 10% respectively of their S from subsoil depths (> 22.5 cm). The extent of the uptake zone reflected the depth of grass and clover rooting. Sulphur uptake occurred from a greater depth (100 cm) in the sandy than silt loam (60 cm). The extent of the S uptake zone also varied on a seasonal basis, with uptake occurring from greater depths under drier soil conditions (Gregg *et al.*, 1977).

High producing grass-clover swards (i.e. > 10,000 kg D.M. ha^{-1} yr^{-1}) may require about 30-35 kg S $ha^{-1}yr^{-1}$ (refer II.1.1.2). However, as little as 10 kg ha^{-1} readily available SO_4-S may be present at any one time (Till and May, 1971). Therefore this pool must be replenished to meet plant requirements. The readily plant available S pool is replenished with the return of SO_4-S in animal excreta, by mineralisation of organic S, with atmospheric S additions, ground and irrigation water S additions and fertiliser S additions.

Sulphur is lost from this pool and the soil-plant-animal cyclic pool, with net immobilisation in the soil organic fraction, losses in drainage waters, and volatilization.

II.1.1.1.2 Organic soil sulphur

In humid-semi-arid regions, most of the topsoil S is in organic form (e.g. Williams and Donald, 1954; Walker and Adams, 1958; Williams and Steinbergs, 1959). Jackman (1964) reported organic S levels ranging from 560-2,000 kg ha^{-1} in the upper 30 cm of a range of representative New Zealand soils. Organic S levels in subsoils are generally much lower (Jackman, 1964; Whitehead, 1964).

Recently May *et al.* (1968) and Till and May (1970a, b; 1971) partitioned the organic soil S into two pools, viz:

(i) an 'active' pool which turned over relatively quickly,

(ii) an 'inert' S pool with a negligible turnover rate.

In their soil 50% of the organic S was held in the 'inert' pool. In the same manner Gregg (1976) identified 'active' and 'inert' organic S pools in several New Zealand soils. However, in his study a much larger proportion, 90%, of the organic S was present in the 'inert' pool.

The 'active' organic S mineralisation rate determines plant availability of the organic S (Till and May, 1970a, b). In Till and May's studies (1970a, b) the 55 kg S ha^{-1} (0-25 cm) present in the active organic S pool turned over rapidly enough to replenish the plant available inorganic SO_4-S pool. Pasture production was unusually low because of the dry conditions. Till and May (1971) concluded that, under favourable climatic conditions when pasture S requirements and SO_4-S leaching losses may be considerably higher the S mineralisation rate may limit productivity.

Under favourable growing conditions in Gregg's (1976) New Zealand study pasture S deficiencies occurred although about 70 kg S ha^{-1} was present in the active S pool at any one time. A slow active S mineralisation rate apparently limited productivity (Gregg, 1976).

Therefore, although a large quantity of S is present in soils in organic form, a major fraction of this S may be held in an 'inert' pool which does not make significant contributions to the plant available S pool. The 'active' organic S mineralisation rate may limit productivity in potentially high producing systems.

II.1.1.2 The plant sulphur pool

The plant S pool comprises that S present in the pasture tops and roots at any one time. This pool will vary greatly in size depending on pasture management practices. A rotationally grazed pasture with a dry matter herbage level of about 3,000 kg ha^{-1} prior to grazing, if adequately supplied with S (> 0.3% (Metson, 1973)) will contain 9 kg S ha^{-1}. Immediately after grazing only 1,000 kg D.M. ha^{-1} may be present, with a S content of only 3 kg S ha^{-1}. The root dry matter level will be more stable. Assuming a dry matter level of 1,000 kg ha^{-1} with a S content of 0.15% (Gregg, 1976) another 1.5 kg S ha^{-1} will be present in the roots.

The annual pasture S turnover figure will be considerably larger. Till and May (1970a) reported that, under unfavourable growing conditions, 15 kg S ha^{-1} (i.e. about 10% of the total cycling S in the soil-plant-animal cycle) was incorporated annually into the plant tops and roots.

New Zealand grass-clover swards producing about 10,000 kg D.M. ha^{-1} yr^{-1} in the pasture tops, if adequately supplied with S, may incorporate about 30 kg S ha^{-1} yr^{-1} in the plant tops. Assuming a top-root production ratio of 3:1 and a root S content of 0.15% (Gregg, 1976), another 5 kg S ha^{-1} will be tied up annually in the roots. Altogether, then, highly productive New Zealand pastures may incorporate about 35 kg S ha^{-1} yr^{-1}.

Plant S is returned to the soil S pools in litter (top residues) and root residues. Shamoot *et al.* (1968) reported that, in a glasshouse investigation, a variety of grasses and clovers returned about 30 gm of root debris/100 gm of fresh root tissue. Assuming root residue S levels are similar to fresh root S contents, only about 1 - 1.5 kg S ha^{-1} will be returned annually to the soil from high producing New Zealand pastures. The contribution made by this S to the various soil S pools has not been investigated.

Sulphur return in litter will vary depending on the level of pasture consumption by grazing animals. With a pasture utilization figure of 75%, 7.5 kg S ha^{-1} may be returned in litter annually from a high producing pasture (10,000 kg D.M. ha^{-1} yr^{-1}) adequately supplied with S.

II.1.1.3 The animal sulphur pool

The animal sulphur pool comprises that S present in the grazing animal at any one time. Animal S amounts to only a small fraction of the total cycling S. For instance, at a stocking rate of 2.5 lactating cows ha^{-1} with a body liveweight in the order of 340-400 kg each and a S content of 0.15% (Maynard, 1937), only 1.3 - 1.5 kg S ha^{-1} will be tied up in the animal.

The annual animal S turnover figure will be larger. Assuming a pasture utilisation figure of 80% with an annual dry matter production figure of 10,000 kg D.M. ha^{-1}, about 24 kg S ha^{-1} will be ingested annually. Both sheep (Till *et al.*, 1973) and dairy cattle (During, 1972) retain about 10% of the S ingested. Therefore most of the S ingested is returned to the pasture in excreta.

Sulphur returned in excreta (i.e. about 90% of the S ingested) is largely in the immediately plant available inorganic sulphate-sulphur form (Barrow and Lambourne, 1962). Sulphur cycling via the animal, therefore, avoids the slow process of plant residue decomposition and S mineralisation, effectively increasing the S cycle turnover rate (Till, 1975). Sulphur cycling via the animal is nevertheless an inefficient process because of both the uneven excretal return distribution pattern and cycling-S losses which occur (refer II.1.2.4).

II.1.2 SULPHUR LOSSES FROM THE CYCLE

Sulphur may be lost from the cycle in surface and subsurface drainage waters, by net immobilisation of S in the soil organic fraction, by volatilisation, in animal products, and in animal excreta returned to unproductive sites.

II.1.2.1 Sulphur drainage water losses

Sulphur is transported (generally as the dissolved SO_4-S ion) in both surface and subsurface drainage waters. Losses from the plant available soil S pool (and the cycling-S pool) occur with

(i) movement over the soil surface, in surface runoff, to streams and with

(ii) movement in percolating (subsurface drainage) water beyond the zone of plant S uptake.

Research findings and the experimental techniques used to investigate S drainage water losses are reviewed.

II.1.2.1.1 Sulphur leaching losses in laboratory and glasshouse studies

Sulphur leaching has been investigated in laboratory and glasshouse studies. Losses ranging from 0-100% of the S applied (i.e. < 50 kg S

ha^{-1}) have been reported in different soils with varying fertiliser and watering techniques. The results of a number of these studies, and experimental techniques used are given in Table I.

Losses in laboratory and glasshouse studies will not refect actual S losses occurring in the field. The amount, velocity and pattern of soil-water movement, the soil solution SO_4-S concentration and hence the extent of S leaching is altered (Harward and Reisenauer, 1966). Several important factors, which are likely to have enhanced S losses in the studies reviewed in Table I, are discussed below.

Air-drying soils enhances S movement in soils (Peverill *et al.*, 1975). Chao *et al.* (1962a), Hogg and Cooper (1964), Hogg (1965), Cooper and Hogg (1966), Hogg and Toxopeus (1966), and Muller and McSweeney (1977) all air-dried soils prior to measuring S leaching losses.

Sieving and bulking to give a homogenous soil sample alters important soil properties (i.e. soil structure, porosity and stratification) which influence soil-water (e.g. Ward, 1967) and hence S movement. Hogg and co-workers (1964, 1965, 1966) sieved and bulked soils before measuring S leaching losses.

'Edge-effects', associated with the soil container interface, promote water and S movement (Till and McCabe, 1976). Only Peverill and Douglas (1976) attempted to avoid this problem by waxing the soil container interface.

'Equilibration' may also be an important factor influencing ion movement. Balasubramaniam *et al.* (1973), for example, found that applying nitrate solution one week prior to, rather than immediately before irrigation, retarded leaching as soil-nitrate equilibrium occurred. In leaching column studies, solid SO_4-S applications to dry soils have generally been followed immediately by intensive simulated rainfall events (e.g. Chao *et al.*, 1962a; Hogg and co-workers, 1964, 1965, 1966). The applied SO_4-S is unlikely to have had time to equilibrate with these soils; whereas a typical rainfall pattern in certain regions would permit equilibration and hence reduce leaching losses.

The presence or absence of plants may be important. In the absence of growing plants, a greater quantity of water and S will be available for leaching. With one exception (i.e. Peverill and Douglas, 1976), plants were absent in the soil leaching column studies outlined

TABLE I Sulphur leaching losses in laboratory and glasshouse studies.

Soil properties	Experimental techniques	Soil pre-treatment procedures	Water applied or quantity leachate	Sulphur fertiliser treatment	Sulphur leached	Reference
(15) soils with widely varying character-istics	Soil leaching column study; 0-175 mm soil depth; plants absent.	soil sieved, bulked and air-dried	25-200 mm water applied	45 kg ^{35}S/ ha^{-1} in gypsum	0-15% fertil-iser S	Chao *et al.* (1962)
(1) Podzol	Undistributed soil leaching column study; 0-100 mm soil depth; plants grown.	-	90 mm water applied	not fertilised	2 kg S ha^{-1}	Peverill and Douglas (1976)
(1) Podzol	Soil leaching column study using Hogg's (1960) leaching technique:- alternate leaching and drying phases; 0-75 mm soil depth; no plants grown	soil sieved, bulked and air-dried	20 mm water applied	110 kg S/ha in gypsum	90% fer-tiliser S	Hogg and Cooper (1964)*
				50 kg S/ha in super-phosphate	81% fer-tiliser S	
				31 kg S/ha in elemental S	19-33% fertil-iser S	
(1) Podzol (3) Yellow-brown sands (1) Organic soil	"	"	400 mm water applied	25 or 50 kg S/ha in super-phosphate	85-100% fertil-iser S	Hogg (1965)*
(1) Yellow-brown pumice soil	"	"	600 mm water applied	17-67 kg S/ha in gypsum or super-phosphate	95-100% fertil-iser S	Cooper and Hogg (1966)*
(41) Yellow-brown pumice soils	"	"	400 mm water applied	25 or 50 kg S/ha in super-phosphate	33-100% fertil-iser S	Hogg and Toxopeus (1966)*
(6) Yellow-brown loams					2-6% fertil-iser S	
(1) Yellow-brown pumice soil (YBPS) (1) Yellow-brown loam (YBL)	Glasshouse pot experiment of 1 years duration; 0-200 mm soil depth; plants grown	soil sieved and bulked when moist	Yellow-brown pumice soil-water applied until 360 mm of leachate collected. Yellow-brown loam-water applied to collect 250 mm leachate	88 kg S/ha in powdered super-phosphate	YBPS 50%, YBL 10% fertil-iser S	Muller and McSweeney (1974)*
				88 kg S/ha in super-phosphate granules	YBPS 17% YBL 0% fertil-iser S	
				88 kg S/ha in gypsum	YBPS 36% YBL 29% fertil-iser S	
				88 kg S/ha as elemental S	YBPS 1%, YBL 2% fertil-iser S	
				88 kg S/ha in powdered super-phosphate plus lime	YBPS 44% YBL 5% fertil-iser S	
(1) Yellow-grey earth (Tokomaru silt loam)	Glasshouse pot trial of 2 years duration 0-180 mm soil depth; plants grown	soil air-dried, sieved and bulked	water applied until 425 mm of leachate collected	106 or 264 kg S/ha applied in super-phosphate	20% fer-tiliser S	Muller and McSweeney (1977)*
				No fertil-iser S applied	51 kg S/ha	

*New Zealand study.

( ) refers to the number of soils studied.

in Table I.

Sulphate-sulphur leaching losses from the upper 7.5 cm of soil have been measured in New Zealand soil leaching column studies. Gregg *et al.* (1977), however, reported that subsoil SO_4-S may be available. As subsoils frequently exhibit a greater ability to adsorb SO_4-S than topsoils, leaching losses from the plant uptake zone are likely to be lower than measured losses from the upper 7.5 cm depth.

For the reasons discussed above S leaching losses in the field are generally likely to be considerably lower than losses occurring (Table I) in the soil leaching column and glasshouse studies.

Laboratory and glasshouse studies have, however, been useful in determining

(i) the influence of soil properties on the extent of S leaching, and

(ii) the relative susceptibility of various forms of fertiliser S to leaching.

Chao *et al.* (1962a) reported that less SO_4-S was leached from SO_4-S retentive than non-retentive soils. Leaching studies undertaken in New Zealand have also shown that the extent of SO_4-S leaching is related to the soil SO_4-S adsorption capacity. Hogg and Toxopeus (1966), for instance, reported lower SO_4-S leaching losses from weakly sorbing yellow-brown pumice soils than SO_4-S retentive yellow-brown loams (Table I).

Muller and McSweeney (1974) attributed the smaller measured SO_4-S leaching losses from a sand than stony silt loam (Table I) to two factors, viz:

(i) organic matter accumulation, and hence fertiliser S immobilisation in the sand, reducing the quantity of SO_4-S liable to leaching,

(ii) a higher soil water holding capacity which reduced the quantity of water percolating through the soil.

Both the chemical and physical form of S fertiliser applied, has been shown to influence S leaching losses in soil column and glasshouse experiments (Hogg and Cooper, 1964; Aylmore *et al.*, 1971; Muller and McSweeney, 1974). Elemental S is less susceptible to leaching than calcium sulphate, in either the anhydrite form in superphosphate or the dihydrate form, gypsum (Hogg and Cooper, 1964; Muller and McSweeney, 1974). Sulphur in granular superphosphate is less susceptible to leaching than S in powdered superphosphate (Aylmore *et al.*, 1971; Muller and McSweeney, 1974).

The application of other fertilisers and accompanying ions in S fertilisers may also influence the extent of S leaching. Chao *et al.* (1962a) found that lime, and phosphate to a lesser extent, promoted SO_4-leaching. Cooper and Hogg (1966) failed to record such an effect; attributable probably to the fact that even prior to liming or phosphate fertilisation virtually no fertiliser SO_4-S was retained by the soil.

II.1.2.1.2 Sulphur leaching losses in lysimeter studies

Lysimetry research findings and the experimental methods involved in these studies are summarised in Table II. Sulphur losses in these studies varied depending on soil properties, fertiliser treatments, and experimental techniques. Sulphur equivalent to 29-90% of that applied in superphosphate or gypsum was leaching in both short-term (McKell and Williams, 1960; Williams *et al.*, 1964; Jones *et al.*, 1968) and long-term studies (Muller, 1975). Although Till and McCabe (1976) also reported large S leaching losses (i.e. 25 kg ha^{-1} yr^{-1}), a negligible fraction of the ^{35}S applied in superphosphate was leached. Elemental S leaching losses were lower, ranging from 2.6 - 58% of that applied (Williams *et al.*, 1964; Jones *et al.*, 1968). Increasing S particle size reduced the extent of leaching (Jones *et al.*, 1968).

Lysimeter studies do not measure actual losses occurring in the field (Stauffer and Rust, 1954; Dreibelbis, 1957; Fried and Broeshart, 1967). However, the techniques used in lysimeter studies investigating S leaching have, as discussed below, been particularly poor.

Till and McCabe (1976) illustrated that free movement of water along soil-container interfaces ('edge-effects') enhanced S losses. Four times as much ^{35}S was leached from the peripheral zone (6.7% of the fertiliser S) as from a central zone of equal area (1.7%) in a lysimeter of 0.2 m^2 surface area. The larger the lysimeter, the smaller the proportional influence of edge-effects (Stauffer and Rust, 1954; Fried and Broeshart, 1967). However, the lysimeters used when measuring S leaching losses have all be comparatively small (i.e. < 0.3 m^2 in surface area).

A prolonged 'soil settling' interval is required prior to experimentation to reverse any soil property changes (occurring as a result of soil disturbance during fulling) which influence water

TABLE II Sulphur leaching losses in lysimeter studies

Soil	Experimental procedures	Sulphur fertiliser treatment	Interim results			Results over entire study interval		Reference
			Years	Average rainfall/yr.	Total S leached	Average rainfall/yr.	Average total S leached from each lysimeter	
Sand	Soil from 0-600 mm depth was layered in a 0.34 m^2 lysimeter; an 8 month 'soil settling' interval prior to 1 year investigation.	Control 22 or 67 kg ^{35}S/ha in gypsum				795 mm	13.0 kg S/ha 77.5% fertiliser S	McKell and Williams (1960)
	The study initiated by McKell & Williams (1960) was continued for another 3 years.	Control 67 kg S/ha in gypsum 67 kg S/ha as coarse or fine elementals	1	266 mm	3.9 kg S/ha 26.7% fertilisers < 1.5 fertilisers	324 mm	5.3 kg S/ha 36.7% fertilisers 15.8% fertilisers	Williams *et al.* (1964)
Sandy loam; loam and a clay	Soil from 0-600 mm depth was sieved, bulked and placed in 0.24 m^2 lysimeters; a 2 week 'soil settling' interval prior to a study of 2 years duration.	56 kg ^{35}S/ha in gypsum 56 kg ^{35}S/ha as fine elemental S 56 kg ^{35}S/ha as coarse elemental S				705 mm	82-98% fertiliser S 21-58% fertiliser S 2.6-11.5% fertiliser S	Jones *et al.* (1968)
Yellow-brown loam	Soil from 0-600 mm depth placed in 0.2 m^2 lysimeter; study of 20 years duration.	Control 272 kg S/ha in powdered super-phosphate in year 1	0-7		53.4 kg S/ha 85% fertiliser S (i.e. 234 kg S ha^{-1})		66 kg S/ha 86% fertiliser S (i.e. 234 kg S/ha)	Muller (1975)*
Loam	Soil from 0-600 mm depth placed in 0.2 m^2 lysimeters; pretreatment procedures not reported study of 252 days duration.	0.5 kg ^{35}S/ha in aqueous $MgSO_4$ or 255 kg ^{35}S/ha in superphosphate				705 mm	25 kg S/ha but < 0.1 kg of the fertiliser S irrespective of S fertiliser rate	Till and McCabe (1976)

*New Zealand study.

movement and nutrient ion movement/unit of percolating water (Stauffer and Rust, 1954; Dreibelbis, 1957). However, indirect evidence suggests that, in McKell and Williams (1960), Williams *et al.* (1964) and Muller's (1975) studies, insufficient time was allowed for 'soil settling'. Consequently, soil property changes influenced the extent of leaching.

In Williams *et al.*'s (1964) study SO_4-S leaching, in an unfertilised soil, occurred to a considerably greater extent in the first year (i.e. 3.92 kg S ha^{-1}) than during the following two years (i.e. average of 0.67 kg S ha^{-1} yr^{-1}) although rainfall was the lowest recorded. This suggests that soil disturbances may have promoted SO_4-S leaching during the earlier part of this investigation. This explanation would also account for the very large leaching loss recorded from this lysimeter (13.0 kg S ha^{-1} yr^{-1}) in the earlier study undertaken by McKell and Williams (1960).

In Muller's (1975) New Zealand lysimeter study, SO_4-S leaching losses from an unfertilised soil were large (averaging 9.1 kg S ha^{-1} yr^{-1}) but erratic, in the first six years of the 20 year study period. Subsequently, losses gradually decreased until, during the last 11 years leaching losses were small and relatively constant at less than 1 kg S ha^{-1} yr^{-1}. Muller (1975) attributed the larger leaching losses observed early in this investigation to the effects of soil disturbances during fulling, on the internal soil drainage pattern.

Till and McCabe (1976) did not measure SO_4-S leaching losses from unfertilised lysimeters. However, the amount of water percolating through 20 replicate fertilised lysimeters varied from 8-59% of that received, indicating a soil disturbance effect. This effect was reflected in widely varying (4.3 - 95.0 kg S ha^{-1} yr^{-1}) SO_4-S leaching losses.

It is not possible to analyse Jones *et al.*'s (1968) results in a similar manner because of the manner in which the data was presented. Experimentation followed only a two week soil settling interval. Soils were sieved and bulked prior to fulling the lysimeters. Both of these factors will influence the extent of S leaching.

Nutrient leaching losses from bare soils tend to be higher than losses from pastures (e.g. Harward and Reisenauer, 1966). The annual resowing of clover when applying S in the American lysimeter studies (McKell and Williams, 1960; Williams *et al.*, 1964; Jones *et al.*, 1968) would probably raise S leaching losses above levels expected under permanent pastures.

For the reasons discussed above it is difficult to interpret the lysimeter results given in Table II in terms of likely S leaching losses occurring in the field under permanent pastures.

II.1.2.1.3 Sulphur drainage water losses in field studies

Sulphur drainage water losses may be most accurately determined in field studies, as the integrated effect of plant uptake, soil properties, aspect, slope and climatic conditions on S movement is measured. The influence of grazing animals on drainage water losses may also be considered. Despite these advantages, few field studies have been undertaken.

Sulphur leaching losses in the few field investigations undertaken have been determined by a variety of methods. May *et al.* (1968), Till and May (1971) and Gregg (1976) monitored the movement of labelled-fertiliser S down the soil profile, with time. Although this may be a very accurate method for investigating leaching, the high cost and dangerous nature of labelled S isotopes limit its widespread use.

Gillman (1973) and During and Cooper (1974) indirectly measured fertiliser S leaching losses from herbage S uptake and soil S levels. This S balance approach is limited in accuracy to the extent that S additions and losses (other than drainage water losses) from the soil are precisely measured.

Kilmer *et al.* (1974) measured S losses in both surface and subsurface drainage water by analysing the drainage water. This approach seems suitable for widespread use when

(i) soils are mole and/or tile drained,

(ii) catchments have an impermeable shallow bedrock, and hence the catchment streamflow may be analysed to determine losses.

Sulphur losses in these field studies varied. May *et al.* (1968), Till and May (1971) and During and Cooper (1974) found that virtually no fertiliser S was leached to subsoil depths, while Gillman (1973) reported massive fertiliser S losses from the upper soil horizons. Gregg (1976) found that an appreciable fraction of the fertiliser S applied was leached to subsoil depths. Sulphur drainage losses from unfertilised catchments in Kilmer *et al.*'s (1974) study were insignificant in relation to annual pasture S requirements.

A detailed examination indicates that the variation in measured S losses between these studies may be explained by differences in soil properties, climatic conditions or incorrect interpretation of the experimental results. Although little S leaching occurred in May *et al.*'s (1968) and Till and May's (1971) studies, rainfall was very low (e.g. 80 mm in 87 days (May *et al.*, 1968)). The quantity of water percolating to subsoil depths was, therefore, probably minimal, severely limiting the extent of possible leaching.

Gillman (1973) concluded that fertiliser S not recovered in the upper 100 cm of soil or by the herbage after three years (i.e. 90% of the 105 kg S ha^{-1} applied in superphosphate, and 73% of the 273 kg ha^{-1} of elemental S applied) was leached beyond the 100 cm soil depth. Lateral surface and/or subsurface transport of fertiliser S (as dissolved SO_4-S and/or discrete fertiliser S particles) in water draining out of the 4 m × 4 m experimental plots may, however, account for the low fertiliser S recovery figures. This soil (having an impermeable clay horizon at the 250 cm depth) was saturated on several occasions (Gillman, 1973) which will tend to favour lateral movement downslope. Lateral movement of S has been observed in a similar soil in the field (Barrow and Spencer, 1959).

In New Zealand, During and Cooper (1974) reported that, in spite of 3,000 mm of excess rainfall (i.e. rain in excess of estimated evapotranspiration) in five years, applied S (< 314 kg S ha^{-1} in gypsum) did not penetrate beyond the 45 cm soil depth. This study was conducted on a highly sulphate retentive soil and apparently the applied S was predominantly retained in adsorbed form in the topsoil.

In contrast, fertiliser S moved to a depth of 60 cm or beyond in one year in several New Zealand soils characterised by their low sulphate adsorption capacities (Gregg, 1976). The amount of rainfall received and soil texture influenced the extent of S movement in these soils. Labelled S was evenly distributed within the upper 60 cm of a sandy loam after 1,112 mm of rainfall while, in another sandy loam receiving 466 mm of rain during the same interval, S did not penetrate beyond the upper 30 cm.

Under a similar rainfall regime, sulphur moved beyond the 60 cm depth in a sandy loam but remained largely in the upper 30 cm of a heavy silt loam.

Gregg (1976) concluded that the effect of SO_4-S leaching must be interpreted in terms of the pasture species composition and their S-uptake zone. In several of the soils studied, subsoil SO_4-S (i.e. SO_4-S below the 30 cm depth) was plant available (Gregg *et al.*, 1977).

A variety of factors will influence the extent of surface runoff (Ward, 1967) and hence S runoff losses including the

a) soil infiltration capacity,
b) soil permeability,
c) soil moisture content,
d) rainfall pattern (i.e. the amount, storm intensity and duration,
e) vegetation type.

For these reasons sulphur runoff losses from both unfertilised and fertilised pastures may vary considerably.

Sulphur surface runoff losses from pastures have only been investigated in conjunction with S subsurface drainage water losses. Kilmer *et al.* (1974) measured total dissolved SO_4-S drainage water losses from 2 steeply sloping, unfertilised catchments receiving, on average, 1,070 mm of rain annually. During a four year period an average of only 2.23 kg S ha^{-1} yr^{-1} was lost in surface and subsurface drainage waters discharged into the catchment streams.

Hamvray and Laften (1971), in the only investigation where S surface runoff losses have been differentiated from subsurface drainage water losses, measured losses from four unfertilised, cropped soils. Losses varied, from 0.3 - 6.1 kg S ha^{-1} yr^{-1}, closely reflecting the amount of water discharged from these gently sloping (3-6% slope) plots. In this study surface runoff was ponded in low-lying depressions for up to eight hours prior to sampling. Water infiltrated into the soil during this interval. Losses from areas not drained in this manner would tend to be higher. However, losses from pastures on this soil are likely to be lower as the denser soil vegetation cover will tend to reduce surface runoff water yields.

Fertiliser S surface runoff losses have not been investigated. Calcium sulphate has a low but significant solubility in water (2 g l^{-1} at $20^{o}C$) and losses could occur by simple dissolution in water flowing over the soil surface. Discrete superphosphate and elemental S particles might also move downslope in surface runoff, particularly when high intensity storms occur soon after fertiliser S applications.

II.1.2.1.4 Conclusions

Sulphur losses in drainage waters have been investigated in laboratory, glasshouse, lysimeter and field studies.

Leaching losses in laboratory, glasshouse and lysimeter studies varied widely. Detailed examination of the techniques involved show that the extent of S movement in these investigations may bear little relationship to losses occurring in the field.

Research approaches used and measured S drainage water losses in field studies have varied. Analysis of tile drainage waters, the most direct approach for measuring leaching losses, has not been used. Surface runoff losses have only been investigated in one overseas study. It is difficult to extrapolate the findings of this study to other sites and agricultural systems (e.g. cropping vs pastural) because of the complexity of the system under consideration.

Further research, investigating the magnitude of drainage water losses, is required under New Zealand conditions.

II.1.2.2 Sulphur immobilisation losses

Plant available soil SO_4-S levels are influenced by mineralisation and immobilisation (i.e. the opposing process) rates. Sulphur is immobilised in the soil organic fraction by microbial incorporation of inorganic soil S and with the return of organically bound S in plant residues and animal excreta. In a steady-state system the rate of immobilisation balances mineralisation and organic soil S levels remain comparatively constant. However, the establishment of grass-clover associations begins a phase of soil organic matter accumulation which is enhanced by the application of fertiliser P and S (e.g. Walker, 1956; Jackman, 1964). Net S immobilisation occurs during this phase, and S immobilised is lost from the S cycle. A number of studies indicate that substantial quantities of S may be immobilised before a new higher steady-state organic matter content is attained.

Hingston (1959), in an Australian investigation, reported net immobilisation of 10-15 kg S ha^{-1} (0-15 cm) yr^{-1} in several fertilised soils under permanent pasture for 3-27 years.

Jackman (1964) found that organic S levels increased by 7.2 - 18.5 kg S ha^{-1} (0-15 cm) yr^{-1} in a range of New Zealand soils under grass-clover pastures for 30 years. Estimates of the half-life for new organic matter steady state contents to be attained in these soils ranged from 2-42 years. Jackman (1964) concluded, however, that these estimates were subject to large errors.

In another New Zealand study, During and Cooper (1974) concluded that 30% (i.e. 55 kg S ha^{-1}) of the fertiliser S applied to a yellow-brown loam over a period of five years, was apparently immobilised in the soil organic fraction.

Burke (1975) reported a two-fold increase in organic soil S levels over a 25 year period. The pasture had been both irrigated and fertilised throughout this period.

These studies indicate that S immobilisation may be an important cycling-S depletion process for an extended period of time after grass-clover pastures are established.

II.1.2.3 Sulphur volatilisation losses

Nicolson (1970) postulated that significant amounts of S may be lost in gaseous forms under aerobic soil conditions at local sites where reducing conditions exist. Recent research findings (Lovelock *et al.*, 1972; Swaby and Fedel, 1973; Sachder and Chhabro, 1974; and Banwart and Bremner, 1976) suggest, however, that losses are likely to be minimal under conditions encountered in pastures. Banwart and Bremner (1976), for instance, found that $\leq$ 0.004% of the S added (at a very high rate of 400 μg S gm^{-1} soil) was lost in volatile compounds over a period of 60 days under aerobic and anaerobic soil conditions. Soils sorb volatile S compounds and the levels of gaseous S detected in these incubation studies must, therefore, be regarded as indicating the minimal level of volatilisation (Banwart and Bremner, 1976). Nevertheless, on the basis of existing research findings, it can only be concluded that volatile S losses are negligible under pastures.

It is generally thought that volatile S losses may be more important under urine spots (e.g. Walker, 1957a). No research has been undertaken to verify or negate this assumption.

II.1.2.4 Sulphur losses associated with grazing animals

Sulphur is lost from the S cycle in animal products and in urine and dung deposited in unproductive sites outside the grazing area. Sulphur deposited in sheep camps may also be effectively lost from the S cycle.

The actual quantity of S lost from the cycle by these means has not been measured. However, losses have been estimated to vary from 3-7 kg S ha^{-1} annually, depending on the type of grazing animal and stocking rates (During, 1972).

In terms of the total quantity of S in the S cycling pool (i.e. 100-300 kg S ha^{-1} (Till and May, 1970a, b; Gregg, 1976)) these losses are likely to be insignificant on an annual basis. However, in the long-term they are likely to limit productivity unless natural S additions are large or fertiliser S is applied.

II.1.2.5 Conclusions

Recent research suggests that sulphur immobilisation losses under grass-clover swards, and losses associated with grazing animals may, in the long-term, considerably deplete the S cycling pool unless balanced by S additions to the cycle. Sulphur volatilisation losses are likely to be negligible. However, the importance of S losses in drainage waters is debatable. Although a few field studies have been conducted overseas, the results of these investigations have been inconclusive. Whilst it is frequently assumed that S leaching is major process responsible for inducing S deficiencies in New Zealand pastures, only Gregg (1976) has monitored S movement within New Zealand soils. Surface runoff S losses have not been investigated in New Zealand. Further investigations into S losses in both surface and subsurface drainage waters are essential to clarify the situation and hence, if possible, improve the efficiency of S use in grazed pastures.

II.1.3 SULPHUR ADDITIONS TO THE S CYCLE

Sulphur may be added to the cycling pool in precipitation, with soil and plant foliar sorption of gaseous S compounds (atmospheric S additions), in ground and irrigation waters, with the weathering of S-bearing minerals and in fertilisers.

II.1.3.1 Atmospheric S additions

Precipitation, collecting S containing gases and particles, may be an important S source replenishing the plant available soil S pool in coastal and thermally active regions, and near swamps and large industrial centres (Whitehead, 1964).

In New Zealand, published rainfall S additions range from less than 1 kg S ha^{-1} to 15 kg S ha^{-1} annually. Muller (1975) reported that, on average, 13.2 kg S ha^{-1} yr^{-1} was added in rainfall in a suburb of Auckland over a 20 year period. Industrial fumes, the emission of H_2S from nearby mudflats and SO_4-S carried in sea-spray contributed to their figure. Sulphur inputs, including dust, of 10 kg S ha^{-1} yr^{-1} have been recorded near Wellington (Miller, 1968). However, S additions in precipitation decrease rapidly on moving inland as illustrated, for a transect of the South Island, in Table III.

Table III Mean values for 3-4 years of SO_4-S in precipitation (excluding dust) for a transect of the South Island (Walker and Gregg (1976) based on Horn's unpublished data).

Site	km from East Coast	km from West Coast	SO_4-S kg ha^{-1} yr^{-1}
Lincoln	22		4.0
Darfield	42		1.7
Torlesse	67		1.9
Cass	100		1.1
Bealey	109		1.0
Arthurs Pass	122	51	3.4
Taipo		29	3.7
Kumara		3	3.6

Sulphur inputs as low as 0.6 kg S ha^{-1} yr^{-1} have been measured at Tara Hills, a remote inland site in central Otago, characterised by very low average annual rainfall (Rukunia Soil Research Station Annual Reports 1959, 1960).

Little information is available on rainfall S inputs at North Island coastal and inland sites. At Marton only 18 km from the coast, annual S additions in 1959-1962 were 2.02, 2.35, 1.95 and 3.80 kg ha^{-1}. Atmospheric and rainfall S levels varied from month to month in an erratic manner (Rukuhia Soil Research Station Annual Reports 1959, 1960, 1961, 1962).

Direct soil absorption of gaseous S compounds may be an important soil S source if atmospheric S levels are high (e.g. Alway *et al.*, 1937). In New Zealand atmospheric S levels have only been measured at a few inland and coastal sites in non-industrialised areas (Rukuhia Soil Research Annual Report 1958). Levels were low.

Atmospheric S may also enter the S cycle by direct foliar absorption of SO_2 (Olsen, 1957; Jensen, 1963). Plants absorb more SO_2 when plant available soil S levels are inadequate (e.g. Cowling *et al.*, 1973). The amount of S entering the S cycle in this manner will be related to atmospheric levels and hence, generally low in New Zealand (Walker and Gregg, 1975).

II.1.3.2 Sulphur additions in irrigation and ground waters

Available SO_4-S enters the cycling S pool in several areas of New Zealand where fluctuating, shallow, ground-waters are influenced by sea water, or weathering of minerals at subsoils depths in weakly weathered soils (Blakemore *et al.*, 1969; Walker and Gregg, 1975). In several soils in Central Otago (Blakemore *et al.*, 1969) ground-water sulphate was available to lucerne but was present at too great a depth for clover S uptake. At a site near Lincoln ground-water deposited SO_4-S within reach of grasses and clovers (Walker and Gregg, 1975). In most soils, however, ground-water does not constitute a source of plant available SO_4-S.

Thorne and Peterson (1954) reported that in America an average of 80 kg S ha^{-1} m is added to soils in irrigation waters. New Zealand pastures are generally not irrigated. In an exception, the Waitaki scheme, about 10 kg S ha^{-1} is applied annually to pastures, in irrigation waters (Sleath, pers. comm.).

II.1.3.3 Sulphur additions from weathering of minerals

Walker and Adams (1958) concluded that the stage is reached fairly early in soil development when weathering of mineral S, in sulphides and sulphates, is an insignificant source of cyclic S. This has been confirmed under New Zealand conditions (Walker and Gregg, 1975); with conversion of sulphides to sulphate, and leaching of sulphate occurring deep within the soil profile.

II.1.3.4 Fertiliser sulphur additions

In most areas of New Zealand, fertiliser S applications are necessary to maintain high pasture production levels (Walker and Gregg, 1975). Generally 25 kg S ha^{-1} is applied annually in a single application, although it is recognised that yellow-brown pumice soils require more frequent S applications at heavier rates (Toxopeus, 1965; Hogg and Toxopeus, 1966). There is evidence that other soils require < 25 kg S ha^{-1} annually to maintain productivity (e.g. During, 1972).

However, actual fertiliser S requirements have not been determined.

Fertiliser S is usually applied as calcium sulphate (anhydrite) in superphosphate. Ammonium sulphate and sulphurized superphosphate (containing both calcium sulphate and elemental S) are applied less frequently in New Zealand.

The rate of release of fertiliser sulphur to the plant available soil pool depends on the type of fertiliser (i.e. chemical S form, associated ions and particle size influencing solubility), soil physico-chemical properties and the rate of water movement over the fertiliser particle (Barrow, 1975; MacLachlan, 1975). Of these, S fertiliser form and particle size can be controlled. Ammonium sulphate is very soluble, while the anhydrite calcium sulphate in superphosphate is sparingly soluble (2 g/litre at 20^{o}C (Barton and Wilde, 1971)). Elemental S is released very slowly as it must first be oxidised to sulphate-sulphur.

The rate of S release and entry into the plant available soil pool decreases with increasing superphosphate or elemental S particle size (Williams, 1969, 1970, 1971).

II.1.3.5 Conclusions

Frequently in New Zealand, S additions to the cycling S pool from natural sources are low. Fertiliser S applications are therefore necessary in many areas to offset losses occurring from the cycle and/or to overcome the productivity limiting effect of slow cycling S turnover rates.

II.1.4 GENERAL CONCLUSIONS

Sulphur deficiencies occur in many areas of New Zealand unless fertiliser S is applied fairly regularly. The S cycle turnover rate may limit productivity. Large drainage water losses in association with low atmospheric S additions may also account for these S deficiencies. Further research is required to determine the relative importance of these factors in inducing S deficiencies in these areas.

II.2 POTASSIUM REVIEW

II.2.1 THE POTASSIUM CYCLE IN GRAZED PASTURES

Pasture K deficiencies frequently occur in many areas of New Zealand. The importance of various processes in inducing these K deficiencies is discussed. Included is a review on the various K pools within the soil-plant-animal cycle, and the processes whereby K is lost from or added to the cycling pool.

II.2.1.1 Soil potassium

Soil potassium is traditionally divided into four categories — water soluble, exchangeable, 'fixed' or specifically adsorbed, and primary mineral K. In practice, however, no distinct boundaries exist between the various forms (e.g. Reitemeir, 1951; Arnold, 1960).

Water soluble K is immediately plant available. Exchangeable K is readily plant available while the fixed and primary mineral K (together comprising the 'non-exchangeable soil K' fraction) is slowly or essentially non-available (e.g. Arnold, 1960; Metson, 1968).

The various forms of soil K tend to be maintained in an exchange equilibrium. A decrease in the level of water soluble K, for instance, will tend to be compensated for by movement from and between the exchangeable and fixed K fractions. Exchangeable K is released rapidly in comparison with the release of fixed K (e.g. Arnold, 1960).

The non-exchangeable K level may increase or decrease with time because of this exchange equilibrium. However, in general, it constitutes a source of plant available K and is regarded as such in this review, rather than a pool within the K cycle or a 'sink' for K from the cycle.

II.2.1.1.1 The readily plant available soil K pool

Water soluble and exchangeable soil K together comprise the readily plant available K pool.

Water soluble K generally comprises < 0.01% of the total soil K, or about 5 kg K ha^{-1} in the topsoil (Thompson and Troeh, 1973). The exchangeable K fraction is comprised of hydrated K ions adsorbed at non-specific sites on clays, silts and organic particles. Exchangeable K is readily replaced by other cations such as Ca, Mn and Mg and is, therefore, readily plant available (Thompson and Troeh, 1972). Most topsoils contain 100-450 kg exchangeable K ha^{-1}, while subsoil K levels are frequently lower (Thompson and Troeh, 1973).

The size of the readily plant available soil K pool is influenced by the extent of the plant K uptake zone. Ozanne *et al.* (1965) have determined, using isotopes, the maximum depth from which various pasture species may obtain K in a sandy loam. The maximum uptake depth reflected the plant species maximum rooting depth. However, greater than 88% of the radioactive K taken up by both ryegrass and subterranean clover varieties was obtained from within the upper 10 cm of soil. Virtually all the labelled K taken up by plants was obtained from the upper 35 cm. No other investigations on the K uptake zone of various grass and clover species have been undertaken.

High producing pastures may require about 300 kg K ha^{-1} annually (II.2.1.2). Most soils contain about 100-450 kg K ha^{-1} readily plant available K in the topsoil (Thompson and Troeh, 1973). Therefore this pool must be continually replenished to meet long term K requirements.

The readily plant available K pool may be replenished by the return of K in plant residues and animal excreta, by the release of non-exchangeable K, with K received in rainfall, and with fertiliser K additions.

Potassium may be lost from the plant available pool, and the K cycle, in drainage waters. Potassium is also lost from this pool with K fixation. If the plant available pool is subsequently depleted fixed K is released. Potassium fixation is, therefore, not a process whereby K is lost permanently from the cycling pool.

II.2.1.2 <u>The plant potassium pool</u>

The plant K pool comprises that K present in the pasture tops and roots at any one time. This pool will vary greatly in size as the dry matter level varies. A rotationally grazed pasture with a dry matter herbage level of about 3,000 kg ha^{-1} prior to grazing, if adequately supplied with K (2.3% (During, 1972)), will contain 60-90 kg K ha^{-1}. Immediately after grazing only 1,000 kg D.M. ha^{-1} may be present. At this stage K in the tops will only amount to about 20-30 kg ha^{-1}. The root dry matter level will tend to be more stable. Assuming a root dry matter level of about 1,000 kg ha^{-1} and a K content of 2-3% (Campkin, pers. comm.) from 20-30 kg K ha^{-1} will be present at any one time in the roots.

The annual pasture K turnover figure will be considerably larger. On an annual basis 200-300 kg K ha^{-1} will be incorporated in the plant tops.

Hopper and Clement (1966) reported that a fertilised ryegrass sward producing 10,000 kg D.M. ha^{-1} annually in the pasture tops, produced root tissue containing about 70 kg K ha^{-1}. With a top:root production ratio of 3:1 (Gregg, 1976) 60-100 kg K ha^{-1} will be incorporated annually into the roots of ryegrass-clover swards.

A variable fraction of the plant K (depending on the pasture utilisation level) is returned to the soil in plant residues. Potassium in the plant residues is readily available for recycling as K is in ionic combination in plants and readily leached from plant residues (Thompson and Troeh, 1973).

II.2.1.3 The animal K pool

The animal potassium pool comprises that K present in the grazing animal at any one time. In relation to the quantity of K in the cycle, K in the animal pool will be negligible. For example, at a stocking rate of 2.5 cattle ha^{-1} with a body liveweight of 350-400 kg each and a K content of 0.19% (Maynard, 1937), only 1.7 - 2.0 kg K ha^{-1} will be present in the animal pool.

The annual animal K pool turnover figure will be considerably larger. Assuming a pasture utilisation figure of 80% at a production level of 10,000 kg D.M. ha^{-1} yr^{-1}, from 160-240 kg K ha^{-1} will be ingested annually.

Cattle retain only about 10% of the K ingested (Davies *et al.*, 1962; Hutton *et al.*, 1967). Sheep retain 28% of the K ingested when fed at a maintenance rate (Grace and Healy, 1974). Therefore most of the K ingested is returned to the pasture in excreta. Research indicates that off-grazing site deposition of excreta and an uneven areal distribution of excreta within the grazing area results in inefficient recycling of this K (Peterson *et al.*, 1956a, b; Davies *et al.*, 1962; Hilder, 1964, 1966; Hopper and Clement, 1966; During and Weeda, 1973).

II.2.2 POTASSIUM LOSSES FROM THE K CYCLE

Potassium is lost from the soil-plant-animal cycle in drainage waters, in animal products, and in animal excreta deposited in unproductive sites outside or within the grazing area.

II.2.2.1 Potassium drainage water losses

Potassium is transported in both surface and subsurface drainage waters. Losses from the readily plant available pool, and hence the K cycle, occur with movement in surface runoff to streams and with leaching beyond the zone of plant K uptake.

Potassium drainage water losses have been investigated in laboratory, glasshouse, lysimeter and field studies. Generally, in the field investigations, losses from cropped and fallowed soils have been determined. However, in this review, only K losses from permanent pastures and the factors influencing the magnitude of these losses are reviewed.

II.2.2.1.1 Potassium leaching losses in laboratory and glasshouse studies

The tendency for K to move in percolating water through a variety of New Zealand topsoils has been investigated in both soil leaching column and glasshouse pot experiments. The experimental techniques used and relevant results of the more comprehensive studies are summarised in Table IV. In these studies, fertiliser K losses varied widely (< 1% - 72%), depending on soil properties and fertiliser treatments. Losses in these investigations are likely to be higher than losses occurring in the field for the reasons discussed earlier (II.1.2.1.1), with respect to S leaching (Munson and Nelson, 1963; Peverill *et al.*, 1975; Ward, 1967).

Laboratory and glasshouse studies (Table IV) have shown that soil properties and fertiliser treatments influence the extent of K leaching. Leaching losses tend to be greater when soils exhibit little ability to fix K. Davies *et al.* (1962), in the only comprehensive study undertaken on K leaching in New Zealand soils exhibiting varying abilities to fix K, reported that a yellow-grey earth and rendzina (containing primary and/or secondary micaeous clay minerals in appreciable quantities (Fieldes, 1968)) lost little K in percolating waters. In contrast, a yellow-brown loam, yellow-brown sand, yellow-brown pumice soil, organic soil and several podzols (lacking K retentive minerals) lost a large fraction of the applied K. Another yellow-brown loam, the Horotiu sandy loam, lost little K in the leachate (Davies *et al.*, 1962). Subsequently, Hogg (1968) reported that this particular yellow-brown loam does fix K.

The chemical type of K fertiliser applied may also influence the extent of K leaching. Davies *et al.* (1962) and Hogg and Cooper (1964) reported that K leaching losses were greater when the associated anion

Table IV Potassium leaching losses in laboratory and glasshouse studies

Soil properties	Experimental techniques	Soil pre-treatment procedures	Water applied or quantity leached	Potassium fertiliser treatment	Potassium leached	Reference
(1) Yellow-brown loam	Undistributed soil cores from 1-150 mm; pasture grown	-	Water applied until 380 mm leachate collected	130 kg K/ha in KCl	1% K applied	Saunders and Metson (1959)
				260 "	4% K applied	
				540 "	14% K applied	
				540 kg K/ha in urine	8% K applied	
				1080 kg K/ha in urine	15% K applied	
(1) Yellow-brown loam	Glasshouse pot trial; 0-150 mm soil depth; pasture growth	N.R.	2,540 mm water applied	'K applied at typical rates under urine spot' in KCl	26% K applied	Davies and Hogg (1960)
				Urine	30% K applied	
(1) Rendzina	Hogg's (1960) leaching technique, 0-70 mm soil	Soil sieved, bulked and air-dried	N.R.	130 kg K/ha in KCl	4% K applied	Davies *et al.* (1962)
(2) Podzols					29% & 68% K applied	
(1) Yellow-grey earth					6% K applied	
(1) Brown-granular clay					2% K applied	
(2) Yellow-brown loams -New Plymouth brown loam					44% K applied	
-Horotiu sandy loam					6% K applied	
(1) Organic soil					31% K applied	
(1) Yellow-brown pumice soil					69% K applied	
(1) Yellow-brown sand					53% K applied	
(1) Podzol	"	"	Water applied until 2,000 mm leachate collected	112 kg K/ha in KCl	27% ditto	Hogg and Cooper (1964)
				" $KHCO_3$	5% ditto	
				" KCl + super	61% ditto	
				" $KHCO_3$ + super	53% ditto	
(1) Yellow-brown sand	"	"	N.R.	250 kg K/ha in KCl	72% ditto	Hogg (1968)
(1) Yellow-brown loam					8% ditto	
(1) Yellow-brown earth	Glasshouse pot trial; 0-200 mm soil depth; pasture grown	Soil sieved and bulked when moist	Water applied until 250 mm leachate collected	105 kg K/ha in KCl	< 1% K applied	Muller and McSweeney (1974)
(1) Yellow-brown pumice soil			Water applied until 360 mm leachate collected		< 5% K applied	
(1) Yellow-grey earth -Tokomaru silt loam	Glasshouse pot trial of 2 years duration; 0-180 mm soil; pasture grown	Soil air-dried, sieved and bulked	Water applied until 420 mm leachate collected	117 kg K/ha in KCl	12% K applied	Muller and McSweeney (1977)
				425 kg K/ha in KCl	6% K applied	

( ) refers to the number of soils studied.

N.R. = not reported.

was susceptible to leaching (e.g. chloride or sulphate cf. phosphates, carbonate or bicarbonate). Hogg and Cooper (1964) results are given in Table IV. Davies *et al.* (1962) did not report on the actual K losses occurring with various K fertilisers.

Applying superphosphate in conjunction with either potash or potassium bicarbonate promotes K leaching (Davies *et al.*, 1962; Hogg and Cooper, 1964). Davies *et al.* (1962) attributed this to the presence of sulphate in superphosphate.

Fertiliser K loss as a fraction of that applied may be influenced by the application rate. Saunders and Metson (1959) found that K losses were proportionally higher when K was applied to a yellow-brown loam at heavy rates. However, Muller and McSweeney (1977) reported that K loss as a fraction of the K applied, to a yellow-brown earth, decreased at heavier rates (Table IV). A difference in soil properties may account for this difference in behaviour at varying K application rates. Fixation will have been promoted at heavier K application rates in the K retentive yellow-grey earth thereby reducing the quantity of K susceptible to leaching. In contrast, losses will tend to be greater at heavier rates on the yellow-brown loam as it is likely to fix little potassium.

II.2.2.1.2 Potassium leaching losses in lysimeter studies

Hogg (1968, 1975) investigated the extent of K leaching in several New Zealand soils in lysimeter studies. An insignificant fraction of the K applied (> 1,100 kg ha^{-1}) in excreta and/or potash was leached beyond the 105 cm depth in either a yellow-brown loam (i.e. 2% in two years (Hogg, 1968)) or yellow-brown pumice soil (i.e. 4% in three years (Hogg, 1975)) under permanent pasture. However, the limited informa- available (Ozanne *et al.*, 1965) suggests that K losses from the upper 10 cm may be more relevant in terms of plant available soil K losses. In Hogg's (1968, 1975) investigations a major fraction of the applied K was leached into the 15-45 cm depth in the yellow-brown loam while movement occurred in the non-retentive pumice soil to a depth of 90 cm.

II.2.2.1.3 Potassium drainage water losses in field studies

Potassium losses in both surface and subsurface drainage waters have been investigated in the field.

No studies undertaken in New Zealand have directly measured drainage water losses. However, Davies *et al.* (1962), using a fertiliser K recovery approach, determined indirectly the likely extent of K leaching in a yellow-brown loam. Yellow-brown loams exhibit little or no ability to fix K and Davies *et al.*'s findings suggest that potassium leaching occurred to a substantial extent. After 39 weeks only 76% of the applied K was accounted for by pasture uptake or in the upper 23 cm of soil. This downward movement of K was of little significance as, after two years, 95% of the K was recovered. The high recovery figure may be due to the sward composition. This sward was dominated by the deep rooting paspalum grass. Under a ryegrass-white clover sward the rooting depth will be shallow and leaching of greater significance.

In overseas field studies, potassium losses in both surface and subsurface drainage waters have been measured directly (Bolton *et al.*, 1970; Kilmer *et al.*, 1974; Burke *et al.*, 1974).

Bolton *et al.* (1970) monitored K leaching losses in tile (70 cm soil depth) discharge waters from ungrazed, unfertilised and fertilised (34 kg K ha^{-1} yr^{-1}) plots in permanent bluegrass pasture. During this seven year study, an average of only 0.12 kg K ha^{-1} and 0.56 kg K ha^{-1} was leached annually from the unfertilised and fertilised plots respectively.

Kilmer *et al.* (1974) measured dissolved K losses from two steeply sloping (i.e. 35-40% sloping) catchments supporting permanent grazed bluegrass swards, under an average annual rainfall of 1,050 mm. Potassium drainage water (surface and subsurface) losses were determined by analysis of the catchment streamflow. In the first year of this study, prior to K fertilisation, 3.71 kg K ha^{-1} were lost from one catchment and 7.30 kg K ha^{-1} lost from the other catchment. The latter catchment was only recently sown in bluegrass and a higher soil erodability factor may account for the higher K loss. There was little evidence of an increase in K losses in the second year when 24 kg K ha^{-1} was applied. An average of only 4.0 kg K ha^{-1} yr^{-1} was lost from both catchments in the three years following K fertilisation.

Burke *et al.* (1974) measured K losses from a poorly drained, heavy textured gley soil in permanent pasture, at a gently sloping site. Surface runoff and subsurface K losses were determined separately. Potassium leached from a fertilised plot was determined by analysis of mole discharge waters. Potassium lost during the six year study interval was insignificant (2.5% or 32.4 kg K ha^{-1}) in relation to the quantity of fertiliser K applied.

Potassium concentrations in surface runoff from an unfertilised, undrained plot closely reflected K concentrations in the rainfall. The actual quantity of K lost varied from 1.12 - 4.20 kg ha^{-1} yr^{-1} depending on the total amount of runoff (ranged from 250-700 mm yr^{-1}). Fertiliser K surface runoff losses varied depending on the soil moisture content and the pattern of rainfall following fertilisation. Wet soil conditions and intense storm events soon after K applications induced large surface runoff losses. On one occasion 12% of the potash K applied (94 kg K ha^{-1}) to both undrained and drained plots, was lost in five days in only 8.4 mm of surface runoff. On another occasion a surface runoff event did not occur until 15 days after the K was applied and then only 5% of the 125 kg K ha^{-1} applied was lost in 21.8 mm of water. Mole drainage generally reduced fertiliser K losses as a greater quantity of water infiltrated into the soil (Burke *et al.*, 1974). Overall, 7.4% (i.e. 96 kg K ha^{-1}) and 2.4% (i.e. 30 kg K ha^{-1}) of the K applied in six years (i.e. 1,250 kg K ha^{-1}) was lost in surface runoff from the undrained and drained plot respectively.

II.2.2.1.4 Conclusions

Potassium leaching losses in laboratory, glasshouse and lysimeter studies have shown that K leaching occurs to a lesser extent in K retentive than non-retentive soils. Findings of the few overseas field investigations undertaken have indicated that, in the situations considered, K surface and/or subsurface drainage water losses were not important cycling-K loss mechanisms. Field research into K leaching in New Zealand soils is meagre. Potassium surface runoff losses have not been measured under New Zealand conditions although large surface runoff events are likely to occur from many New Zealand soils in winter months. There is a need for the direct measurement of both surface and sub-surface K drainage water losses under New Zealand conditions to confirm the findings of overseas studies.

II.2.2.2 Potassium losses associated with grazing animals

Potassium is lost from the soil-plant-animal cycle in animal products and excreta deposited in unproductive areas outside and within the grazing area.

In a recent study (New Zealand Dairy Exporter, July 1978) it was found that 64 kg K ha^{-1} was lost annually from high producing New

Zealand dairy farms; 10 kg K ha^{-1} in milk and culled animals, and 54 kg K ha^{-1} in excreta deposited in dairy sheds, races and unproductive areas within the grazing area.

Potassium losses attributable to sheep is likely to be lower. During (1972) suggested that 20% of the K ingested by sheep is lost in wool, culled animals and excreta deposited in unproductive sites. In a high producing New Zealand pasture, with an animal intake figure of 220 kg K ha^{-1} yr^{-1} K losses associated with sheep might, therefore, amount to about 45 kg K ha^{-1}.

II.2.2.3 Conclusions

The limited published information suggests that K losses associated with the grazing animal may amount to an important fraction of the cycling K. Further research is necessary in New Zealand to determine the significance of K drainage water losses in inducing pasture deficiencies.

II.2.3 POTASSIUM ADDITIONS TO THE K CYCLE

Potassium may be added to the plant available soil K pool, and hence the K cycle, with the release of non-exchangeable soil K, in rainfall, and by the application of K fertilisers.

II.2.3.1 Non-exchangeable K additions

Non-exchangeable soil K may be an important source of plant available soil K in soils containing the primary micaeous minerals (biotite and muscovite), basic glass and/or the secondary clay minerals, illite and vermiculite (e.g. Fieldes and Swindale, 1954; Metson, 1968). The following review on non-exchangeable K is based on Fieldes and Swindale's (1954) findings and Reitemeir's (1951), Arnold's (1960), Fieldes' (1968), Metson's (1968) and Schroeder's (1974) review papers.

Potassium is released into the plant available soil K pool with weathering of primary minerals. The readily weathered micaeous mineral, biotite, releases K more rapidly than the comparatively resistant micaeous mineral, muscovite. Basic glass is readily weathered and the mineral K released quickly.

The secondary micaeous clay minerals contain 'fixed' or specifically adsorbed K. The weakly weathered illitic clay minerals contain mainly, 'native' fixed K (i.e. K fixed during the formation of secondary clay minerals during weathering of the primary micaeous minerals). Vermiculite, in contrast, contains little 'native' fixed K but the expanding type, clay vermiculite, exhibits a marked capacity to fix K when water soluble and exchangeable K levels increase (i.e. contains 'added' fixed K). Depletion of the plant available pool results in the release of fixed K. The more severe the available K depletion, the higher the rate of K release. 'Native' fixed K is released more slowly than 'added' fixed K.

The important role that non-exchangeable soil K may play in achieving or maintaining high pasture production levels is illustrated by the results of a New Zealand study undertaken by Metson and Hurst (1953). Pasture production and available soil K levels remained virtually constant over a four year trial period although about 1,000 kg K/ha was removed from the K-cycle in animal excreta not returned to the pasture. Metson and Hurst (1953) concluded that the release of non-exchangeable K in this recent soil, occurred at a rate sufficient to continuously replenish the plant available K pool.

The zonal and intrazonal New Zealand soils can be subdivided into three groups on the basis of their ability to offset K losses from the cycling pool, by the release of non-exchangeable K (Metson, 1968; During, 1972), including:

(a) Group 1. Non-exchangeable K is released at a rate sufficient to meet plant requirements at high levels of pasture production. This group includes the brown-grey earths; southern yellow-grey earths; the weakly weathered southern and central yellow-brown earths, and the young red and brown loams.

(b) Group 2. Non-exchangeable potassium is released too slowly to maintain high levels of pasture production. This group includes the more strongly weathered yellow-brown earths.

(c) Group 3. Non-exchangeable K is almost or entirely absent. Included in this group are the yellow-brown pumice soils; yellow-brown loams; brown granular loams; brown granular clays; organic soils, and the older red and brown loams. Pastures on these soils tend to be consistently K-responsive.

In recent and related soils ('azonal' soils) the nature of the alluvial parent material and the degree of weathering (affecting the soil mineral composition), influences the importance of non-exchangeable K as a source of plant available K.

II.2.3.2 Potassium rainfall additions

Potassium is added to the plant available soil pool in precipitation. Measured additions from this source in New Zealand (< 6.83 kg K ha^{-1} yr^{-1} — Rukuhia Soil Research Station Annual Report 1962) are, however, negligible in relation to pasture K requirements.

II.2.3.3 Fertiliser potassium additions

In recent years the incidence of pasture K deficiencies in New Zealand has become fairly widespread, reflecting an overall increase in production levels. Regular K applications are necessary to ensure high pasture production levels over large areas of the North Island and in some regions of the South Island (During, 1972).

Potassium is generally applied in the highly soluble fertiliser potash, at a rate of about 150 kg kg^{-1} annually. However, actual fertiliser K requirements may be considerably less. During (1972) concluded that the limited field evidence published, indicated that K-responsive New Zealand pastures require only 30-100 kg K ha^{-1} annually, depending on animal stocking rates and the rate at which non-exchangeable K is released. Recent field study results (the New Zealand Dairy Exporter, July 1978) agree with During's findings.

II.2.3.4 Conclusions

Non-exchangeable K may be an important source of plant available K in New Zealand soils containing appreciable quantities of primary and secondary micaeous minerals, or basic glass. When non-exchangeable K is not released at a rate sufficient to offset losses K fertilisation is essential to attain, and subsequently maintain, high pasture and animal production levels.

II.2.4 GENERAL CONCLUSIONS

Potassium deficiencies frequently occur in New Zealand pastures. The K cycle turnover rate is unlikely to limit productivity. Potassium losses from the cycling pool must, therefore, exceed K additions. Undoubtedly, K losses associated with the grazing animal may play an important role in inducing pasture K deficiencies. Further investigations are necessary, however, to determine the significance of K drainage water losses in inducing K deficiencies under New Zealand conditions.

CHAPTER III METHODS AND MATERIALS

III.1 SOIL PROPERTIES

Studies investigating the magnitude of S and K drainage water losses from the Tokomaru silt loam were conducted. The Tokomaru silt loam is a weakly leached, moderately-strongly gleyed soil type belonging to the yellow-grey earth soil group. Yellow-grey earth soils occur extensively throughout the Manawatu and Wairarapa areas and in mid Hawkes Bay, Otago, Marlborough and Canterbury.

The Tokomaru silt loam occurs on the flat to rolling (< 12% slopes) high terraces of the Manawatu and Rangitikei rivers (Cowie, 1972). Together the Tokomaru silt loam flat and rolling phases cover a total area of 8,910 ha. Mean annual rainfall over this region ranges from 860-1,140 mm (Cowie, 1972).

The average annual rainfall recorded at the experimental site is 1,020 mm (Scotter, unpubl.).

Profile description of the Tokomaru silt loam

The following profile description is based on the reports of Cowie (1972) and Pollok (1974).

A slightly mottled silt to heavy silt loam, the A horizon, extends to a depth of approximately 35 cm. Internal drainage is slightly imperfect and Fe and Mn concretions occur in the lower part of this horizon.

A mottled clay loam to clay, the B horizon, extends to a depth of about 75 cm. Iron and Manganese concretions are present and internal drainage is impeded.

A frazipan, situated at a depth of about 75-145 cm overlies a sandy clay loam.

Pasture roots are abundant in the upper 20-25 cm and a few extend into the B horizon.

Clay mineralogy

The A and B horizons have a clay content of about 23% and 30% respectively. This clay fraction is comprised almost entirely of 2:1 micaeous clay minerals. Mica and illite are the principal clays although vermiculite and interstratified clays are also abundant. Clay size feldspar particles occur in limited quantities (Pollok, 1974).

Although non-exchangeable K levels are likely to be high because of the composition of the clay fraction, exchangeable K levels are low throughout the profile at about 0.2 me./100 gm (Pollok, 1974).

Kaolinite and halloysite (i.e. 1:1 clays) are present only in trace amounts and allophane is absent (Pollok, 1974). Therefore, as in other yellow-grey earth soils (Metson, 1969), the SO_4-S retention capacity is low (i.e. 5% (Muller and McSweeney, 1977)).

III.2 FIELD TECHNIQUES USED FOR INVESTIGATING SO_4-S AND K SURFACE RUNOFF LOSSES

III.2.1 FIELD METHODS (1976)

In 1976 water soluble SO_4-S and K surface runoff losses from both undrained and drained plots on the Tokomaru silt loam were measured over a 41 day period from May 28 to July 8.

Description of the surface runoff plots and flow monitoring installations

Site descriptions for the four plots (plots 1-4 inclusive) from which runoff losses were measured, are given in Table V. These runoff plots were bordered on two sides and upslope with wooden boards placed in the soil to a depth of 10 cm and extending 8 cm above the surface to prevent runoff from entering the trial area. On the downslope edge plastic guttering sunk into the soil to be level with the ground surface, collected runoff from each plot and discharged it into large polyethylene containers. Child's stage recorders monitored surface runoff from plots 1 (undrained) and 3 (drained). Water discharged into the storage containers from plots 2 (undrained) and 4 (drained) was measured at the conclusion of two runoff events, at the beginning of the study. Virtually the same quantity of water was discharged from these plots as from the respective drained or undrained plot where Child's stage recorders monitored flow rates. Subsequently, therefore, the amount of water discharged from plots 1 and 2; and plots 3 and 4, was assumed to be the same.

Fertiliser S and K applications

All plots had a recent history of regular S and K fertiliser applications. In late October 1975, 200 kg 15% potassic superphosphate was allied to all plots. In 1976, superphosphate (57 kg S ha^{-1}) and potash (50 kg K ha^{-1}) was applied to plots 1 and 4 on May 28 (Table V).

Pasture management

The runoff plots were fenced off to grazing animals and the grass-clover swards mown immediately prior to this investigation.

Runoff sampling procedure

At the conclusion of each runoff event, during the interval May 28 to July 8, a water sample was taken from each of the polyethylene containers. These samples, collected in polyethylene bottles, were millipore filtered (< 0.4 μm) within 12 hours of sampling and subsequently stored at $-1^{\circ}C$ until analysed for SO_4-S and K.

This runoff study was terminated on July 8 as cattle gained entry to the plots damaging the wooden boards and plastic guttering.

II.2.2 FIELD METHODS (1977)

In 1977, water soluble SO_4-S and K surface runoff losses from undrained pastures on the Tokomaru silt loam were measured.

Description of the runoff plots and flow monitoring installations

Four runoff plots (plots 5-8 inclusive) were laid down in a catchment adjacent to that from which 1976 runoff losses were measured. Site description for the four plots are given in Table V.

The construction of these plots was as outlined for plots 1-4. Child's stage recorders were installed to monitor flow rates at plots 5 and 8. It was assumed that a similar quantity of water was discharged from the plot immediately adjacent to each of these plots.

Fertiliser S and K applications

All plots had a recent history of regular S and K fertiliser application. In early November 1976, 380 kg of 15% potassic super-

Table V Site descriptions of the surface runoff plots used in 1976 (plots 1-4 inclusive) and 1977 (plots 5-8 inclusive) and fertiliser S and K treatments.

	1	2	3	4	5	6	7	8
Area m^2	41	41	41	41	55	55	55	55
Slope	6^{o} 30′							
Aspect	SW	SW	NE	NE	SW	SW	SW	SW
Drainage status	undrained	undrained	drained*	drained*	undrained	undrained	undrained	undrained
S kg ha^{-1}	57	-	-	57	55	55	-	-
K kg ha^{-1}	50	-	-	50	55	55	-	-

*mole (45 cm depth) and tile (75 cm depth) drained.

phosphate was applied to all plots. On June 10, 1977, 55 kg S ha^{-1} was applied to plots 5 and 6 in liquid superphosphate (Table V). Liquid superphosphate was obtained by dissolving solid superphosphate in water over a period of several days. This was applied in preference to solid superphosphate to permit another investigation to be undertaken at the same time.

On July 1, 1977, potash was applied to plots 5 and 6 at a rate of 55 kg K ha^{-1} (Table V).

Pasture management

All four plots were mown and fenced off to grazing animals two weeks before the study was due to commence. However, during this intervening period cattle obtained entry to plots 5 and 6 for a 24 hour period from June 5-6. Although, subsequently, the soil surface in plots 5 and 6 was puggy and excreta had been deposited on these plots the study was undertaken.

Runoff sampling procedure

Runoff samples were taken from each of the collecting tanks at the conclusion of each runoff event occurring after June 10 until surface runoff events ceased to occur in mid-September. These samples were millipore filtered within 12 hours of collection and stored at $-1^{o}C$ until analysed for S and K.

III.3 FIELD TECHNIQUES USED FOR INVESTIGATING SO_4-S AND K LEACHING LOSSES

Description of the field plots and flow monitoring installations

Eight field plots had been laid down and flow monitoring equipment installed for another study. These facilities were used in the present study.

These eight plots (plots 1-8 inclusive), each 1,250 m^2 in area, were situated on flat land ($0-1^{o}$ slope) adjacent to the 1976 surface runoff plots (Plate I). Four plots (plots 5-8 inclusive) had been irrigated over the spring-autumn period in each of the preceding five years.

The experimental area was originally mole and tile drained about 35 years previously, but remoled about five years ago. Each plot was

Plate I View of the subsurface drainage plots.

Plate II Apparatus used manually to sample and obtain 'representative' samples of, the percolate.

independently drained. Mole drains of 2 m spacings at a depth of 45 cm, discharged water into a single tile drain at a depth of 75 cm. The tile discharge flow rate for each plot was monitored continuously by flow meters designed by the M.A.F.

Fertiliser S and K applications

Before 1975 fertiliser S and K had been applied regularly to all plots. In 1975 and again in mid-1976, 380 kg of 15% potassic superphosphate was applied to plots 1, 4, 5 and 8. In late 1976 380 kg of 15% potassic superphosphate was applied to plots 2, 3, 6 and 7.

In 1977 dissolved SO_4-S and K concentrations in water discharged from each of the eight plots, were monitored for a six week period before fertiliser S and K was applied to four of these plots.

Fertiliser S and K was applied to selected paired plots in 1977. The four non-irrigated plots were paired on the basis that mean SO_4-S concentrations in the three flow events occurring during the interval May 18 to July 1 were similar and/or that mean concentrations in these flows varied in a similar manner. The four irrigated plots were paired on the same basis. Paired plots included 1 and 3, 2 and 4, 5 and 7, and 6 and 8. Subsequently, on July 1, superphosphate, at the rate of 43 kg S ha^{-1} and potash at a rate of 56 kg K ha^{-1} was applied to one of each of these paired plots, namely, plots 2, 3, 6 and 7.

Pasture management

All plots were rotationally grazed by sheep. The dates on which the various plots were grazed, and stocking rates, are given in the Appendix, Table 1.

Tile drainage water sampling procedure

Plastic tubing holed at regular intervals along its length was inserted vertically in the tile drains at the outfall points (Plate II). A fraction of the water flowing through the tile drains entered the tubing through these holes and was drained away into large polyethylene containers. The water collected in this manner comprised a constant proportion of the quantity discharged as the lower the water level in the drains the fewer the number of holes submerged. Water in the polyethylene containers was sampled 24 hourly, or at more frequent intervals depending on the intensity of the storm event. These water samples were millipore filtered within 12 hours of collection and stored at $-1^{o}C$ until analysed for SO_4-S and K.

To ensure that SO_4-S and K losses as determined from these 'representative' samples accurately reflected SO_4-S and K losses from tile drains, losses determined from representative samples were compared with losses determined from samples taken manually at frequent intervals during several flow events.

Losses from both plots 5 and 8 were compared. Initially, water discharge from plots 5 and 8 was manually sampled at 15 minutes over a period of 6½ hours during a flow event on May 25-26. These samples were millipore filtered within an hour of collection and stored overnight before determining SO_4-S and K levels.

Instantaneous flow rates when these samples were taken were obtained from the automatic flow meter data. Total soluble SO_4-S and K losses were then determined from average concentrations and average flow rates between samplings.

These values were compared with losses determined from a 'representative' sample collected at the conclusion of the 6½ hour sampling interval, and the flow data.

A close relationship was established (Table VI) between SO_4-S losses determined by both procedures. Potassium losses from plot 5 were also in close agreement. However, there was a very poor relationship between manual and representative determinations of K loss from plot 8. The K leaching loss was underestimated using the representative sample approach. The water discharged from plot 8 was discoloured because of a high fine sediment content. In contrast, water discharged from plot 5 was clear. These findings suggest that solution K may have been retained by clay particles in the collecting containers before the representative sample was taken and filtered. Potassium retention in the manually obtained samples apparently occurred to a considerably lesser extent because these samples were filtered within a hour of collection.

Water discharged from plot 8 was again intensively manually sampled on June 17. Samples were taken at regular 10 minute intervals over a five hour period and filtered within half-an-hour of collection. Sulphate-sulphur and potassium losses determined from analyses of these samples and flow data, and a 'representative' sample and flow data were compared. The results, outlined in Table VI, show a much

Table VI Soluble sulphate-sulphur and potassium tile drainage water losses on May 25-26 and June 17, determined from frequently, manually obtained samples of the discharge water and from a representative sample.

Date	Plot	Load (gm/plot)			
		SO_4-S		K	
		Discharge water sampled regularly (15 minute intervals)	Representative sample	Discharge water sampled regularly (15 minute intervals)	Representative sample
May 25-26	5	59.4	63.0	47.1	49.9
	8	32.7	33.5	32.6	24.5
		(10 minute intervals)		(10 minute intervals)	
June 17	8	19.3	19.0	7.6	7.5

closer relationship for K and confirm the earlier established strong relationship between SO_4-S losses measured by both procedures. On this occasion water discharged from plot 8 was discoloured at the beginning of the flow event but rapidly became clear. These results appear to confirm the suggestion that when the sediment content in the drainage water was high, K retention by the clay fraction substantially reduced measured dissolved K losses in the representative samples.

Water discharged from plots 7 and 8 had a high sediment content only after lengthy dry periods. Water discharged from the remaining plots was clear. Therefore, overall the representative sampling procedure for determining SO_4-S and K leaching losses was considered adequate.

III.4 SOIL SAMPLING

Soil samples were taken from each of the eight leaching plots at 2-3 weekly intervals during the period May 18 to October 13. Twelve samples taken from depths 0-10 cm, 10-20 cm, 20-40 cm and 40-60 cm in each plot were bulked, sieved (< 4 mm) and frozen at $-5^{o}C$ until analysed for SO_4-S and K levels.

III.5 RAINFALL MEASUREMENT AND SAMPLING FOR S AND K LEVELS

Rainfall was recorded by a Lambrecdt 30 day continuous recorder located adjacent to the subsurface drainage plots.

Rainfall S and K additions were determined by analysing rain collected in a glass container. This container was placed adjacent to the subsurface drainage plots, in the ground but extending about 45 cm above the surface in an area fenced off to grazing sheep. It was installed on May 5, 1977 and thereafter samples were collected at irregular intervals on May 25, June 17, June 27, July 5, August 12, September 9, September 30, and October 30. These samples were millipore filtered and stored at $-1^{o}C$ until analysed for S and K levels.

III.6 LABORATORY PROCEDURES

All chemical analyses were done in duplicate or, in the case of excess variation, until results agreed to within 5%.

III.6.1 Water chemical analyses

Soluble sulphate-sulphur levels in the rainfall and drainage waters were determined on millipored samples. Ten ml aliquots were evaporated to dryness overnight in an oven at $80^{\circ}C$ and S levels measured by the method of Johnson and Nishita (1952). In this method sulphur is reduced by heating with a mixture of hydriodic acid, hypophosphorus acid and formic acid. The H_2S released is reacted with zinc acetate to form ZnS. Acidification of the ZnS solution releases hydrogen sulphide which reacts with P-aminodimethylaniline to form methylene blue. The intensity of the methylene blue formation, indicating the SO_4-S content, was measured colorimetrically in a Unicam SP 600 series 2 spectrophotometer at 670 mμ.

Soluble potassium levels in the rainfall and drainage waters were determined by emission spectrophotometry. Strontium nitrate was added to filtered water samples (to give a strontium ion concentration of 2,000 ppm) preventing interference by calcium and magnesium when measuring potassium concentrations. Potassium concentrations were then measured on a Perkin-Elmer 306 A.A. Spectrophotometer at a wave-length of 383 nm, using an air-acetylene flame.

III.6.2 Soil chemical analyses

Soil SO_4-S levels: A 6 gm (oven dry weight) moist, soil sample was shaken for one hour with 30 ml of distilled water. The suspension was centrifuged and millipore filtered. A 5 ml aliquot of this extract was then evaporated to dryness overnight and the S content determined by the method of Johnson and Nishita (1952).

Phosphate-extractable soil SO_4-S levels in several soil samples were also measured to determine the likely size of the chemically adsorbed SO_4-S soil fraction. Soil samples from depths 0-10 cm and 40-60 cm were shaken with $Ca(H_2PO_4)_2.H_2O$ containing 500 ppm P, as proposed by Fox *et al.* (1964). Extraction of S determination procedures were as outlined previously in relation to water soluble SO_4-S levels.

Water and PO_4-extractable SO_4-S levels were similar (Table VII) indicating that a limited quantity of absorbed SO_4-S was present in the Tokomaru silt loam.

Table VII Water soluble and PO_4-extractable soil SO_4-S levels in the Tokomaru silt loam prior to fertilisation.

Soil depth interval (cm)	Sample No.	SO_4-S ($\mu g.gm^{-1}$)	
		Water soluble	PO_4-extractable
0-10	1	8.65	9.45
	2	13.40	12.35
40-60	1	11.80	14.80
	2	16.30	18.80

Soil potassium status: A 15 ml aliquot of the extract obtained by shaking 6 gm (oven dry weight) of moist soil with 30 ml of distilled water for one hour was analysed for water soluble soil K. Strontium nitrate (2,000 ppm St) was added and K concentrations determined by emission spectrophotometry.

Ammonium acetate extractable soil K levels were also determined. Six gm of moist soil (oven dry weight basis) was shaken for one hour with 1 N NH_4OAc (pH 7), centrifuged and filtered. Potassium concentrations in the extracts were determined by emission spectrophotometry.

CHAPTER IV RESULTS AND DISCUSSION

IV.1 SULPHUR

IV.1.1 SULPHUR SURFACE RUNOFF LOSSES

IV.1.1.1 Surface runoff (1976)

Water was discharged from the two undrained and two drained runoff plots on seven and six occasions respectively during the interval May 28 and July 8. At this stage the study was terminated as dairy cows obtained entry to the plots damaging runoff collection apparatus. Storm events during this interval were generally intense and of long duration (> 24 hours). The first runoff event from the undrained plots occurred on June 6. Water was not discharged from the drained plots until June 12.

Total dissolved SO_4-S losses, fertiliser S losses, mean dissolved SO_4-S concentrations in the runoff, and the amount of water discharged from the undrained and drained plots are given in Table VIII. Fertiliser S losses were calculated by subtracting SO_4-S lost from the unfertilised plot from that lost from the associated fertilised plot.

TABLE VIII Dissolved sulphate-sulphur surface runoff losses in 1977, the quantity of water discharged from both undrained and drained plots and mean SO_4-S concentrations in the runoff.

Plot	Treatment	SO_4-S loss kg ha^{-1}	Fertiliser S loss kg ha^{-1}	Mean SO_4-S concentration $\mu g\ ml^{-1}$	Water yield $m^3\ ha^{-1}$
1	Undrained, fertilised*	5.5	4.6	6.5	843
2	Undrained, unfertilised**	0.9		1.0	
3	Drained, unfertilised	0.2		0.8	241
4	Drained, fertilised	1.2	1.0	5.0	

*57 kg ha^{-1} S applied in (solid) superphosphate on May 28, 1976.

**S fertiliser not applied in 1976.

The addition of S fertiliser, and artificial subsurface drainage influenced the magnitude of SO_4-S runoff losses considerably.

Only a negligible fraction of that S required annually by grass-clover pastures was removed from the unfertilised, undrained and drained plots in runoff waters.

Sulphur fertilisation enhanced runoff losses approximately six-fold. In only six weeks a significant fraction of the applied S (8.0% or 46 kg SO_4-S ha^{-1}) was discharged in runoff water from the undrained plot. Only 1.8% of S applied in superphosphate (1 kg SO_4-S ha^{-1}) was lost from the drained plot.

Mole and tile drainage reduced SO_4-S losses from the unfertilised and fertilised plots approximately 4.5-fold. A greater volume of water infiltrated into the drained soil resulting in a 3.5-fold reduction in the surface runoff water yield. This reduction in water yield contributed in part to the lower SO_4-S runoff losses. Mean SO_4-S concentrations in runoff from the drained plots were also lower, probably as less water moved downslope over the drained plots resulting in less soil and fertiliser particle disturbance.

Figure 1 illustrates that SO_4-S concentrations were highest in water discharged from the fertilised plots in the first runoff event following fertilisation. Subsequently SO_4-S concentrations fell as less fertiliser S was available for transport in runoff water. Calcium sulphate is only sparingly soluble and the gradual reduction in concentrations observed is a reflection of this. The application of 57 kg S ha^{-1} to undrained and drained plots continued to influence SO_4-S concentrations in runoff, and hence runoff losses, six weeks after fertilisation. Total surface runoff losses in 1976 may, therefore, have been considerably greater than the losses measured in this six week study.

IV.1.1.2 Surface runoff (1977)

Water was discharged from the four undrained plots on 14 occasions during the experimental period June 10 to September 19. The first runoff event occurred only one day after S was applied. The total quantity of dissolved SO_4-S lost from each plot in surface runoff waters during this interval, mean dissolved SO_4-S concentrations in the runoff, and the amount of water discharged from the adjacent plots are given in Table IX.

Figure 1 Mean dissolved SO_4-S concentrations in surface runoff from each plot in each flow event (1976).

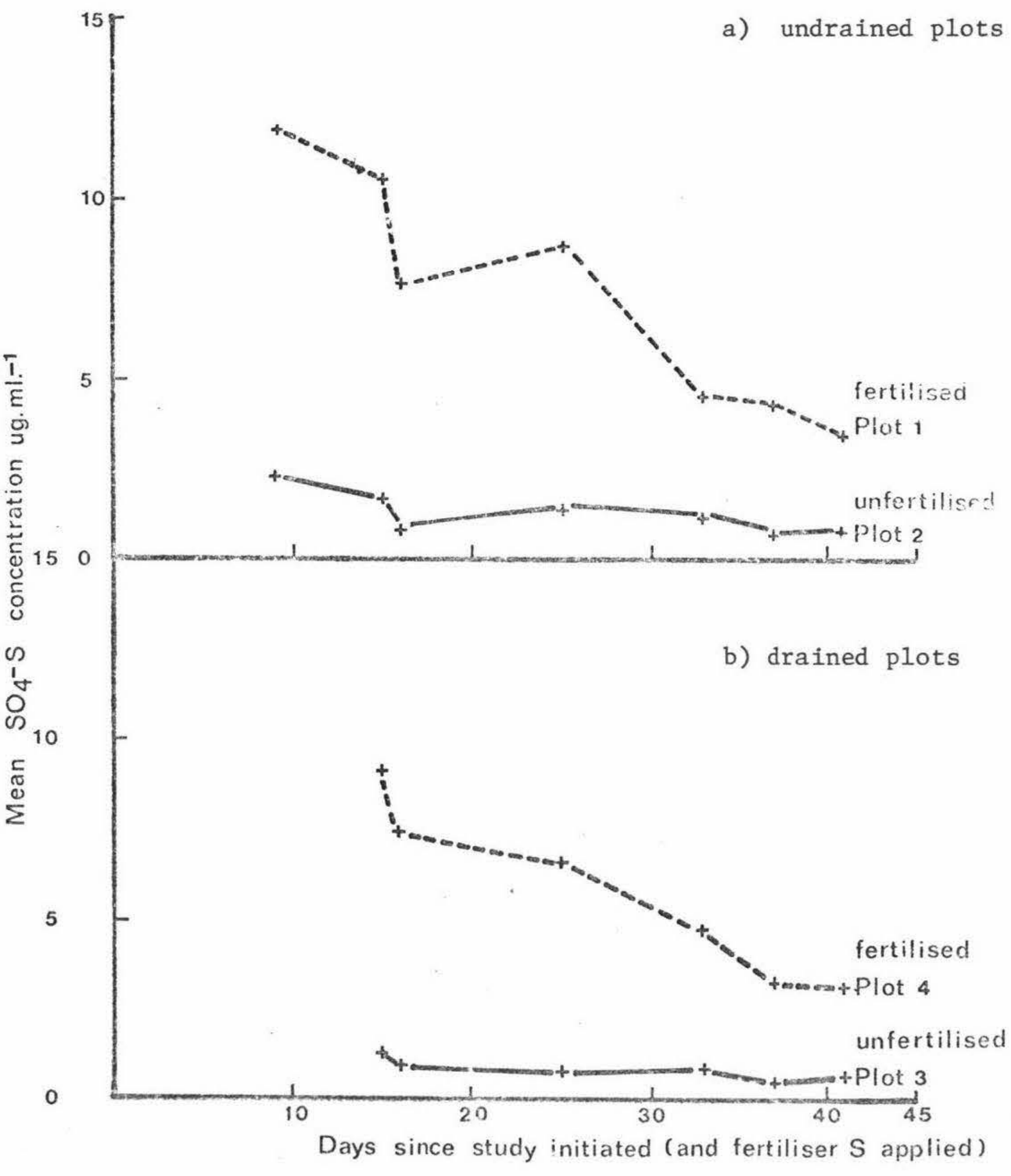


Table IX Dissolved SO_4-S surface runoff losses in 1977, the quantity of water discharged from the adjacent paired plots and mean SO_4-S concentrations in the runoff.

Plot	Treatment	SO_4-S loss kg ha^{-1}	Mean SO_4-S concentration $\mu g\ ml^{-1}$	Water yield $m^3\ ha^{-1}$
5	Fertilised*, grazed**	8.4	6.7	1250
6	" "	7.6	6.1	
7	Unfertilised, ungrazed	0.8	0.7	1157
8	" "	0.8	0.7	

*55 kg ha^{-1} S applied in liquid superphosphate on June 10, 1977.
**25 hour grazing event from June 5-6.

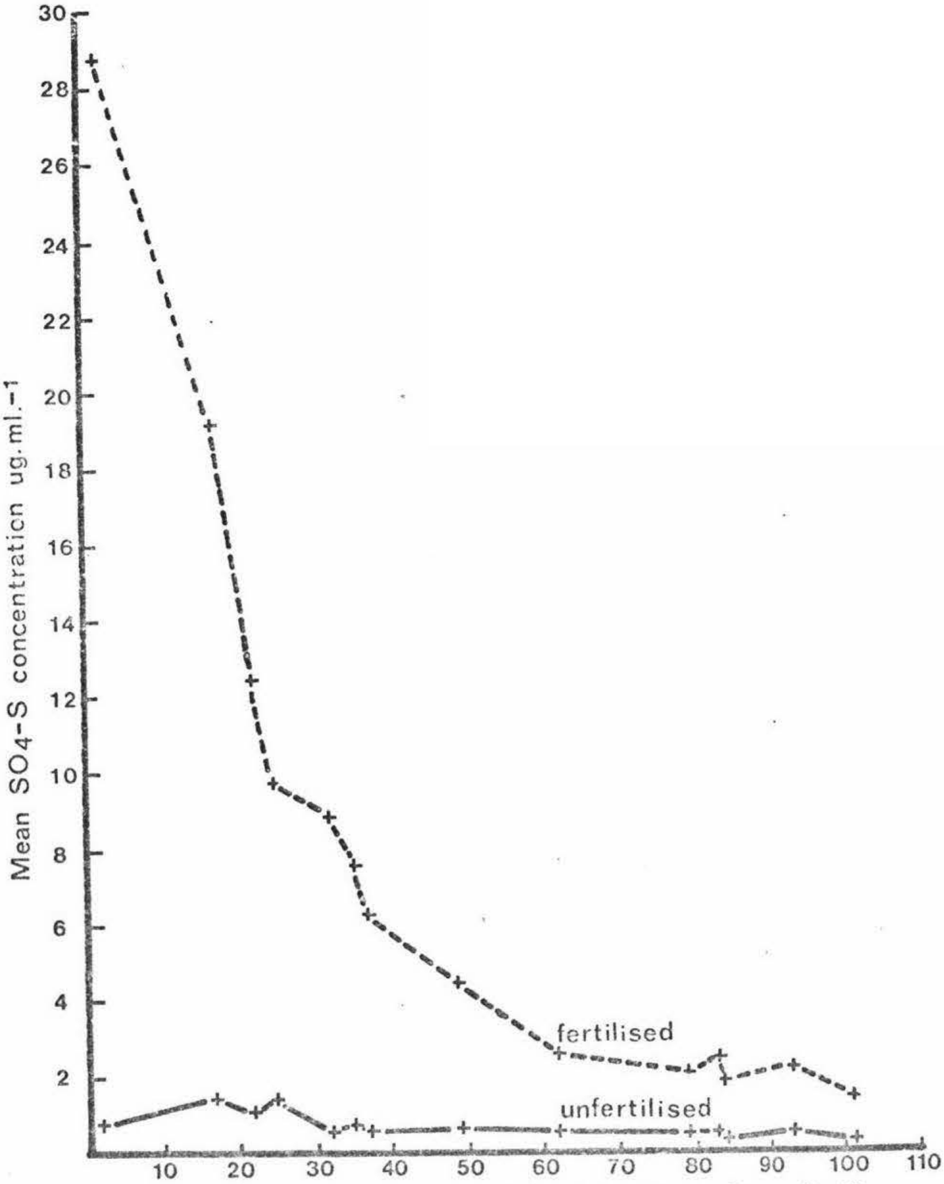
Only a negligible fraction of that S required annually by grass-clover pasture was discharged from the unfertilised plots (0.8 kg SO_4-S ha^{-1}) as dissolved SO_4-S.

A considerably greater quantity of SO_4-S was lost from the fertilised plots (8.0 kg SO_4-S ha^{-1}). Both S fertilisation and grazing cattle, which obtained entry to plots 5 and 6 just prior to this study, may have enhanced runoff losses.

The larger SO_4-S losses associated with the fertilised, grazed plots were the result of a greater water yield in addition to higher mean SO_4-S concentrations in the runoff (Table IX). The higher mean water yield may be attributable to the grazing cattle, with soil surface plugging reducing the extent of water infiltration. The higher SO_4-S concentrations may reflect both fertiliser and excretal S (subsequently referred to FE) transport downslope in runoff waters. Because of the experimental design it is not possible to isolate a possible cattle effect on runoff losses from a fertiliser effect. However, their combined effect was to increase losses occurring during the following three month winter-spring interval by, on average, 7.2 kg SO_4-S ha^{-1}.

Mean dissolved SO_4-S concentrations in water discharged from the unfertilised and fertilised plots in each flow event are presented in Figure 2. As S was applied in liquid superphosphate, rapid entry of the applied S into the soil and hence, a sharp decline in runoff concentrations to levels approaching concentrations in runoff from unfertilised plots might be expected. Concentrations initially fall

Figure 2 Mean dissolved SO_4-S concentrations in surface runoff from unfertilised and fertilised plots in each flow event (1977).



rapidly from a peak in the flow event immediately following fertilisation. Later, however, there was a more gradual decrease. This suggests that S entering the soil was retained to some extent, in a zone subsequently flushed by surface runoff water. This may result with rain disturbing the soil surface layer and/or with soil water lateral movement and discharge at the surface downslope.

At all stages throughout the three month study, SO_4-S concentrations in runoff from the fertilised grazed plots were higher than concentrations in runoff from the unfertilised plots. Hence an application of 55 kg S ha^{-1} in liquid superphosphate and/or a 24 hour grazing event enhanced surface runoff losses throughout this interval.

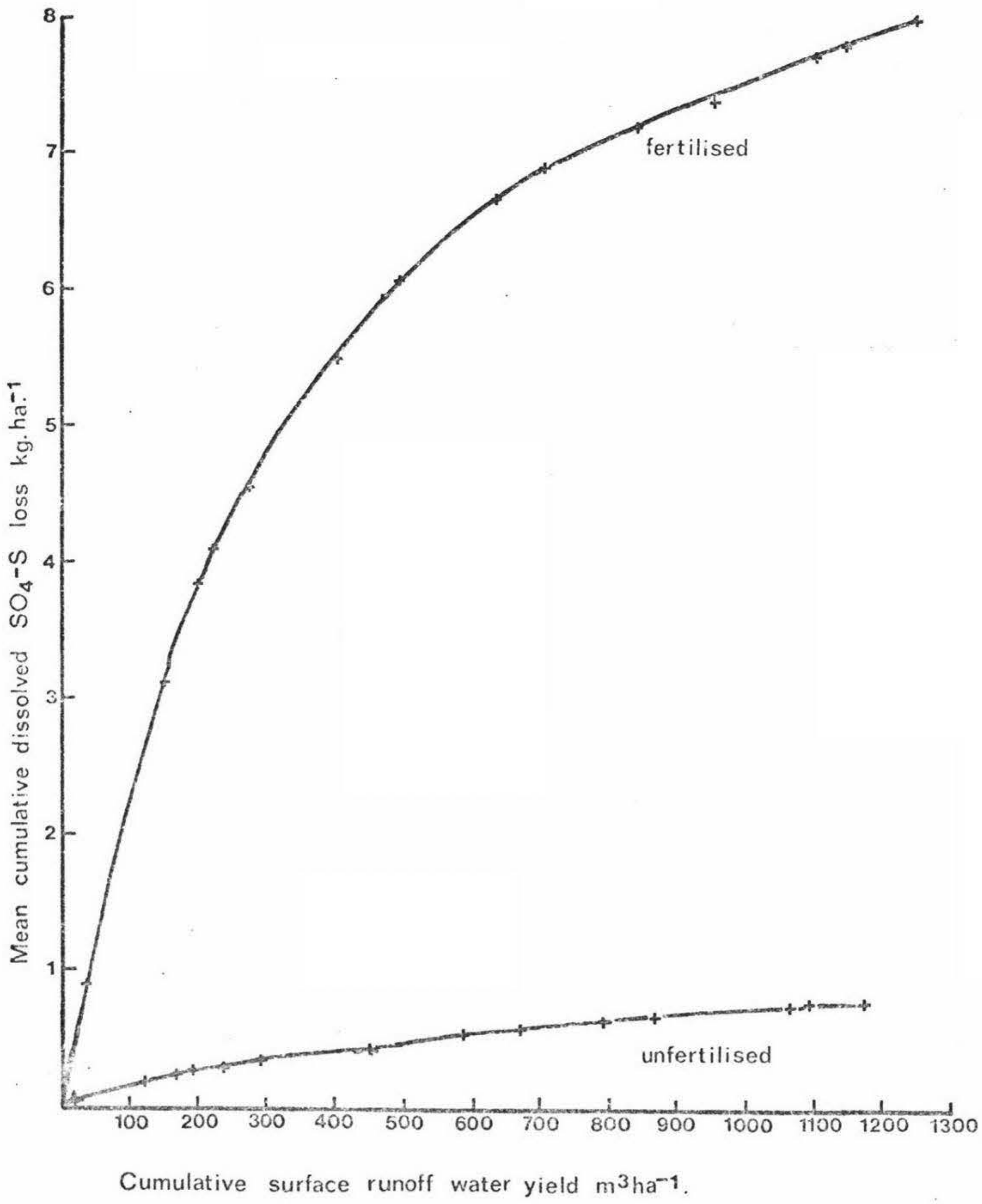
The FE S loss pattern within this three month interval may be determined from the relationships existing between cumulative mean SO_4-S loss from the fertilised grazed, and unfertilised plots, and water yield in each flow event. These relationships are given in Figure 3. As expected, most of the FE S lost was transported downslope in the first few runoff events following fertilisation and grazing. On average, 10% of the total FE S lost was removed in the first runoff event (occurring two days after fertiliser S was applied and six days after grazing) in only 31 m^3 ha^{-1} of water. A further 40% (i.e. 50% cumulative loss) of the total FE S lost was transported downslope in two further events in 171 m^3 ha^{-1} of water. Altogether, approximately 85% of the total FE S lost was removed in the first 625 m^3 ha^{-1} of water discharged (50% of the total water yield) from the fertilised plots.

In both of these runoff investigations, fine soil particles markedly discoloured runoff from the undrained plots. Adsorbed and organically bound S associated with this sediment fraction was not determined. Total S runoff losses from these plots will therefore have been greater than measured losses.

IV.1.1.3 <u>A comparison between runoff losses in 1976 and 1977</u>

Measured losses from undrained plots in 1976 (i.e. in 841 m^3 ha^{-1} of runoff) may be compared with SO_4-S losses in the initial 840 m^3 ha^{-1} of runoff water discharged from undrained plots in 1977.

Figure 3 Cumulative SO_4-S surface runoff losses from unfertilised and fertilised plots in 1977.



Sulphate-sulphur losses from undrained, unfertilised plots in 1976 and 1977 in this runoff water were similar (0.9 and 0.8 kg SO_4-S ha^{-1} respectively).

Additional SO_4-S lost from the fertilised plots in 1976 (57 kg S ha^{-1} applied) and 1977 (55 kg S ha^{-1} applied) totalled 4.6 and 6.5 kg ha^{-1} respectively. This difference largely reflected a greater loss from the plots fertilised in 1977 in the first 250 m^3 ha^{-1} of water discharged (Table X). The application of solution S immediately (i.e. within one day) prior to the occurrence of a runoff event resulted in a large runoff loss in 1977. The application of S in 1976 in a form less susceptible (i.e. solid superphosphate) to rapid transport in runoff water resulted in a comparatively small loss initially. The prolonged (nine day) interval between fertilisation and the occurrence of a runoff event in 1976 probably also contributed to the reduced loss; with infiltration of a fraction of the applied S occurring in rainwater received during the intervening period.

Table X The fertiliser (1976) and fertiliser and excretal S (1977) loss pattern in the initial 840 m^3 ha^{-1} of runoff waters discharged in 1976 and 1977

Cumulative runoff yield m^3 ha^{-1}	SO_4-S discharged in		
	m^3 ha^{-1} runoff	1976	1977
		kg ha^{-1}	
250	250	1.9	4.0
420	170	1.2	1.1
840	420	1.5	1.4

The observed similarity in losses occurring in the following 590 m^3 ha^{-1} of runoff was unexpected considering the different forms of fertiliser S applied. The finding, however, supports the earlier proposal that a fraction of the applied solution S (in fertiliser and urine) was retained in a zone subsequently flushed by runoff water.

IV.1.2 SULPHUR LEACHING LOSSES

IV.1.2.1 Dissolved SO_4-S tile drainage water losses

Water was initially discharged from tiles draining plots 5, 6, 7 and 8 (i.e. irrigated plots) on May 18, 1977; plots 2 and 4 on May 31; and plots 1 and 3 on June 3. Altogether 12-13 flow events occurred before the tile drainage season concluded on September 21. Dissolved SO_4-S losses in the drainage water, mean SO_4-S concentrations in the leachate, and the amount of water discharged from each of the eight plots in 1977 are given in Table XI (see p.65).

On average, 11 kg ha^{-1} SO_4-S was leached from the four unfertilised plots. This quantity of SO_4-S comprises an important fraction (approximately 30%) of the S required annually by grass-clover pastures.

Leaching losses from the S fertilised plots were generally considerably larger. The influence of S fertilisation on the magnitude of SO_4-S leaching losses was determined over the 17 week interval July 1 to September 21 by comparing losses from the replicate unfertilised and fertilised plots. Dissolved SO_4-S losses in the three flow events preceding fertilisation varied between the eight plots. The effect of this variation on SO_4-S losses from the replicate unfertilised and fertilised plots after July 1 was reduced using covariance analysis, and adjusted mean SO_4-S obtained (Table XII).

Table XII Actual and adjusted mean SO_4-S tile drainage water losses from unfertilised and fertilised plots during the interval July 1 to September 21, 1977.

Treatment	Actual SO_4-S loss kg ha^{-1}	Adjusted SO_4-S loss* kg ha^{-1}
Unfertilised plots	6.56	7.12
Fertilised plots	12.14	11.58
		Difference 4.47 ± 1.47**

*Covariance analysis – F-test 8.47 significant.
**Difference significant at the 95% confidence level.

A comparison between these adjusted mean SO_4-S loss values shows that a significantly greater quantity of dissolved SO_4-S was leached from the fertilised than unfertilised plots. Sulphur fertilisation (43 kg ha^{-1}) increased SO_4-S tile drainage water losses by 4.47 ± 1.47 kg ha^{-1}, representing 10.4% of the applied S.

The manner in which fertilisation influenced the extent of SO_4-S movement in percolating water throughout this 17 week interval may be determined by comparing SO_4-S concentrations in leachate from the unfertilised and fertilised plots.

Mean dissolved SO_4-S concentration for each flow event in 1977

Table XI Dissolved SO_4-S lost in tile discharge water from each of the eight plots during 1977, the quantity of water discharged from each plot and mean SO_4-S concentrations in the leachate.

Plot	Treatment	SO_4-S loss $kg\ ha^{-1}$	Water yield $m^3\ ha^{-1}$	Mean SO_4-S concentration $\mu g\ ml^{-1}$
1	NF	9.23	1,096	8.4
2	F	14.36	1,640	8.8
3	F	15.98	1,344	11.9
4	NF	5.87	1,552	3.8
5	NF*	19.84	2,096	9.5
6	F*	16.14	1,720	9.4
7	F*	21.24	1,960	10.8
8	NF*	8.99	1,848	4.9

F = 43 kg S ha^{-1} applied on July 1, 1977.

NF = Plots not fertilised in 1977.

*Irrigated plots.

(determined for each plot from total dissolved SO_4-S loadings and total flow data) for 'paired unfertilised and fertilised plots' (III.3) are given in Figure 4. Dissolved SO_4-S concentrations in leachate from the unfertilised plots tended to remain comparatively stable throughout the tile drainage season. Sulphate-sulphur concentrations in leachate from the fertilised plots increased after fertiliser was applied on July 1. The pattern of these increases suggest that fertiliser S was leached in several 'waves'. For example, sulphate-S concentrations in leachate from plot 7 in particular (but also plots 3 and 6) increased immediately after fertilisation. This may reflect rapid fertiliser S leaching down cracks in the Tokomaru silt loam which develop over the summer due to earthworm activity and soil shrinkage (Scotter, pers. comm.). Subsequently, concentrations fell prior to a more gradual increase in concentrations in leachate from all the fertilised plots. This delayed fertiliser effect will reflect the comparatively slow leaching of most of the applied S fertiliser through the soil bulk. Hydrodynamic dispersion and SO_4-S soil interaction (i.e. adsorption) will have dispersed the leaching front resulting in the gradual increases observed.

Although this field trial was designed principally to measure leaching losses from unfertilised and fertilised plots, the trial design also enabled the effect of irrigation on S leaching losses to be measured.

The wide variation in dissolved SO_4-S losses from replicate unfertilised and fertilised plots (Table XI) reflected, in part, a wide variation in the quantity of water discharged from the replicate plots (Table XI). Plots irrigated the summer preceding this study lost, on average, an additional 500 ℓ water ha^{-1} (Table XIII). These

Table XIII Mean dissolved SO_4-S tile drainage water leaching losses from non-irrigated and irrigated plots in 1977, and mean water yields.

Treatment	Mean SO_4-S loss kg ha^{-1}	Mean water yield kg ha^{-1}
Non-irrigated	11.36	1408
Irrigated	16.53	1906
Difference	5.17 n.s.	498 n.s.

n.s. = not significant.

Figure 4 Mean dissolved SO_4-S concentrations in leachate discharged from paired unfertilised and fertilised plots in each tile drainage event in 1977.

a) Plots 3 and 1.

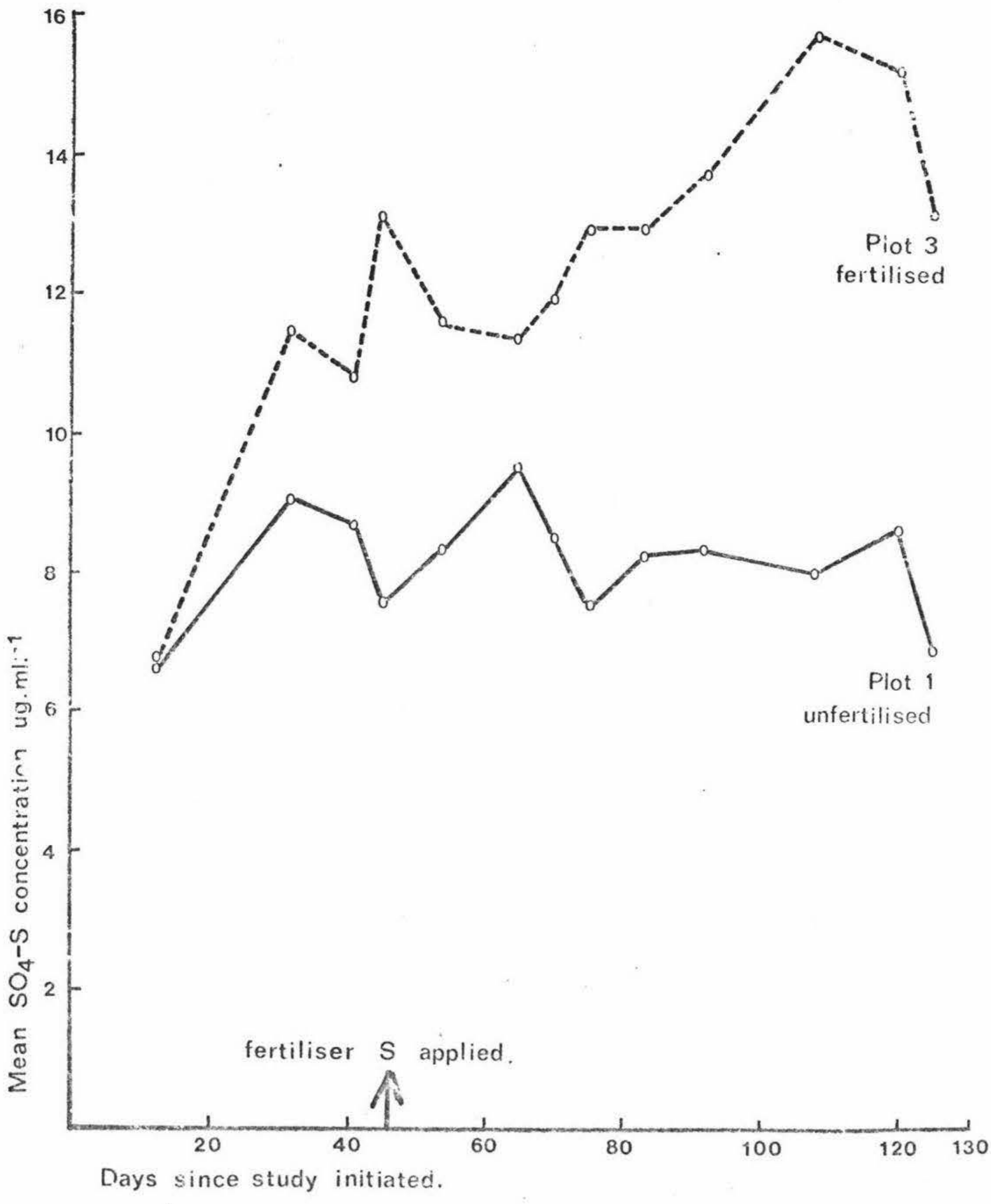


Figure 4 Mean dissolved SO_4-S concentrations in leachate discharged from paired unfertilised and fertilised plots in each tile drainage event in 1977.

b) Plots 2 and 4.

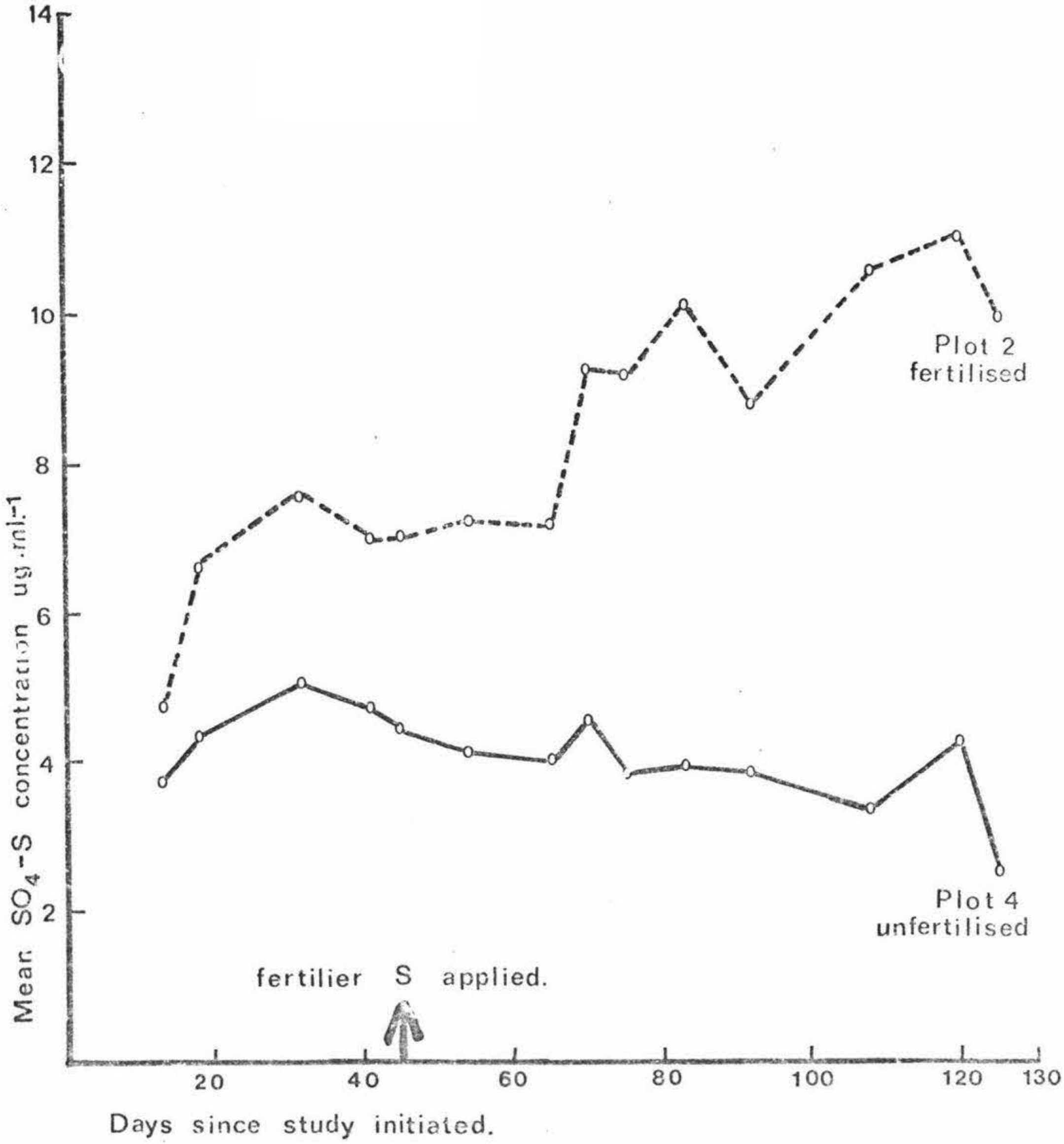


Figure 4 Mean dissolved SO_4-S concentrations in leachate discharged from paired unfertilised and fertilised plots in each tile drainage event in 1977.
c) Plots 7 and 5.

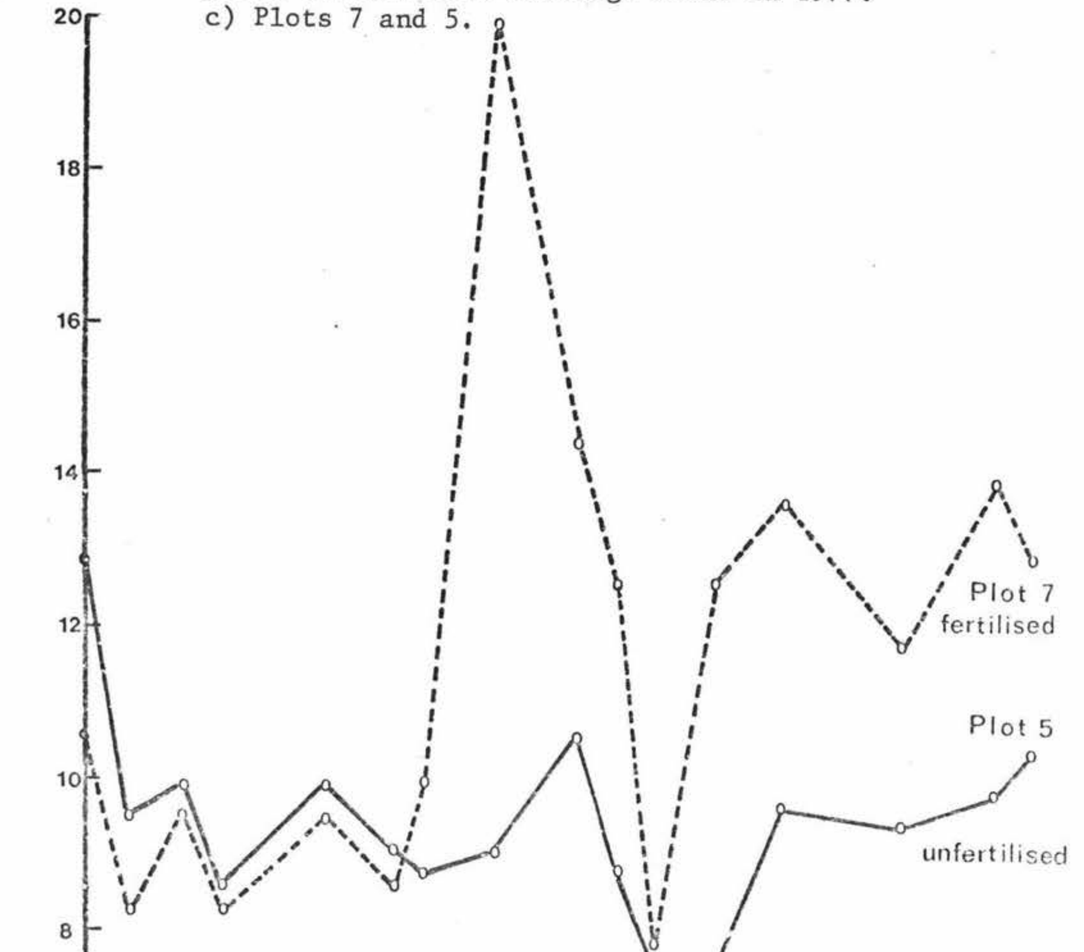
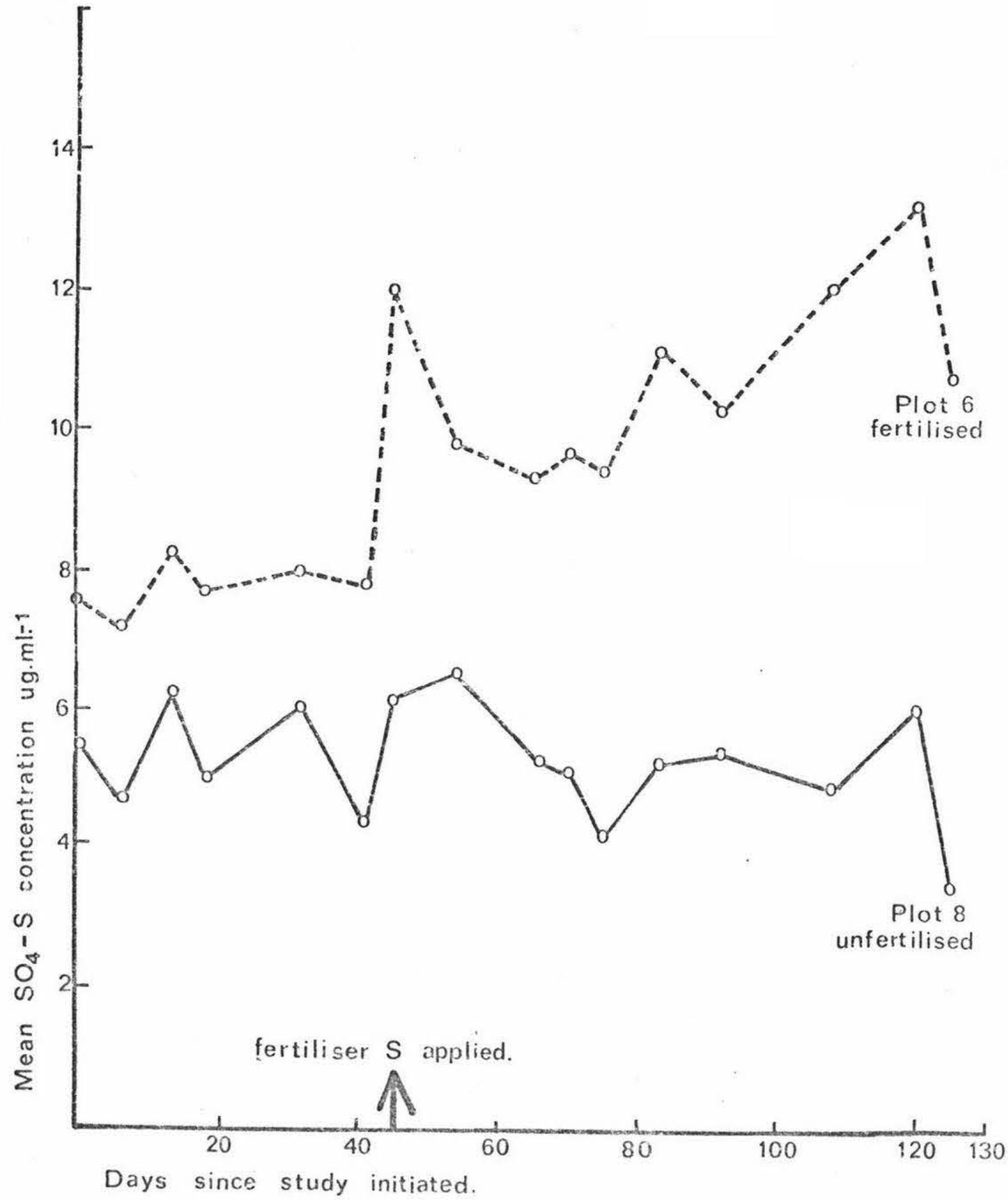


Figure 4 Mean dissolved SO_4-S concentrations in leachate discharged from paired unfertilised and fertilised plots in each tile drainage event in 1977.

d) Plots 6 and 8.



higher water yields were associated with greater SO_4-S leaching losses. On average, an additional 5.2 kg ha^{-1} SO_4-S was lost from the irrigated plots (Table XIII). However, this increase was not statistically (t-test) significant, probably due to the lack of replicates rather than the absence of an effect.

In this study, total dissolved SO_4-S leaching losses from the upper 50 cm of soil in all plots may have been underestimated. D. Scotter (pers. comm.) and M. Turner (pers. comm.) using different methods calculated that significantly more water was lost from these plots in 1977 than that measured via the tile drains. Scotter calculated water yields from rainfall figures and soil moisture contents, determined at regular intervals in 1977. Turner predicted water yields from the relationship established between rainfall values and the amount of leachate collected from these plots in the preceding five years. They suggest that cracks may have developed in the fragipan and water seepage beyond the pan may have occurred during winter. Water seepage through the Tokomaru silt loam fragipan has been observed (B. Clothier) at a nearby site. If this were the case dissolved SO_4-S will have by-passed the tiles in percolating water. The measured SO_4-S losses in this study therefore represent minimal values.

IV.1.2.2 Prediction of SO_4-S tile drainage water losses

The prediction of dissolved SO_4-S losses in subsurface drainage waters from soil analytical data (water soluble soil SO_4-S levels — Appendix, Table 2) was investigated.

Two parameters were selected to describe the transport of dissolved SO_4-S in subsurface drainage waters:

(i) mean dissolved SO_4-S concentrations in selected flows, and

(ii) total dissolved SO_4-S loadings in these flow events.

Mean dissolved SO_4-S concentrations were regressed against water soluble SO_4-S contents of various soil depth intervals to 60 cm. Sulphate-sulphur levels at a particular soil sampling were related to SO_4-S concentrations in the flow event immediately following the soil sampling.

Correlation coefficients for the relationships, water soluble soil SO_4-S levels vs mean dissolved SO_4-S concentrations in the drainage water are given in Table XIV.

Table XIV Relationship between mean dissolved SO_4-S concentration in tile drainage water and water soluble soil SO_4-S levels at different depths expressed as correlation coefficients.

Soil depth cm	r
0-10	0.590**
10-20	N.D.
0-20	0.707**
20-40	0.581**
0-40	0.769**
40-60	N.D.
0-60	0.735**

**Highly significant ($P < 0.01$).

N.D. Relationships not determined as visual assessment of the graph, mean dissolved SO_4-S concentration vs water soluble SO_4-S level suggested only poor relationships existed.

Highly significant relationships existed between mean dissolved SO_4-S concentrations in the drainage water and water soluble SO_4-S levels at all depths considered. The strongest linear relationship was obtained, however, when the water soluble SO_4-S content of the upper 40 cm of soil was considered (Figure 5). This indicates that dissolved SO_4-S was leached from all depths in the upper 40 cm of soil in individual flow events.

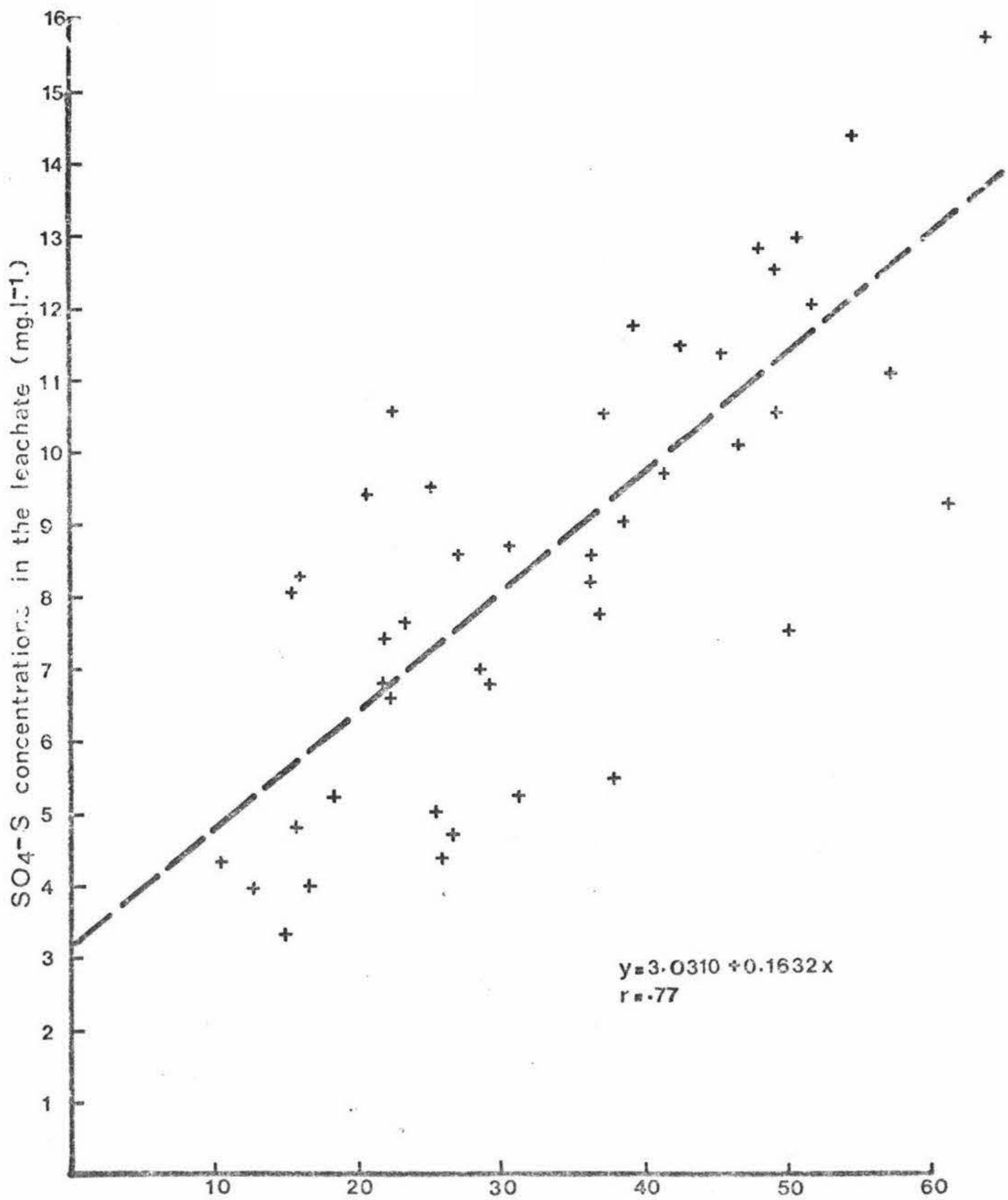
As the mole drains were situated at a depth of 45 cm, an improved relationship may have been obtained if water soluble SO_4-S levels in the 40-45 cm depth had also been considered. This could not be confirmed as the soil was not sampled at this depth.

The highly significant relationships observed above indicate that the wide variations reported earlier in SO_4-S losses from replicate plots were partly attributable to differences in SO_4-S levels in these replicate plots.

Total dissolved SO_4-S loadings in each flow event immediately following soil sampling were also regressed against water soluble SO_4-S levels in the upper 40 cm of soil. Sulphate-sulphur loadings were not significantly related to water soluble soil SO_4-S levels.

As mean dissolved SO_4-S concentrations in the leachate but not total dissolved SO_4-S loadings, were related to water soluble SO_4-S levels in the soil, the quantity of water discharged was the prime

Figure 5 Relationship between water soluble SO_4-S (0-40 cm) levels and SO_4-S concentrations in the leachate.



factor influencing the relative quantity of SO_4-S lost from plots in each flow event.

IV.1.2.3 Fertiliser S recovery in the soil

Mean water soluble SO_4-S levels in plots 2, 3, 6, and 7 (i.e. plots subsequently fertilised) on July 1, and plots 1, 4, 5 and 8 did not differ significantly prior to fertilisation (Table XV). Fertiliser S present as water soluble SO_4-S in the upper 60 cm of soil at each soil sampling after July 1 may, therefore, be determined by comparing SO_4-S levels in the unfertilised and fertilised plots. T-test comparisons (Table XV) showed that a significant fertiliser effect existed at all samplings. Fifteen weeks after fertilisation, 28 kg ha^{-1} of the 43 kg S ha^{-1} applied in superphosphate was recovered as water soluble SO_4-S in the upper 60 cm of soil.

Table XV The average quantity of water soluble SO_4-S present in plots 2, 3, 6, 7 (0-60 cm) in excess of that present in plots 1, 4, 5, 8 (0-60 cm) prior to and after fertilisation.

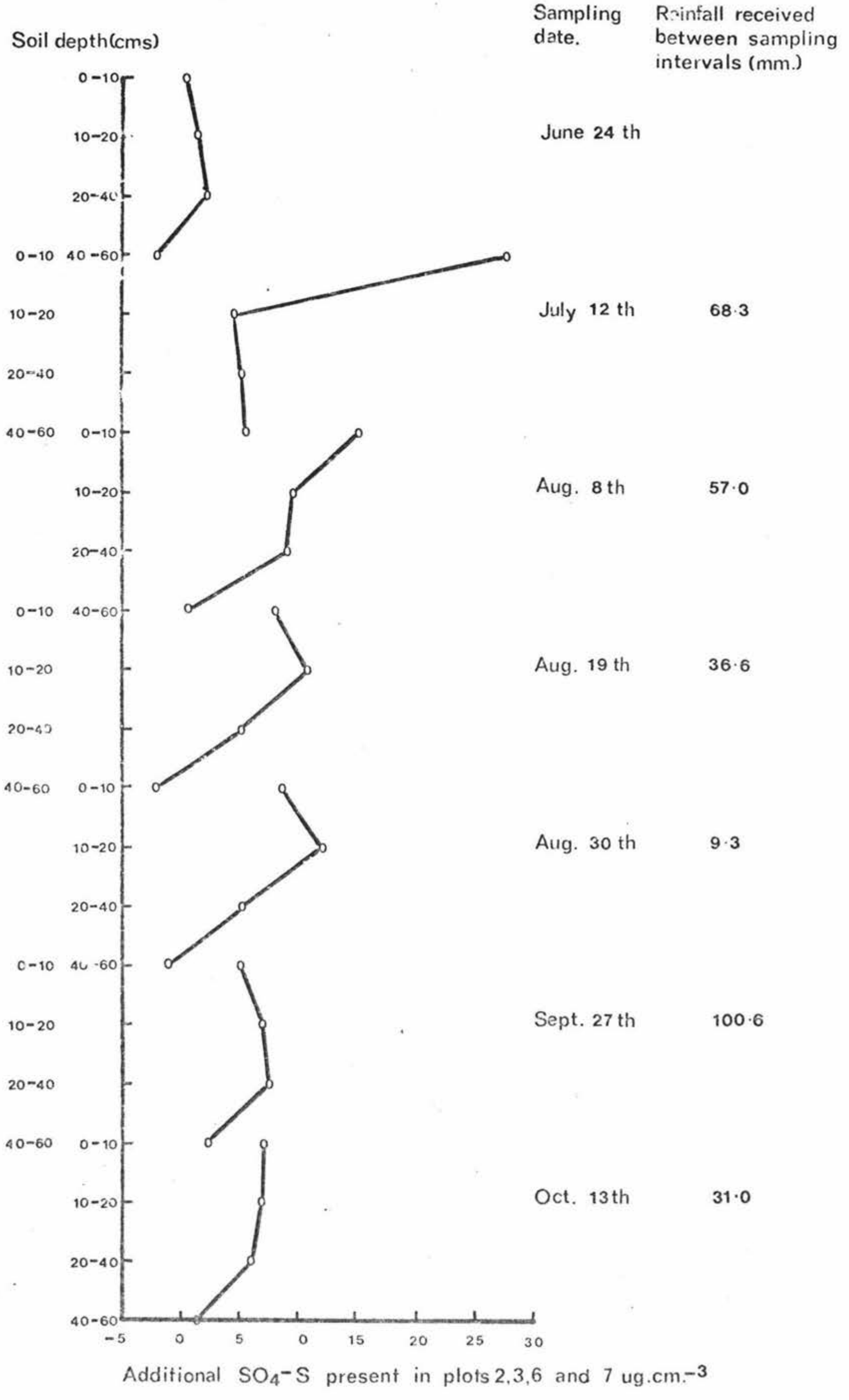
Date	SO_4-S (kg ha^{-1})
June 24	0.9
July 12	54.4*
August 3	35.0**
August 19	25.2*
August 30	29.2*
September 27	33.4**
October 13	29.1**

*significant ($P < 0.05$).

**highly significant ($P < 0.01$).

Differences in mean water soluble SO_4-S levels in plots 2, 3, 6 and 7 and plots 1, 4, 5 and 8 at each soil depth sampled immediately prior to and after S was applied are graphed in Figure 6. Prior to fertilisation SO_4-S levels at each depth in plots 2, 3, 6 and 7 closely approximated levels in plots 1, 4, 5 and 8. Hence differences occurring after July 1 indicate the fertiliser S distribution pattern within the upper 60 cm of soil. On July 12, eleven days after fertilisation, most of the applied S was recovered in the upper 10 cm of soil. Sulphate-S levels below the 10 cm depth in the fertilised

Figure 6 The average quantity of water soluble soil SO_4-S (0-60 cm) present in plots 2,3,6 and 7 in excess of that present in plots 1,4,5 and 8 at each sampling prior to and after fertilisation, and rainfall received between sampling intervals.



plots were also slightly higher than corresponding levels in the unfertilised plots indicating that a small fraction of the applied S was rapidly leached down the profile. This was reflected in higher dissolved SO_4-S concentrations in tile drainage waters from the fertilised plots (IV.1.2.1).

Under the leaching conditions which prevailed, with time, a progressively larger fraction of the fertiliser S in the upper 60 cm of soil was recovered below the 0-10 cm depth. By August 19 fertiliser S in the upper 60 cm was concentrated at the 10-20 cm depth. Fertiliser S leaching occurred to a minimal extent over the interval August 19-30, evidenced by the similar fertiliser S distribution patterns. Little rainfall was, however, received during this interval (Figure 6) and no tile flow events occurred. Fertiliser S in the upper 60 cm of soil was evenly distributed throughout the upper 40 cm on October 13 when this study was concluded.

Although fertiliser S losses in tile drainage water amounted to only 4.5 kg S ha^{-1}, losses from the plant uptake zone may have been considerably larger. The fertiliser S distribution pattern (Figure 6) shows that substantial amounts of S moved beyond the topsoil depth of 20 cm. Although plant roots penetrated to the maximum soil depth sampled (60 cm) at this site, evidence (During, 1972; Gregg, 1976) suggests that in heavy textured soils plants obtain most of their S from the topsoil. In this study measured fertiliser SO_4-S leaching losses from this active zone of uptake totalled 18.23 kg ha^{-1} (Table XVI), or 50% of the applied S. Total fertiliser S leaching loss may have been even larger. Some S may have been,

(i) leached beyond the 60 cm depth and/or

(ii) leached beyond the 20 cm depth and subsequently adsorbed.

Table XVI Measured fertiliser S leaching loss from the upper 20 cm of soil in 1977.

SO_4-S tile drainage water loss (kg ha^{-1})	4.47
SO_4-S recovered in the 20-60 cm depth (ka ha^{-1})	13.76
Total leaching loss:	18.23

Despite the large fertiliser S leaching loss, an application of 43 kg SO_4-S ha^{-1} in autumn maintained the water soluble SO_4-S content of the upper 20 cm of soil in spring (Table XVII) at a level adequate to meet pasture S requirements for an extended length of time. In contrast, in spring, insufficient water soluble SO_4-S was present in the upper 20 cm of the unfertilised plots (Table XVII) to meet pasture S requirements for an extended length of time unless this pool was subsequently replenished at a relatively rapid rate.

Table XVII Mean water soluble SO_4-S contents of the upper 20 cm of soil in the replicate plots in autumn before the tile drainage season commenced, and spring after the tile drainage season had concluded.

Plots	Water soluble SO_4-S content kg ha^{-1}	
	May 18 prior to topdressing	October 13
1, 4, 5, 8 (unfertilised)	19.4	7.9
2, 3, 6, 7 (fertilised)	23.1	22.2

IV.1.3 RAINFALL SULPHUR ADDITION

Rain received, S concentrations in the rain and dissolved S rainfall additions measured over irregular intervals throughout the interval May 12 to October 30, 1977, are given in Table XVIII.

Measured S concentrations suggest that S concentrations do not vary in a consistent manner on a seasonal basis. Therefore, assuming that the mean S concentration in rain received in the remaining seven months of 1977 was similar, with an annual rainfall figure of 960 mm (Scotter, unpubl. data), approximately 5.5 kg ha^{-1} of S was received in the rainfall during 1977.

IV.1.4 GENERAL DISCUSSION

Surface runoff

Findings of the present runoff studies are of particular importance as no earlier studies have investigated the magnitude of S runoff losses from pastures.

In this study the 'unfertilised' treatment represents the situation where fertiliser S is applied in spring (October-November). It can be

Table XVIII Rain received S, concentrations in the rain and total rainfall addition over the interval May 12 to October 30, 1977.

Interval between sampling the rain collected	Dissolved S concentrations ($\mu g.ml^{-1}$)	Rain received (mm)
May 12 - 25	0.47	67
May 25 - June 17	0.38	80
June 17 - 27	0.65	46
June 27 - July 7	0.35	39
July 7 - August 2	0.56	78
August 2 - September 2	0.42	74
September 2 - 30	1.00	97
September 30 - October 7	0.80	28
October 7 - 30	0.62	9

Total rainfall S addition over the period May 12 to October 30 = 3.1 kg ha^{-1}.

concluded from the results that S losses from superphosphate applied in the previous spring will be negligible, irrespective of whether the pastures are drained or undrained.

The fertiliser treatments in these studies represent situations where superphosphate is applied in late autumn. Results show that autumn applied fertiliser S losses in runoff from undrained pastures may be substantial.

Dissolved SO_4-S surface runoff losses measured in the present studies may differ somewhat from the actual losses occurring from large scale areas (paddocks or catchments). In large scale areas the erosional power of runoff water is likely to be significantly greater due to the greater velocities attained in moving large distances downslope. Ponding of surface runoff and subsequent SO_4-S entry into the soil at the base of slopes will tend to reduce runoff losses. Nevertheless, important factors governing runoff losses, including soil infiltration characteristics and the rainfall pattern will be the same. Therefore losses are likely to be of a similar order of magnitude.

In the present study no attempt was made to predict runoff losses from soil data, as done by Sharpley *et al.* (1977) in relation to P surface runoff losses. This would seem a useful field for research.

Leaching

The 'unfertilised' treatment in the leaching study also represents the situation where S is applied in spring. Findings indicate that in this situation leaching losses from drained, grazed pastures will be substantial. Losses from pastures fertilised in late autumn will be significantly higher.

The rapid movement of fertiliser S observed in this study closely reflects the pattern of fertiliser S movement reported by Gregg (1976) in several Canterbury soils (yellow-brown earths and recent alluvial soils) which are also characterised by low SO_4-S retention capacities.

Fertiliser S leached beyond the 20 cm soil depth in the present investigation (18.2 kg S ha^{-1} or 42% of the applied S) exceeds that fraction of the applied S leached from the Tokomaru silt loam in Muller and McSweeney's (1977) glasshouse investigation (average 11.5 kg S ha^{-1} yr^{-1} or 10% of the applied S). The comparatively small fertiliser S loss reported by Muller and McSweeney (1977) is, however, surprising as unfertilised soils in this glasshouse study lost, on average, 25 kg S ha^{-1} yr^{-1}.

Attempts to predict tile drainage S losses from soil data in the present study met with moderate success. Since it is relatively simple to measure leaching losses from drained pastures on the Tokomaru silt loam it would seem worthwhile more fully to investigate soil SO_4-S/discharge relationships.

Total drainage water losses

In the present study it was not possible to conduct the surface runoff and subsurface leaching experiments on similar land. The surface runoff plots were gently sloping (6° 5') whereas the surface drainage plots were flat (0-1°). Surface runoff losses from the subsurface drainage plots would have been lower because of increased infiltration following ponding at the soil surface. Subsurface drainage water losses from the runoff plots would be lower because a greater fraction of the water will move downslope as surface runoff. Nevertheless, the results indicate that total tile drainage and surface runoff losses from drained pastures fertilised in spring would have exceeded 7.5 kg dissolved SO_4-S ha^{-1} yr^{-1}. Losses from the pastures fertilised in autumn would have exceeded 15.0 kg dissolved SO_4-S ha^{-1} yr^{-1}.

Total drainage water losses from undrained pastures were not investigated. Losses are also likely to be high, as any reduction in leaching losses at sloping sites (as a consequence of reduced infiltration) will tend to be offset by the larger surface runoff losses observed. The relationship between drainage water losses from undrained and drained pastures could be further investigated.

The results suggest that where drained pastures were fertilised in spring S received in the rain in 1977 was likely largely to offset drainage water losses. A significant net S loss (in relation to annual pasture S requirements) will have occurred from pastures irrigated the preceding summer and/or fertilised in autumn. Measured surface runoff losses also indicate that S received in the rain was unlikely to offset likely total drainage water losses from undrained pastures.

The importance of leaching and surface runoff as loss mechanisms in the Tokomaru silt loam may be illustrated by comparing measured losses with reported immobilisation losses and losses associated with grazing animals. Drainage water S losses exceed losses associated with grazing animals (i.e. 3-7 kg S ha^{-1} yr^{-1} (During, 1972)). Losses from pastures fertilised in spring are generally low in comparison with immobilisation losses reported in a range of New Zealand pastural soils (i.e. 7.2 - 18.5 kg S ha^{-1} (0-15 cm) yr^{-1} (Jackman, 1964)). However, measured drainage water losses from pastures fertilised in autumn are generally high in comparison to immobilisation losses.

IV.2 POTASSIUM

IV.2.1 POTASSIUM SURFACE RUNOFF LOSSES

IV.2.1.1 Surface runoff (1976)

Dissolved K lost from each of the four runoff plots during the interval May 28 to July 8, fertiliser K losses and mean concentrations in the runoff are given in Table XIX.

Table XIX Dissolved K surface runoff losses in 1976 and mean K concentrations in the runoff.

Plot	Treatment	K loss kg ha^{-1}	Fertiliser K loss kg ha^{-1}	Mean K concentrations $\mu g\ ml^{-1}$
1	Undrained, fertilised*	2.6	1.5	3.1
2	Undrained, unfertilised**	1.1		1.3
3	Drained, unfertilised	0.3		1.2
4	Drained, fertilised	0.6	0.3	2.5

*50 kg K ha^{-1} in potash on May 28, 1976.
**K fertiliser not applied in 1976.

Potassium lost from each of the four plots was negligible in relation to annual pasture K requirements. Both K fertilisation and drainage influenced the magnitude of these losses.

Potassium fertilisation enhanced losses from undrained and drained plots 2.5- and 2-fold respectively. Fertiliser K runoff losses were, nevertheless, minimal in relation to the quantity of K applied ($\leqslant$ 3%).

Mole and tile drainage influenced runoff losses to a considerably greater extent than K fertilisation. Drainage reduced the K lost from unfertilised plots 3.5-fold. This reduction reflected the 3.5-fold reduction in water yield associated with mole and tile drainage. Potassium runoff losses from fertilised plots were reduced 4.5-fold by mole and tile drainage. This reduction was a reflection of both a lower mean dissolved K concentration in the runoff and a lower water yield.

Mean K concentrations in runoff from the four plots in each flow event are given in Figure 7.

The lower initial K concentration in runoff from the fertilised drained than undrained plot (Figure 7) indicates that a greater fraction of the applied K had infiltrated into the drained plot before a flow event occurred. However, concentrations in runoff from the undrained plot fell rapidly from a peak in the flow event immediately following fertilisation. This pattern is probably a reflection of the highly soluble nature of potash. Most of the fertiliser K not lost in the first few flow events apparently entered the soil and subsequently was not susceptible to transport in surface runoff. Despite this rapid infiltration of fertiliser K, fertilisation continued to influence K concentrations in runoff (Figure 7) from the undrained plots in particular, throughout this six week study.

IV.2.1.2 <u>Surface runoff (1977)</u>

Dissolved K lost from each of the four undrained plots during the interval June 10 to September 19, the amount of water discharged from plots 5 and 6, and 7 and 8, and K losses prior to after July 1 when 55 kg K ha^{-1} was applied to plots 5 and 6, are given in Table XX.

Only a negligible fraction of that K required annually by grass-clover pastures was transported in surface runoff waters from the unfertilised plots (i.e. plots 7 and 8). Considerably more dissolved K was lost from plots 5 and 6 both prior to and after fertilisation (four-fold increase).

A 24 hour grazing event enhanced losses prior to fertilisation. This increase reflected in part a larger surface runoff water yield. Dissolved K concentrations in the runoff water from plots 5 and 6 were also considerably higher (Figure 8), reflecting excretal K movement in the runoff water.

An immediate increase in the mean K concentration in runoff from plots 5 and 6 followed K fertilisation (Figure 8). This <u>increase</u> in

Figure 7 Mean dissolved K concentrations in surface runoff from each plot in each flow event (1976).

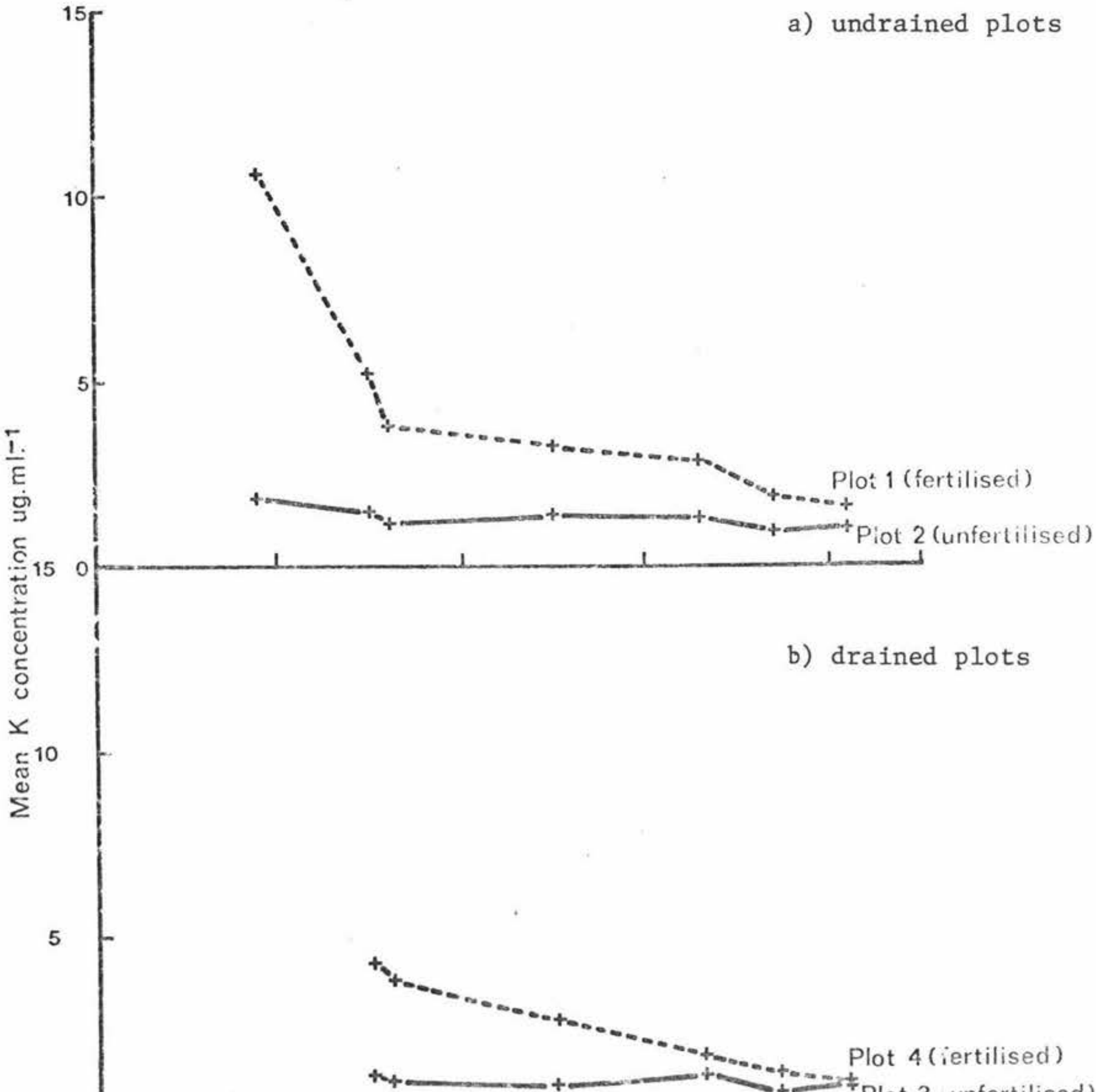


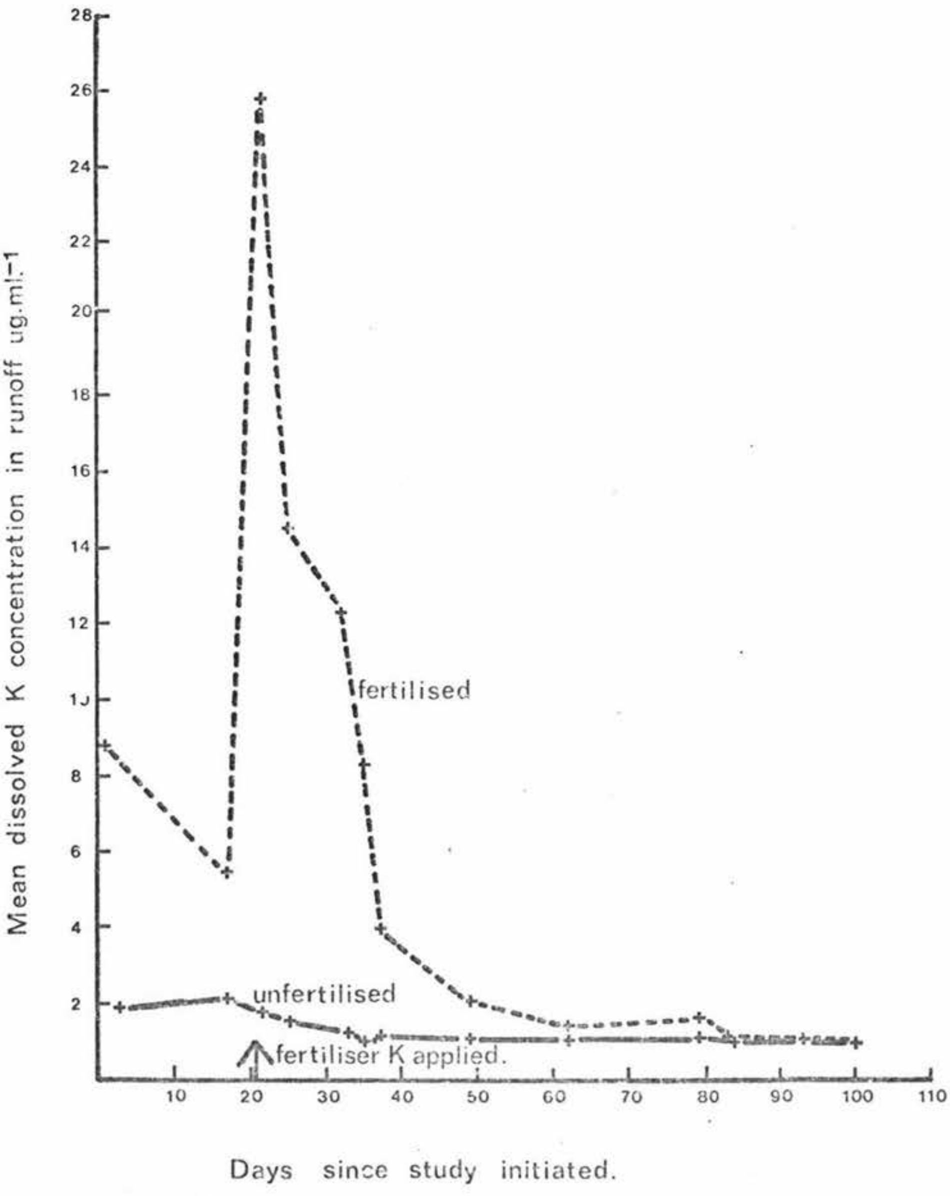
Table XX Dissolved potassium surface runoff losses in 1977, losses prior to and after fertilisation of two of the four plots, and water yields.

Plot	Treatment	June 10 - July 1		July 1 - September 19		June 10 - September 19
		K loss kg ha^{-1}	Water yield m^3 ha^{-1}	K loss kg ha^{-1}	Water yield	K loss kg ha^{-1}
5	Fertilised*, grazed	0.7	156	4.6	1094	5.3
6	Fertilised, grazed	1.1		4.7		5.8
7	Unfertilised** ungrazed	0.2	120	1.2	1037	1.4
8	Unfertilised, ungrazed	0.2		1.1		1.3

*55 kg ha^{-1} K applied in potash on July 1, 1977.

**Fertiliser K not applied in 1977.

Figure 8 Mean dissolved K concentrations in surface runoff from unfertilised and fertilised plots in each flow event (1977).



concentration presumably reflected fertiliser K transport downslope. Mean K concentrations fell rapidly in subsequent flow events and by August 10 (61 days after K was applied) K runoff levels closely approximated K concentrations in runoff from the unfertilised plots. Fertiliser (and excretal) K was subsequently not liable to transport in surface runoff water.

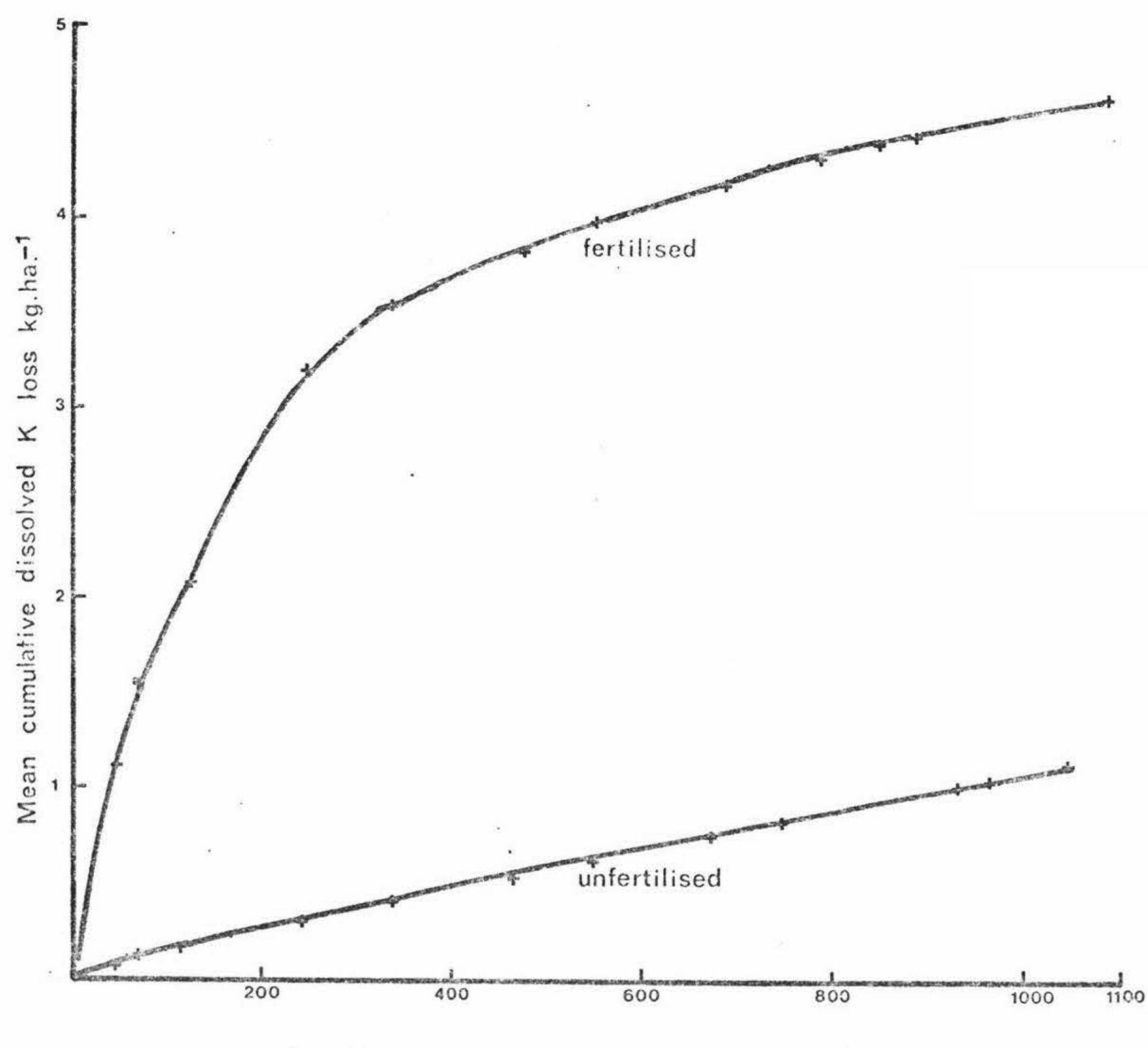
The pattern of fertiliser (and excretal) K loss after July 1 may be determined by comparing mean cumulative K loss curves for the unfertilised and fertilised plots (Figure 9). Probably only a comparatively small quantity of excretal K was lost after fertilisation and hence, most of the fertiliser K lost in runoff was transported downslope in the first few flow events following fertilisation. In the flow event occurring only two days after fertilisation, 32% of the total applied K lost was lost in only 47 m^3 ha^{-1} of water. Another 23% of the total K lost, was transported downslope in a further 68 m^3 ha^{-1} of water in two additional flow events. Altogether 95% of the applied K lost in runoff was discharged in the first 547 m^3 ha^{-1} (i.e. 50% of the total water yield) of runoff water.

In these studies, K losses in sediment discharged in the surface runoff were not measured. Sediment markedly discoloured runoff waters from undrained plots. This sediment was likely to contain K in appreciable quantities due to the K retentive nature of the clay fraction (2:1 clays dominate) in the Tokomaru silt loam. Total K surface runoff losses from unfertilised and fertilised plots (in particular the undrained plots) may, therefore, have been considerably underestimated by measuring dissolved K runoff losses.

IV.2.1.3 A comparison between runoff losses in 1976 and 1977

Losses from unfertilised plots in 1976 and 1977 in the initial 840 m^3 ha^{-1} of runoff (discharged after K was applied to the associated fertilised plots) were similar. Additional K lost from the fertilised plots was equivalent to 3.0% (1.5 kg K ha^{-1}) and 6.3% (3.5 kg K ha^{-1}) of the fertiliser K applied in 1976 (50 kg K ha^{-1}) and 1977 (55 kg K ha^{-1}) respectively. The K loss pattern in this runoff water (summarised in Table XXI) shows that the larger total K loss in 1977

Figure 9 Cumulative K surface runoff losses from unfertilised and fertilised plots in 1977.



reflected a greater loss in the first 250 m^3 ha^{-1} of water discharged. Transport of solution K (received in urine) in runoff water may partly account for the greater loss in 1977. However, the more important factor was likely to be the different rainfall patterns immediately following fertilisation. The occurrence of several flow events within four days of fertilisation would probably account for the large K loss in 1977. In contrast the prolonged interval (nine days) between fertilisation and the occurrence of a runoff event in 1976 would favour a relatively small K loss, as recorded; with a larger fraction of the applied K infiltrating into the soil in the intervening period.

Table XXI The fertiliser (1976) and fertiliser excretal K (1977) loss pattern in the initial 840 m^3 ha^{-1} of runoff water discharged in 1976 and 1977.

Cumulative runoff yield	m^3 ha^{-1} runoff	K discharged in 1976	K discharged in 1977
		kg ha^{-1} (% fertiliser K applied)	
250	250	0.8 (1.6)	2.9 (5.3)
420	170	0.3 (0.6)	0.3 (0.5)
840	420	0.4 (0.8)	0.3 (0.5)

IV.2.2 POTASSIUM LEACHING LOSSES

IV.2.2.1 Dissolved K tile drainage water losses

Dissolved K leaching losses and mean dissolved K concentrations in leachate from each of the eight plots in 1977 are given in Table XXII.

Dissolved K leached from the four unfertilised plots was negligible in relation to annual pasture K requirements. Potassium losses from the fertilised plots in 1977 were also low.

The influence of K fertilisation on tile drainage water losses over the 17 weeks interval, July 1 to September 21, was determined using covariance analysis, as losses from the eight plots in the three flow events prior to K fertilisation varied considerably. The 'adjusted mean K loss values' thus obtained for the unfertilised and fertilised plots did not differ significantly (Table XXIII). Only a negligible fraction (1.3%) of the applied K was leached in tile drainage waters.

Table XXII Dissolved K lost in tile discharge waters from each of the eight plots during 1977 and mean K concentrations in the leachate.

Plot	Treatment	K loss kg ha^{-1}	Mean K concentration µg ml^{-1}
1	NF	4.85	4.4
2	F	4.83	3.0
3	F	4.53	3.4
4	NF	3.21	2.1
5	NF*	8.10	3.9
6	F*	3.02	1.8
7	F*	3.82	1.9
8	NF*	2.49	1.4

F = 55 kg ha^{-1} K applied on July 1, 1977.

NF = Plots not fertilised in 1977.

*Irrigated plots.

Table XXIII Actual and 'adjusted' mean K tile drainage water losses from unfertilised and fertilised plots during the interval July 1 to September 21, 1977.

Treatment	Actual mean K loss kg ha^{-1}	Adjusted mean K loss* kg ha^{-1}
Unfertilised plots	2.32	2.06
Fertilised plots	2.51	2.77
	Difference	0.71 n.s.

*Covariance analysis F-test 1.52 — not significant.

n.s. = not significant.

A comparison between mean K concentrations in leachate from paired unfertilised and fertilised plots in each flow event during 1977 (Figure 10) suggests that K fertilisation did, however, enhance K concentrations immediately after K was applied. This effect was most pronounced in plot 7 and probably reflects the rapid leaching of a small fraction of the applied K down cracks in the soil profile. Potassium concentrations in water discharged from the fertilised plots decreased rapidly again (Figure 10), approaching values expected in the absence of a K fertiliser effect. Fertiliser K entering the soil was, therefore, almost entirely retained in forms not susceptible to movement in percolating water.

Irrigation did not influence dissolved K leaching losses (Table XXIV). While a significantly greater quantity of water was discharged from the irrigated than non-irrigated plots in 1977, the mean K concentration in leachate from the irrigated plots was lower.

Table XXIV Mean dissolved K tile drainage water leaching losses from non-irrigated and irrigated plots in 1977, mean water yields, and mean K concentrations in the leachate.

Treatment	Mean dissolved K loss kg ha^{-1}	Mean dissolved K concentration $\mu g\ ml^{-1}$	Mean water yield $m^3\ ha^{-1}$
Non-irrigated plots	4.36	3.21	1408
Irrigated plots	4.35	2.23	1906

As discussed earlier (IV.1.2.1), leaching water may have percolated beyond the 45 cm depth in these eight plots. Therefore, total dissolved K leaching losses will have been underestimated by measuring tile drainage water losses. Nevertheless, the magnitude of these tile drainage water losses indicate that total K leaching losses are likely to be low.

IV.2.2.2 Prediction of K tile drainage water losses

The possibility of predicting dissolved K losses in tile drainage waters from water soluble soil K levels (Appendix Table 3) and ammonium acetate (a.a.) extractable K levels (Appendix Table 4) were investigated.

Two parameters were selected to describe the transport of K in

Figure 10 Mean dissolved K concentrations in leachate discharged from paired unfertilised and fertilised plots in each tile drainage event in 1977.

a) Plots 1 and 2.

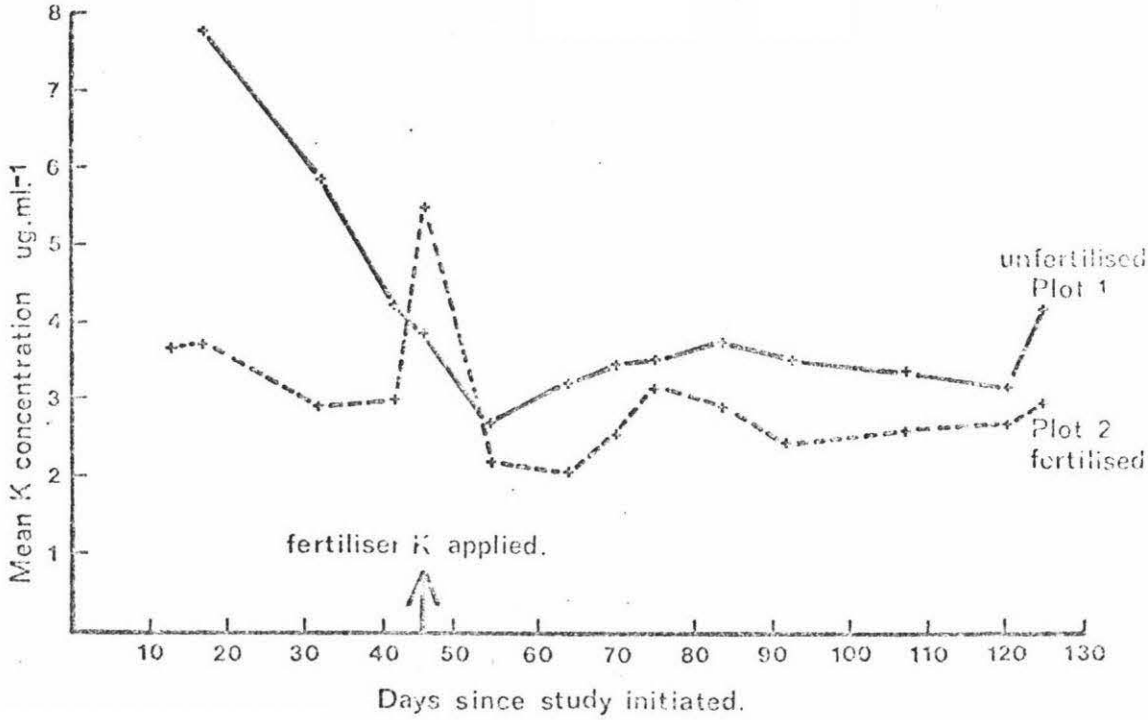


Figure 10 Mean dissolved K concentrations in leachate discharged from paired unfertilised and fertilised plots in each tile drainage event in 1977.

b) Plots 3 and 4.

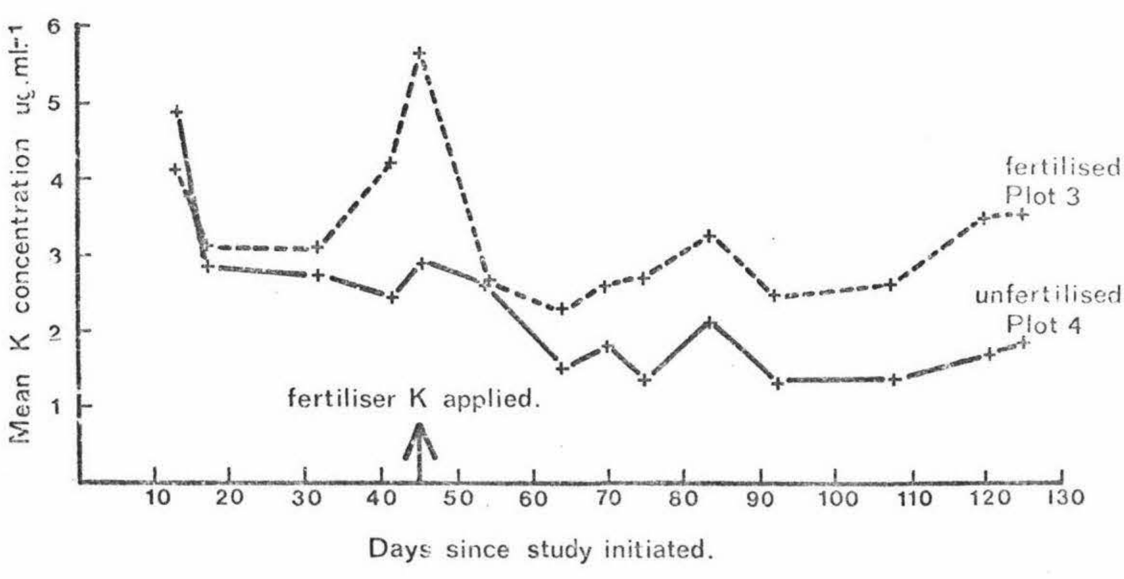


Figure 10 Mean dissolved K concentrations in leachate discharged from paired unfertilised and fertilised plots in each tile drainage event in 1977.

c) Plots 5 and 6.

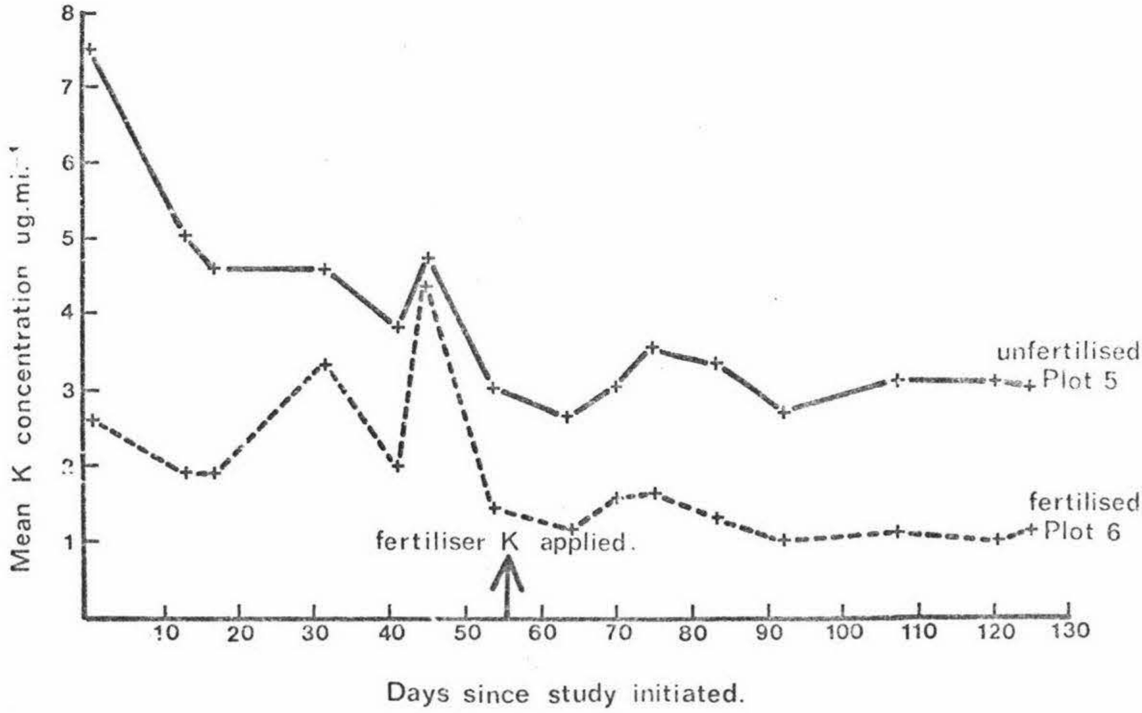
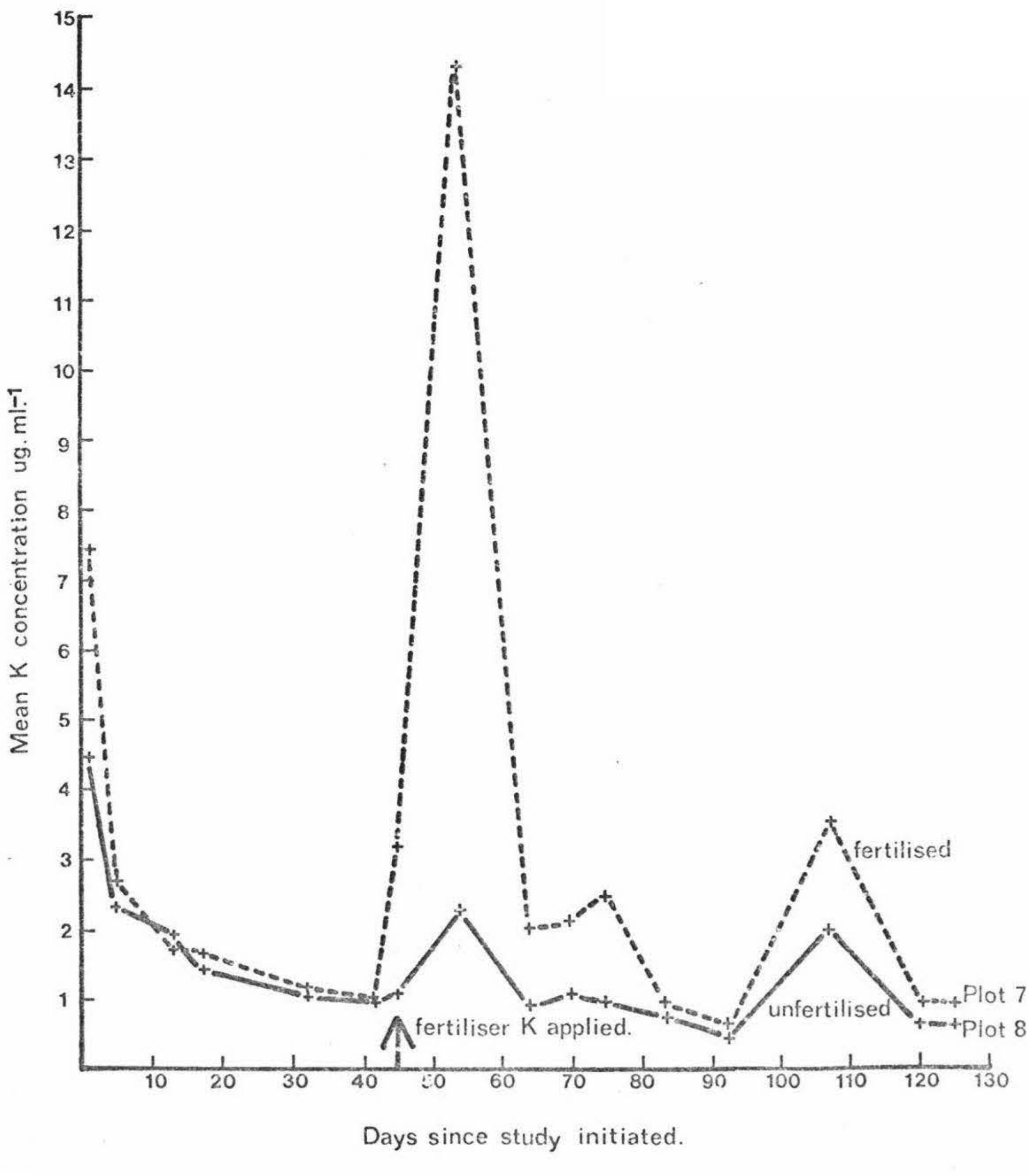


Figure 10 Mean dissolved K concentrations in leachate discharged from paired unfertilised and fertilised plots in each tile drainage event in 1977.

d) Plots 7 and 8.



subsurface drainage waters, viz.:

(i) mean dissolved K concentrations in selected flow events,

(ii) total dissolved K loadings in these flow events.

Mean dissolved K concentrations and loadings were regressed against K contents of the 20-40 cm, 40-60 cm, 0-40 cm, and 0-60 cm soil intervals. These soil intervals were selected from visual assessment of the graphs, K concentration and K loadings vs soil K levels at all depths. In all instances potassium levels at a particular soil sampling were paired with dissolved K concentrations and K loadings in the drainage event immediately following soil sampling.

Significant (5% level) correlations existed only between mean dissolved K concentrations in the drainage water and water soluble ($r = 0.368$) and ammonium acetate extractable K ($r = 0.293$) in the upper 40 cm of soil.

Potassium loadings were not correlated with soil K levels.

These very poor relationships may be due to several factors including:

(i) selection of soil parameters which do not describe the quantity of K susceptible to leaching and/or

(ii) imprecise characterisation of the soil K status (water soluble and a.a. extractable K).

Water soluble and extractable (a.a.) K levels varied widely (frequently in the order of 30 to 100 kg ha^{-1} (0-60 cm) respectively) over relatively short sampling intervals of 2-3 weeks. These variations, in general not attributable to K fertilisation, exceed the level of change that might be expected in the absence of K fertilisation. It appears, therefore, that the soil sampling techniques may have been inadequate.

The field plots were grazed on a rotational basis for several years prior to, and during, this study. Occasional sampling of K enriched excretal spots and/or K depleted areas may explain the extreme variability in measured K levels. Soil SO_4-S levels discussed earlier did not display such marked variability. However, SO_4-S applied in urine would tend to leach down the profile effectively reducing the application rate.

IV.2.2.3 Fertiliser K recovery in the soil

As only a negligible fraction of the applied K was leached in tile drainage waters, it seems reasonable to assume that this K was largely retained in the upper 60 cm of soil. However, water soluble and ammonium acetate minus water soluble (AA-WS) soil K contents of the 0-10, 10-20, 20-40, 0-40, and in the upper 60 cm of soil in the four unfertilised and four fertilised plots did not significantly differ (t-test) at any sampling after fertiliser K was applied.

Several factors may explain this negligible fertiliser K recovery including:

(i) the extreme variability which existed in extractable K levels (Appendix – Tables 3 and 4) between the replicate plots at each soil sampling (a reflection of non-representative soil sampling), and

(ii) the retention of applied K in forms not extracted with water or ammonium acetate.

The amount of K applied (55 kg ha^{-1}) was very low in relation to the total quantity of AA-WS K already present in the upper 60 cm of soil (average of 564 kg K ha^{-1} on June 24). Therefore, even if representative samples had been obtained, it would be difficult to detect a significant fertiliser effect on AA-WS K levels in the 0-60 cm depth.

IV.2.3 RAINFALL K ADDITIONS

Only 1.40 kg K ha^{-1} was received in the rain over a period of 21 weeks from May 12 to October 30, 1977 (Table XXV).

Measured K concentrations in the rain (Table XXV) were lowest in late winter-early spring. However, even if, as the figures suggest, K concentrations were higher throughout the late spring-early autumn interval, with a yearly rainfall figure of 960 mm (Scotter, unpubl. data), K received in 1977 was unlikely to exceed 3.5 kg ha^{-1}.

Table XXV Rain received, K concentrations in the rain and the total K received during the interval May 12 to October 30, 1977.

Interval between sampling the rain collected	Dissolved K concentrations ($\mu g\ ml^{-1}$)	Rain received (mm)
May 12 - 25	0.47	67
May 25 - June 17	0.38	80
June 17 - 27	0.65	46
June 27 - July 7	0.35	39
July 7 - August 2	0.56	78
August 2 - September 2	0.42	74
September 2 - 30	1.00	97
September 30 - October 7	0.80	28
October 7 to 30	0.62	9

Total rainfall K addition over the period May 12 to October 30 = 1.4 kg ha^{-1}

IV.2.4 GENERAL DISCUSSION

Surface runoff

Results of the present study are important as potassium surface runoff losses from New Zealand pastures have not previously been investigated.

The unfertilised treatment in this study represents the situation where fertiliser K is applied in spring. It may be concluded from the results that losses of fertiliser (potash) K applied in late spring from both drained and undrained pastures on the Tokomaru silt loam will be negligible. Larger losses occur, particularly from undrained pastures, if fertiliser K is applied in autumn. Fertiliser K lost will comprise a small but variable fraction of the K applied, depending on the rainfall pattern immediately following fertilisation.

Losses in the present study are similar to losses reported by Burke *et al.* (1974) in Ireland. In the latter investigation, losses from recently unfertilised pastures were small, ranging from 1.1 - 4.2 kg K ha^{-1} yr^{-1}. Fertiliser K losses from undrained and drained pastures (averaging 7.4% and 2.4% respectively) varied depending on the rainfall pattern immediately following fertilisation. Potassium losses were considerably lower if pastures were tile drained.

Results of the present study also indicate that grazing cattle enhance K runoff losses. Although a grazing effect on nutrient runoff losses other than K have been reported (e.g. Sharpley *et al.*, 1977), this is the first reported finding with regard to potassium.

For reasons discussed with regard to S (IV.1.4), measured dissolved K runoff losses from the small plots used in the present study may differ slightly from losses occurring from paddocks or catchments.

Leaching

The commonly made assumption that K leaching occurs to a minimal extent in K-retentive New Zealand soils in the field was substantiated by findings in the present field investigation.

Results of this study indicate that K losses from pastures fertilised in spring or autumn will be insignificant in relation to the quantity of K applied or annual pasture K requirements.

Leaching losses in this study (averaging 4.36 kg ha^{-1}) closely parallel losses reported in overseas field studies (Bolton *et al.*, 1970; Burke *et al.*, 1974; Kilmer, 1974). In these overseas studies, K tile or catchment drainage water losses from fertilised, grazed and ungrazed pastures were low ($\leq$ 5.5 kg K $ha^{-1} yr^{-1}$).

A greater quantity of water was discharged from the irrigated than non-irrigated plots. However, K concentrations in the leachate were lower. These results suggest that a pool of readily leached soil K existed which was depleted to a greater extent in the irrigated than non-irrigated plots by the greater quantity of water percolating through the soil. The existence of such a pool of readily leached soil K was not supported by soil analyses, as very poor relationships existed between measured soil K levels and K leaching losses. These poor relationships observed may, however, be due to incorrect selection of measured soil K parameters to describe the level of readily leached K and/or imprecise determinations of the soil K status.

Total drainage water losses

In the present investigation surface runoff and leaching losses were measured at different sites on the Tokomaru silt loam. Nevertheless, the results of these studies indicate that, irrespective of whether fertiliser K is applied in autumn or late spring, total drainage water K losses from drained pastures were unlikely to exceed 5.0 kg K ha^{-1} in 1977.

The importance of the leaching component of drainage water losses from undrained pastures was not investigated. However, potassium leaching losses from undrained pastures are likely to be smaller than losses from drained pastures because of reduced water infiltration. Hence total drainage water losses from undrained pastures fertilised in spring are also likely to be low. Research is required to confirm this hypothesis. Fertiliser K lost from undrained, gently sloping pastures fertilised in autumn may be significantly higher because of a larger surface runoff loss. This loss will, however, only comprise a small fraction of the applied K.

Rainfall analyses indicated that total drainage water losses from drained pastures were likely to be largely offset by K received in the rain in 1977.

A comparison between measured drainage water losses and reported losses associated with grazing animals (e.g. 64 kg K ha^{-1} on high producing dairy farms (New Zealand Dairy Exporter, July 1978); 45 kg K ha^{-1} on sheep farms (During, 1972)) indicates that surface runoff and leaching were unimportant K loss mechanisms within the soil-plant-animal cycle. Results indicate that the occurrence of pasture K deficiencies on K retentive yellow-grey earth soils is not attributable to drainage water losses.

CHAPTER V CONCLUSIONS

This study has shown that surface and subsurface drainage are important S loss mechanisms in the Tokomaru silt loam, a low SO_4-S retentive yellow-grey earth soil.

Subsurface drainage losses from grazed pastures fertilised in spring (average 11 kg ha^{-1}) were likely to comprise an appreciable fraction of the total losses occurring from the soil-plant-animal cycle. The application of superphosphate S in late autumn resulted in the loss of an appreciable fraction (10.4% or 4.5 kg S ha^{-1}) of this fertiliser S (43 kg ha^{-1}) in the tile drainage water. Fertiliser S lost from the major plant S uptake zone (0-20 cm) was considerably greater.

The significance of surface runoff as a loss mechanism depends on the method of drainage and fertiliser practices. Surface runoff was not an important S depleting process

(i) at drained or undrained, gently sloping sites if fertiliser S was applied in spring, or

(ii) at drained sites if fertiliser S was applied in autumn.

However, autumn applied fertiliser S (solution and solid superphosphate S) losses were significant ($\geq$ 8%). Surface runoff is likely to be an important drainage component in all the yellow-grey earth soils. As most of these soils are undrained and superphosphate is frequently applied in autumn, this loss mechanism will be important.

Total drainage water losses were likely to comprise an appreciable fraction of the total S losses occurring from the soil-plant-animal cycle. However, where superphosphate was applied in late spring, drainage water losses from non-irrigated drained pastures were likely to be balanced by S received in the rain. Rainfall additions would not balance losses from irrigated pastures fertilised in spring or pastures fertilised in late autumn.

For maximum efficiency it would be preferable to apply superphosphate to weakly SO_4-S retentive soils such as the Tokomaru silt loam at times other than late autumn, winter or early spring. Under the conditions likely to prevail at this time fertiliser S drainage water losses may comprise an appreciable fraction of the S applied. Consideration should be given to applying elemental S when conditions favour leaching.

Drainage water (surface and subsurface) losses of K are low even when fertiliser K is applied at a time when conditions favour losses. Surface runoff is a more important loss mechanism than leaching but will only be of consequence when heavy rain immediately follows fertilisation.

CHAPTER VI SUMMARY

A review of relevant literature showed that little research had been undertaken on the magnitude of S and K drainage water losses. The principal aim of this study was, therefore, to investigate the extent of S and K movement in surface and subsurface drainage waters in a yellow-grey earth soil. To evaluate the possible significance of these losses in inducing S and K pasture deficiencies, rainfall S and K additions were investigated. An attempt was made to predict S and K losses in tile drainage waters from soil S and K levels.

Dissolved S and K surface runoff losses from unfertilised and fertilised pastures were measured at gently sloping undrained (1976, 1977), and mole and tile drained (1977) sites on the Tokomaru silt loam.

Dissolved SO_4-S tile drainage water losses from four unfertilised, and four S and K fertilised, pastures in 1977 were measured. Two unfertilised and two fertilised plots had been irrigated each summer of the preceding five years. Fertiliser S and K leaching was also monitored from changing soil levels, determined at 2-3 weekly intervals over the autumn-spring interval.

Rainfall received during the interval May 12 to October 30, 1977 was analysed to evaluate likely annual S and K additions from this source.

Subsurface dissolved SO_4-S tile drainage water losses from unfertilised, non-irrigated plots in 1977 averaged 7.50 kg ha^{-1} Unfertilised plots irrigated the preceding summer lost an additional 6.7 kg SO_4-S ha^{-1} (i.e. a total average of 14.2 kg SO_4-S ha^{-1}).

The addition of superphosphate (43 kg S ha^{-1}), after the tile drainage season had begun, significantly enhanced subsequent leaching losses. Approximately 10% of the applied S was leached in tile drainage waters before the drainage season concluded 17 weeks later. In total 15.2 kg SO_4-S ha^{-1} was discharged from the two non-irrigated, fertilised plots in 1977. The two irrigated, fertilised plots lost, on average, 18.64 kg SO_4-S ha^{-1}.

In addition to the loss of 4.5 kg ha^{-1} fertiliser S in tile drainage water, another 13.8 kg ha^{-1} of this applied S was recovered, 15 weeks after fertilisation, as water soluble SO_4-S leached beyond the 20 cm depth (i.e. below the depth from which plants are likely to obtain most of their S requirements).

An application of 43 kg S ha^{-1} in July nevertheless maintained the average SO_4-S content of the upper 20 cm of soil in spring, at a fairly high level (22.2 kg water soluble SO_4-S ha^{-1}). Water soluble SO_4-S levels in the unfertilised plots in spring were considerably lower (average 7.9 kg water soluble SO_4-S ha^{-1} 0-20 cm).

Surface runoff SO_4-S losses from gently sloping unfertilised, undrained and drained plots were low. Only 0.9 kg SO_4-S ha^{-1} was discharged from an unfertilised, undrained pasture over a period of six weeks in 1976. Only 0.2 kg ha^{-1} was lost from a drained plot during this interval. On average, 0.8 kg SO_4-S ha^{-1} was discharged in surface runoff waters from unfertilised, undrained pastures throughout a three month interval in 1977.

S fertilisation increased SO_4-S runoff losses. An appreciable fraction (8%) of the S applied in autumn 1976 was lost from an undrained plot in six weeks. Mole and tile drainage reduced the fertiliser S runoff loss to a minimal fraction (1.7%) of the S applied. Undrained pastures, fertilised and grazed in 1977 (one 24 hour cattle grazing event) lost considerably more SO_4-S in surface runoff (i.e. on average, an additional 7.2 kg SO_4-S ha^{-1}) than unfertilised plots.

Regression analyses indicated that dissolved SO_4-S concentrations in tile drainage waters, but not SO_4-S loadings, were significantly related to water soluble soil SO_4-S levels. It was concluded that losses may be predicted within a reasonable degree of accuracy from soil SO_4-S levels, determined at frequent intervals during the drainage season, if the quantity of water percolating through the soil is measured.

A total of 3.1 kg S ha^{-1} was received in the rain over a 22 week interval in 1977. The results indicate that S received in the rain throughout 1977 was likely largely to offset drainage water losses from the unfertilised, non-irrigated pastures. A net loss of S from the unfertilised, irrigated pastures and fertilised pasture was likely to have occurred. Surface runoff losses from undrained, fertilised pastures in 1977 were likely to be largely offset by S received in the rain.

From these results it was concluded that SO_4-S leaching is an important S depleting process in the Tokomaru silt loam. Surface runoff is not an important process unless undrained pastures are fertilised in autumn or winter, when an appreciable fraction of the applied S may be lost.

Dissolved K tile drainage water losses from unfertilised and fertilized grazed pastures in 1977 averaged 4.66 and 4.05 kg ha^{-1} respectively. Irrigation did not enhance K leaching. Potassium fertiliser (55 kg ha^{-1}) did not influence measured water soluble and ammonium acetate extractable soil K levels and hence fertiliser K leaching within the upper 60 cm could not be monitored.

Dissolved K surface runoff losses from unfertilised, undrained pastures on the Tokomaru silt loam in a six week winter interval in 1976, and throughout winter in 1977, were low, averaging 1.1 kg ha^{-1} and 1.35 kg ha^{-1} respectively. Unfertilised, mole and tile drained runoff plots lost only 0.3 kg ha^{-1} in 1976.

The addition of potash fertiliser increased K runoff loss from both drained (1976) and undrained (1976, 1977) plots. Fertiliser K losses varied. A minimal fraction (3.1%) of the K applied (50 kg K ha^{-1}) to an undrained plot in 1976 was discharged in the surface runoff. Only 1.7% of the K applied was discharged from a drained plot. In 1977, grazing (one 24 hour cattle grazing event) and K fertilisation (55 kg K ha^{-1}) enhanced runoff losses from undrained plots by, on average, 4.20 kg ha^{-1}. Most of the fertiliser and excretal K lost was transported downslope in the first few runoff events following treatment.

Only 1.06 kg K ha^{-1} was received in the rainfall over a 22 week interval in 1977.

The results, therefore, indicate that K received in the rain in 1977 was unlikely to balance K drainage water losses from drained pastures. The small net loss resulting would deplete the soil K to a negligible extent. Surface runoff losses from the undrained, unfertilised pastures would be offset by rainfall K additions. Runoff losses from the undrained, fertilised pastures would not be balanced by K received in the rain.

From these findings it was concluded that the occurrence of K deficiencies in high producing pastures on K retentive yellow-grey earth soil is not attributable to extensive K movement in surface and subsurface drainage waters.

No relationship was found between measured water soluble or ammonium acetate extractable soil K levels and leachate K concentrations or loadings.

APPENDIX TABLE 1 Grazing dates and stocking rates

Plot	Intervals when grazed from May to October incl.	Stocking rates store lambs/ha^{-1}
1	3/5 - 4/5	592
	1/6 - 3/6	592
	11/7 - 15/7	280
	10/8 - 12/8	112
	7/9 - 12/9	160
	30/9 - 4/10	176
2	2/5 - 3/5	592
	25/5 - 27/5	592
	27/6 - 29/6	592
	8/8 - 10/8	224
	12/9 - 14/9	336
3	11/5 - 13/5	592
	22/6 - 24/6	592
	3/8 - 8/8	88
	4/9 - 7/9	192
	11/10 - 14/10	688
4	23/5 - 25/5	592
	29/6 - 1/7	592
	3/8 - 8/8	72
	4/9 - 7/9	144
	8/10 - 14/10	208
5	4/5 - 5/5	592
	7/6 - 9/6	592
	18/7 - 19/7	400
	21/7 - 25/7	96
	18/8 - 24/8	72
	20/9 - 27/9	144
6	5/5 - 6/5	592
	13/6 - 16/6	592
	15/7 - 18/7	280
	28/8 - 29/8	192
	28/9 - 30/9	264
7	16/5 - 18/5	592
	4/7 - 8/7	392
	27/8 - 1/9	72
	1/9 - 2/9	208
	27/9 - 30/9	304
8	18/5 - 20/5	592
	4/7 - 8/7	240
	27/8 - 2/9	80
	27/9 - 30/9	304

APPENDIX TABLE 2 Water soluble SO_4-S levels at various depth intervals in each of the eight plots, at each sampling ($\mu g/cm^3$ soil).

Date	Soil depth sampled (cm)	Plot 1	2	3	4	5	6	7	8
May 18th	0-10	8.72	11.96	14.01	8.59	15.55	8.90	10.57	8.90
	10-20	5.86	12.61	7.67	10.00	10.90	13.20	13.60	9.05
	20-40	7.98	13.66	13.04	9.54	10.89	13.97	12.60	10.03
	40-60	14.50	16.04	8.60	15.02	19.85	10.04	13.77	18.63
May 31st	0-10	5.78	6.26	6.16	3.81	5.38	4.74	6.94	10.29
	10-20	6.55	6.30	5.88	2.44	5.56	5.05	7.31	4.66
	20-40	14.58	4.82	4.90	2.15	8.36	6.76	11.03	5.25
	40-60	14.58	9.33	10.58	2.77	15.31	10.11	15.50	13.88
June 24th	0-10	6.39	4.28	6.10	5.15	4.89	6.30	6.03	5.29
	10-20	6.34	6.55	6.97	6.15	8.13	9.20	7.81	4.45
	20-40	8.86	8.82	14.70	7.64	12.82	10.61	11.39	8.06
	40-60	14.21	8.20	12.15	15.71	16.82	16.04	16.80	14.47
July 12th	0-10	10.50	61.40	23.37	6.34	5.64	33.43	21.00	5.27
	10-20	3.15	7.60	6.63	3.34	4.07	9.01	11.68	6.77
	20-40	5.81	18.43	7.67	3.45	6.39	9.47	10.91	9.56
	40-60	8.76	16.69	11.91	6.69	16.98	16.33	21.71	11.23
Aug. 3rd	0-10	3.46	16.63	19.63	4.27	3.54	18.28	20.44	3.35
	10-20	2.65	15.35	12.83	2.31	3.69	12.92	10.02	4.03
	20-40	5.00	7.32	9.11	3.09	7.35	13.01	9.85	5.48
	40-60	15.56	9.28	11.39	4.94	11.66	11.39	15.76	13.25
Aug. 19th	0-10	3.30	8.37	14.42	6.37	1.81	13.80	10.35	2.97
	10-20	2.58	11.40	22.59	1.61	2.56	11.50	9.14	4.10
	20-40	6.84	9.53	16.88	4.48	5.39	7.94	8.28	5.19
	40-60	12.96	8.21	11.55	11.55	13.12	11.39	9.44	10.94
Aug. 30th	0-10	6.26	12.88	16.07	3.67	4.56	14.36	11.29	5.11
	10-20	2.33	12.81	21.99	3.47	2.52	15.18	9.42	1.92
	20-40	3.43	5.88	12.94	3.90	6.76	11.03	9.33	4.38
	40-60	10.66	8.42	9.64	5.72	18.92	10.98	10.82	8.99
Sept. 27th	0-10	5.08	11.15	8.50	4.10	3.35	8.73	19.74	4.68
	10-20	3.94	8.13	9.42	1.99	2.56	11.66	14.09	2.90
	20-40	8.13	13.16	13.82	4.85	5.51	13.60	12.20	6.95
	40-60	18.71	15.07	11.91	7.13	13.01	16.36	15.76	12.20
Oct. 13th	0-10	3.53	7.96	7.78	3.11	4.91	8.94	7.88	2.84
	10-20	3.40	11.30	7.94	3.09	5.48	10.42	12.07	5.23
	20-40	6.84	15.19	14.88	5.22	8.20	14.96	11.57	8.57
	40-60	11.99	14.86	15.10	13.82	12.56	16.69	14.58	17.42

APPENDIX TABLE 3 Water soluble k levels at various depth intervals in each of the eight plots, at each sampling ($\mu g/cm^3$ soil).

Date	Soil depth sampled (cm)	Plot 1	2	3	4	5	6	7	8
May 18th	0-10	39.4	70.0	32.8	54.9	53.7	32.7	3.5	38.3
	10-20	13.8	42.3	6.1	13.9	15.3	10.0	6.1	8.1
	20-40	6.4	35.0	14.4	8.7	9.6	7.1	2.5	7.2
	40-60	9.8	15.0	15.8	9.6	8.5	18.6	9.3	11.8
May 31st	0-10	69.5	32.5	18.5	21.9	44.9	17.8	20.8	31.2
	10-20	31.4	12.6	12.8	11.9	26.2	11.6	11.9	13.2
	20-40	19.6	14.1	14.2	9.0	22.2	14.9	20.3	20.4
	40-60	13.8	20.9	13.7	11.6	25.4	14.5	5.1	16.5
June 24th	0-10	51.0	24.9	23.8	17.6	42.9	15.2	7.1	15.5
	10-20	18.5	11.0	15.0	11.9	23.1	10.3	5.4	10.1
	20-40	40.3	15.2	28.4	13.5	22.2	9.9	10.6	20.5
	40-60	22.6	19.6	17.2	13.8	13.9	16.0	4.8	21.4
July 12th	0-10	24.0	67.8	15.5	13.9	11.5	34.0	12.8	25.6
	10-20	12.5	21.5	5.2	10.3	4.6	14.1	5.2	13.0
	20-40	9.5	13.8	7.2	12.5	10.9	10.6	6.0	8.2
	40-60	6.3	12.8	30.2	9.4	15.9	11.6	6.1	10.0
Aug.3rd	0-10	14.2	60.2	28.2	12.8	16.2	16.8	18.6	12.4
	10-20	10.1	18.6	15.0	9.0	15.3	10.3	3.7	7.4
	20-40	16.8	13.3	17.6	11.1	27.5	17.7	14.0	13.7
	40-60	24.9	35.3	27.4	19.6	7.3	61.9	28.0	21.6
Aug.19th	0-10	19.8	13.5	20.8	25.5	11.9	13.7	5.8	11.9
	10-20	16.3	14.2	9.6	15.9	8.7	8.5	2.7	5.4
	20-40	17.1	9.8	12.0	13.6	10.6	9.0	6.6	5.3
	40-60	17.1	12.2	15.9	16.2	6.6	7.2	10.2	10.5
Aug.30th	0-10	21.9	15.7	13.5	12.0	10.4	15.4	6.0	6.1
	10-20	14.3	10.0	9.3	5.6	6.1	11.4	3.5	5.0
	20-40	14.1	8.2	10.7	10.6	12.3	11.8	6.7	9.1
	40-60	12.0	14.9	14.0	6.8	8.9	6.6	7.6	9.9
Sept.27th	0-10	13.0	24.3	25.7	12.1	12.0	12.4	6.1	7.3
	10-20	7.5	18.7	12.8	10.2	7.7	9.4	3.7	5.1
	20-40	8.5	13.0	11.1	10.5	16.4	10.2	6.1	8.0
	40-60	9.1	11.9	12.7	10.8	4.8	16.8	13.7	4.0
Oct.13th	0-10	22.8	29.9	16.8	9.3	36.3	13.1	7.0	7.6
	10-20	14.2	20.3	9.5	8.6	16.7	10.2	7.7	5.0
	20-40	14.6	15.1	16.2	15.5	19.7	11.5	11.4	11.4
	40-60	13.7	41.5	11.3	17.3	19.2	23.4	20.0	13.3

APPENDIX TABLE 4 Ammonium acetate k levels at various depth intervals in each of the eight plots at each sampling ($\mu g/cm^3$ soil).

Date	Soil depth sampled (cm)	Plot 1	2	3	4	5	6	7	8
May 18th	0-10	225	431	224	309	295	213	49	204
	10-20	168	328	86	111	142	80	84	83
	20-40	119	351	101	72	130	60	31	47
	40-60	110	201	105	53	110	57	45	20
May 31st	0-10	340	193	146	203	258	120	147	197
	10-20	180	171	100	76	169	60	82	89
	20-40	116	164	111	69	127	77	54	61
	40-60	87	101	87	60	69	52	31	24
June 24th	0-10	387	244	241	207	307	140	63	218
	10-20	207	138	157	113	214	70	33	76
	20-40	178	125	121	85	175	69	32	59
	40-60	66	70	74	52	70	49	33	36
July 12th	0-10	203	476	175	195	148	248	97	229
	10-20	151	246	73	83	79	142	50	133
	20-40	142	248	77	177	91	91	47	82
	40-60	86	83	67	90	69	79	32	31
Aug.3rd	0-10	174	420	279	161	151	143	177	164
	10-20	127	198	163	86	97	67	101	91
	20-40	129	157	137	64	89	60	107	68
	40-60	95	102	134	43	79	59	52	40
Aug.19th	0-10	228	147	180	232	144	120	59	132
	10-20	161	108	95	164	101	57	30	66
	20-40	131	95	87	137	89	65	55	44
	40-60	81	65	68	80	74	35	30	26
Aug.30th	0-10	234	198	113	153	118	159	80	64
	10-20	191	118	69	79	95	118	67	50
	20-40	204	138	71	85	90	83	78	37
	40-60	117	111	90	53	76	97	38	32
Sept.27th	0-10	157	273	202	133	136	100	69	87
	10-20	116	214	125	124	91	77	38	69
	20-40	107	199	111	68	80	66	32	64
	40-60	98	112	72	71	76	44	22	37
Oct.13th	0-10	231	270	149	114	271	121	71	59
	10-20	170	193	68	96	172	91	57	52
	20-40	126	126	80	85	114	71	55	38
	40-60	61	154	119	69	106	53	33	30

BIBLIOGRAPHY

Allaway, W.H. and J.F. Thompson (1966).
Sulphur in the nutrition of plants and animals. Soil Sc. 101: 240-247.

Allway, F.J., A.W. Marsh and W.J. Methley (1937).
Sufficiency of atmospheric sulphur for maximum crop needs. p. 229-238. In Proc. Soil Sc. Soc. Am. 2.

Arnold, P.W. (1960).
Nature and mode of weathering of soil potassium reserves. J. Sc. Fed. Agric. 11: 285-292.

Aylmore, L.A.G., M. Karim and J.P. Quirk (1971).
Dissolution of gypsum, monocalcium phosphate and superphosphate fertilisers in relation to particle size and porous structure. Aust. J. Soil. Res. 9: 921-932.

Balasubramaniam, V., Y. Kanchiro, P.S. Rao and R.E. Green (1973).
Field study of solute movement in a highly aggregated Oxisol with intermittent flooding. I. Nitrate. J. Environ. Qual. 2: 359-362.

Banwart, W.L. and J.M. Bremner (1976).
Volatilisation of sulphur from unamended and sulphate treated soils. Soil Bio. Biochem. 8: 19-22.

Barrow, N.J. (1969).
Effects of adsorption of sulphate by soil on the amount of sulphate present and its availability to plants. Soil Sc. 108: 193-201.

__________ (1974).
Western Australia. p.32-41. In MacLachlan, K.D. ed. Handbook of sulphur in Australian agriculture. C.S.I.R.O., Melbourne, Australia.

__________ (1975).
Reactions of fertiliser sulphate in soil. p.50-57. In MacLachlan, K.D. ed. Sulphur in Australasian agriculture. Sydney University Press.

Barrow, N.J. and L.J. Lambourne (1962).
Partition of excreted nitrogen, sulphur, and phosphorus between faeces and urine of sheep fed pasture. Aust. J. Agric. Res. 13: 461-471.

Barrow, N.J. and K. Spencer (1939).
Lateral movement of fertiliser sulphur. J. Aust. Inst. Agric. Sc. 25: 208-209.

Barton, A.F.M. and N.M. Wilde (1971).
Calcium sulphate as a fertiliser. The dissolution rates of gypsum and anhydrite. N.Z. J. Sc. 14: 608-620.

Bates, T.E. (1971).
Factors affecting critical nutrient concentrations in plants and their evaluation : A review. Soil Sc. 112: 116-130.

Blakemore, L.C., T.W. Collie and A.J. Metson (1968).
Sulphur (Ch. 7.8) p. 103-109. In Soils of New Zealand, N.Z. Soil Bur. Bull. 26 (2), Govern. Printer, Wellington.

Blakemore, L.C., T.E. Ludecke, M.J. Leamy and A.J. Metson (1969).
Study of the pattern of sulphur responses shown by dryland lucerne on some brown-grey earths. N.Z. J. Agric. Res. 12: 333-351.

Bolton, E.F., J.W. Aylesworth and F.R. Hore (1970).
Nutrient losses through tile drains under three cropping systems and two fertility levels on a Brookston clay soil. Can. J. Soil Sc. 50: 275-279.

Burke, A.S. (1975).
Effect of long-term irrigation on stony soils of the Canterbury Plains. N.Z. J. Expt. Agric. 1: 131-138.

Burke, W., J. Mulqueen and P. Bulter (1974).
Fertiliser losses in drainage water from a surface water gley. Irish J. Agric. Res. 13: 204-214.

Chao, T.T., M.E. Harward and S.C. Fang (1962a).
Movement of ^{35}S-tagged sulphate through soil columns, p.27-37. In Proc. Soil Sc. Soc. Am. 26.

———— (1962b).
Adsorption and desorption phenomena of sulphate ions in soils. p.243-247. In Proc. Soil Sc. Soc. Am. 26.

Copper, M. and D.E. Hogg (1966).
Leaching losses of sulphate from superphosphate and gypsum applied on a soil from rhyolitic pumice. N.Z. J. Agric. Res. 9: 345-349.

Cowie, J.D. (1972).
Extended legend of soil map of the Kairanga County, N.I., N.Z. Explanatory notes. N.Z. Soil Bur. Publ. 538.

Cowie, J.D., B.S. Kear and G.E. Orbell (1977).
Soils and agriculture of the Kairanga County, N.I., N.Z. N.Z. Soil Bur. Bull. 33.

Cowling, D.W., L.H.P. Jones and D.R. Lockyer (1973).
Increased yield through correction of sulphur deficiencies in ryegrass exposed to sulphur dioxide. Nature 243: 479.

Davies, E.B. and D.E. Hogg (1960).
Potassium losses in pastures. N.Z. J. Agric. 100: 491-492.

Davies, E.B., D.E. Hogg and H.G. Hopewell (1962).
Extent of return of nutrient elements by dairy cattle: Possible leaching losses. p. 715-720. In Trans. Jt. Meet. Comm. IV and V Int. Soil Sc., N.Z.

Dreibelbis, F.R. (1957).
Soil type and land use effects on percolation of soil water through monolith lysimeters. p. 358-363. In Proc. Soil Sc. Soc. Am. 18.

During, C. (1972).
Fertilisers and soils in New Zealand farming. N.Z. Dept. Agric. Bull. No.409, pp. 312. Govern. Printer, Wellington.

During, C. and M. Cooper (1974).
Sulphate nutrition and movement in a soil with high sulphate sorption characteristics. N.Z. J. Expt. Agric. 2: 45-51.

During, C. and W.C. Weeda (1973).
Some effects of cattle dung on soil properties, pasture production and nutrient uptake. II. Influence of dung and fertiliser on sulphate sorption, pH, C.E.C. and the K, Mg, Ca and N economy. N.Z. J. Agric. Res. 16: 431-438.

Ensminger, L.E. (1954).
Some factors affecting adsorption of sulphate by Alabama soils. p. 259-264. In Proc. Soil Sc. Soc. Am. 18.

Fieldes, M. (1968).
Clay mineralogy (Ch. 6.3) p. 22-39. In Soils of New Zealand. N.Z. Soil Bur. Bull. 26 (2). Govern. Printer, Wellington.

Fieldes, M. and L.D. Swindale (1954).
Chemical weathering of silicates in soil formation. N.Z. J. Sc. Tech. 36B: 140-154.

Fox, R.L., R.A. Olson and H.F. Rhoades (1964).
Evaluating the S-status of soil by plant and soil tests. p. 243-246. In Proc. Soil Sc. Soc. Am. 28.

Freney, J.R. (1961).
Some observations on the nature of organic sulphur compounds in soil. Aust. J. Agric. Res. 12: 424-432.

Freney, J.R., N.J. Barrow and K. Spencer (1962).
A review of certain aspects of sulphur as a soil constituent and plant nutrient. Pl. Soil 17: 295-308.

Fried, M. and H. Broeshart (1967).
The soil-plant system in relation to inorganic nutrition. N.Y. Academic Press. pp. 358.

Gillman, G.P. (1973).
Studies on some deep sandy soils in Cape York Peninsula, North Queensland. 3. Losses of applied phosphorus and sulphur. Aust. J. Expt. Agric. An. Husb. 13: 418-422.

Grace, N.D. and W.B. Healy (1974).
Effect of ingestion of soil on faecal losses and retention of Mn, Ca, P, K and Na in sheep fed two levels of dried herbage. N.Z. J. Agric. Res. 17: 73-78.

Gregg, P.E.H. (1976).
Field investigations into the fate of fertiliser sulphur added to soil pasture systems. Thesis Ph.D., Lincoln College.

Gregg, P.E.H., K.M. Goh and D.W. Brash (1977).
Isotopic studies on the uptake of sulphur by pasture plants. II. Uptake from various soil depths at several field sites. N.Z. J. Agric. Res. 20: 229-233.

Hamvray, J.J. and J.M. Laften (1971).
Plant nutrient losses from the outlet terraces. J. Environ. Qual. 3: 351-356.

Harward, M.E. and H.M. Reisenauer (1966).
Reactions and movement of inorganic soil sulphur. Soil Sc. 101: 326-335.

Hilder, E.J. (1964).
The distribution of plant nutrients by sheep at pasture. p.241-248. In Proc. Aust. Soc. Anim. Prod. 5.

——————— (1966).
Distribution of excreta by sheep at pasture. p. 977-980. In Proc. X Int. Grassld. Cong., Helsinki.

Hingston, F.J. (1959).
The loss of applied P and S from soils under pasture in West Australia. J. Aust. Inst. Agric. Sc. 25: 209-213.

Hogg, D.E. (1965).
Studies on leaching losses of S from pumice soils, yellow-brown loams and sands. p. 123-128. In Proc. 27th Conf. N.Z. Grassld. Ass.

——————— (1968)
Lysimeter studies of K losses from urine applied to pasture. p. 631-638. In Trans. 9th Int. Cong. Soil Sc. 3.

——————— (1975)
Lysimeter studies of nutrient losses from urine and dung applied on pasture. N.Z. Soil News 23 (4): 110-112.

Hogg, D.E. and M. Cooper (1964).
Laboratory studies on loss of P, S and K from Te Kopuru sand. N.Z. J. Agric. Res. 7: 364-374.

Hogg, D.E. and M.R.J. Toxopeus (1966).
Studies on the retention of sulphur by yellow-brown pumice soils. N.Z. J. Agric. Res. 9: 93-97.

Hopper, M.J. and C.R. Clement (1966).
The supply of K to grassland. An integration of field, pot and glasshouse investigations. p. 237-246. In Trans. Int. Soc. Soil Sc. Comm II and IV, Aberdeen.

Hume, I.D. and P.R. Bird (1970).
Synthesis of microbial protein in the rumen. IV. The influence of the level and form of dietary S. Aust. J. Agric. Res. 21: 315-322.

Hutchinson, K.J. (1973).
Short communication, III World Conf. Animal Prod., Melbourne, Australia.

Hutton, J.B., K.E. Jury and E.B. Davies (1967).
Studies of the nutritive value of New Zealand dairy pastures. V. The intake and utilisation of K, Na, Ca, P and N in pasture herbage by lactating dairy cattle. N.Z. J. Agric. Res. 10: 367-388.

Jackman, R.H. (1964).
Accumulation of organic matter in some New Zealand soils under permanent pasture. I. Pattern of change of organic C, N, S and P. N.Z. J. Agric. Res. 7: 445-471.

Jensen, J. (1963).
Some investigations on plant uptake of sulphur. Soil Sc. 93: 63-68.

Johnson, C.M. and H. Nishita (1952).
Micro-estimation of sulphur in plant materials, soil and irrigation waters. Anal. Chem. 24: 736-742.

Jones, M.B., W.E. Martin and W.A. Williams (1968).
Behavior of sulphate-sulphur and elemental sulphur in three Californian soils in lysimeters. p. 535-540. In Proc. Soil Sc. Soc. Am. 32.

Kilmer, V.J., J.W. Gilliam, J.F. Lutz, R.T. Joyce and C.D. Eklund (1974).
Nutrient losses from fertilised grassed watersheds in Western North Carolina. J. Environ. Qual. 3 (3): 214-219.

Lovelock, J.E., R.J. Magg and R.A. Rasmussen (1972).
Atmospheric dimethyl sulphide and the natural sulphur cycle. Nature, London, 237: 452-53.

MacLachlan, K.D. (1975).
The residual value of a sulphur fertiliser. p. 58-67. In MacLachlan, K.D. ed. Sulphur in Australasian agriculture, Sydney University Press.

May, P.F., A.R. Till and A.M. Downes (1968).
Nutrient cycling in grazed pastures. I. A preliminary investigation on the use of ^{35}S gypsum. Aust. J. Agric. Res. 19: 531-543.

McKell, C.M. and W.A. Williams (1960).
A lysimeter study of fertiliser sulphur on an annual rangeland. J. Range Mgmt. 13: 113-117.

McNaught, K.J. (1958).
Potassium deficiency in pastures. I. Potassium content of legumes and grasses. N.Z. J. Agric. Res. 1: 148-181.

Metson, A.J. (1968).
The long-term potassium supplying power of New Zealand soils. p. 621-630 In Trans. 9th Int. Cong. Soil Sc., Australia. 3.

———— (1969).
Sulphur status of New Zealand soils. p. 73-84. In Proc. 12th Tech. Conf. Fert. Manu. Res. Ass.

———— (1973).
Sulphur in forage crops. The Sulphur Inst. Tech. Bull. No.20. pp. 24.

Metson, A.J. and F.B. Hurst (1953).
Effects of sheep dung and urine on a soil under pasture at Lincoln, Canterbury, with particular reference to K and N equilibria. N.Z. J. Sc. Tech. 35A: 327-359.

Miller, R.B. (1968).
Flows and cycles of macro- and micro-elements in a forest soil and its environment. p. 323-331. In Trans. IX Int. Cong. Soil Sc. 4.

Muller, F.B. (1975).
Sulphur received in rainfall and leached from a yellow-brown loam. N.Z. J. Sc. 18 (2): 234-252.

Muller, F.B. and G. McSweeney (1974).
Effect of granulation of superphosphate on movement of phosphorus and sulphur in two soils. N.Z. J. Expt. Agric. 2: 53-62.

————————————— (1977)
Movement of plant nutrients through Tokomaru silt loam. p. 87-97. In Proc. Tech. Conf. N.Z. Fert. Manu. Res. Ass. 1.

Munson, R.D. and W.L. Nelson (1963).
Movement of applied potassium in soils. J. Agric. Food Chem. 11: 193-201.

Nicolson, A.J. (1970).
Soil sulphur balance studies in the presence and absence of growing plants. Soil Sc. 109: 345-350.

Olsen, R.A. (1957).
Adsorption of sulphur dioxide from the atmosphere by cotton plants. Soil Sc. 84: 107-111.

Ozanne, P.G., C.J. Asher and D.J. Kirton (1965).
Root distribution in a deep sandy soil and its relationship to the uptake of added potassium by pasture plants. Aust. J. Agric. Res. 16: 785-800.

Petersen, R.G., H.L. Lucas and W.W. Woodhouse (1956a).
The distribution of excreta by freely grazing cattle and its effect on pasture fertilisation. I. Excretal distribution. Agron. 7: 440-444.

Petersen, R.G., W.W. Woodhouse and H.L. Lucas (1956b).
The distribution of excreta by freely grazing cattle and its effect on pasture fertilisation. II. Effect of returned excreta on the residual concentration of some fertiliser elements. Agron. 7: 444-449.

Peverill, K.L., G.P. Briner and L.A. Douglas (1975).
Changes in extractable sulphur and potassium levels in soils due to oven drying and storage. Aust. J. Soil Res. 13: 69-75.

Peverill, K.L. and L.A. Douglas (1976).
Use of undistributed cores of surface soil for investigating leaching losses of sulphur and potassium. Geoderma 16: 193-199.

Pollok, J. (1975).
A comparative study of certain New Zealand and German soils formed from loess. Thesis PhD., University of Bonn. pp. 312.

Reitemeir, R.F. (1951).
Soil potassium. p. 113-164. In Norman, A.G. ed. Adv. Agron. 3. Academic Press Inc., N.Y.

Sachder, M.S. and P. Chhabra (1974).
Transformations of ^{35}S-labelled sulphate in aerobic and anaerobic conditions. Pl. Soil 41: 335-341.

Saunders, W.M.H. and A.J. Metson (1959).
Fate of potassium applied to pasture on a soil derived from andesitic ash. N.Z. J. Agric. Res. 2: 1211-1231.

Schroeder, D. (1974).
Relationships between soil potassium and the potassium nutrition of the plant. p. 53-63. In Proc. 10th Cong. Int. Potash Inst., Budapest.

Shamoot, S., L. McDonald and W.V. Bartholomew (1968).
Rhizo-decomposition of organic debris in soil. p. 817-820. In Proc. Soil Sc. Soc. Am.

Sharpley, A.N., R.W. Tillman and J.K. Syers (1977).
Use of laboratory extraction data to predict losses of dissolved inorganic phosphate in surface runoff and tile drainage. J. Environ. Qual. 6: 33-36.

Spencer, K. (1963).
The residual value of a sulphatic fertiliser applied to a basaltic soil. Aust. J. Expt. Agric. Anim. Husb. 3: 180-183.

Stauffer, R.S. and R.H. Rust (1954).
Leaching losses, rainfall and percolation from eight Illinois soils. Agron. J. 47: 207-211.

Swaby, R.J. and R. Fedel (1973).
Microbial production of sulphate and sulphide in some Australian soil. Soil Bio. Biochem. 5: 773-781.

Thompson, L.M. and F.R. Troeh (1973).
Soils and soil fertility. 3rd ed. McGraw-Hill Inc. pp.459.

Till, A.R. (1975).
Sulphur cycling in grazed pastures. p.68-75. In MacLachlan, K.D. ed. Sulphur in Australasian agriculture. Sydney University Press.

Till, A.R. and T.P. McCabe (1976).
Sulphur leaching and lysimeter characterization. Soil Sc. 121: 44-47.

Till, A.R. and P.F. May (1970a).
Nutrient cycling in grazed pastures. II. Further observations with ^{35}S gypsum. Aust. J. Agric. Res. 21: 253-260.

——————————— (1970b).
Nutrient cycling in grazed pastures. III. Studies on labelling of the grazed pasture system by solid ^{35}S gypsum and aqueous Mg $^{35}SO_4$. Aust. J. Agric. Res. 21: 455-463.

——————————— (1971).
Nutrient cycling in grazed pastures. IV. The fate of ^{35}S following its application to a small area in a grazed pasture. Aust. J. Agric. Res. 22: 391-340.

Thorne, D.W. and H.B. Peterson (1954).
Irrigated soils - Their fertility and management. 2nd ed. Blackiston, N.Y. pp. 392.

Toxopeus, M.R.J. (1964).
Investigations into the fertiliser requirements of pumice soils. p. 162-171. In Proc. Ruakura Farmers' Conf.

Walker, T.W. (1956).
The accumulation of organic matter in grassland soils. p. 409-416. In Trans. 6th Int. Cong. Soil Sc.

——————— (1957).
The sulphur cycle in grassland soils. J. Brit. Grassld. Sc. 12: 10-18.

Walker, T.W. and A.F.R. Adams (1958).
Studies on soil organic matter. I. Influence of phosphorus content of parent material on accumulation of C, N, S and organic P in grassland soils. Soil Sc. 85: 307-318.

Walker, T.W. and P.E.H. Gregg (1975).
The occurrence of sulphur deficiencies in New Zealand. p. 145-153 In MacLachlan, K.D. ed. Sulphur in Australasian agriculture. Sydney University Press.

Ward, R.C. (1967).
Principles of Hydrology. London: McGraw-Hill Publ. Co. Ltd.

Warth, F.J. and T.S. Krishan (1937).
Sulphur and sulphur balance experiments with sheep. Ind. J. Vet. Sc. An. Husb. 5: 319-331.

Whitehead, D.C. (1964).
Soil and plant nutrition aspects of the sulphur cycle. Soil Ferts. 27: 1-8.

Williams, C.H. (1968).
Seasonal fluctuations in mineral sulphur under subterranean clover pastures in southern New South Wales. Aust. J. Soil Res. 6: 131-139.

——————— (1969).
Moisture uptake by surface applied superphosphate and movement of the phosphate and sulphate into the soil. Aust. J. Soil Res. 7: 307-316.

——————— (1970).
Effect of particle size on the availability of the phosphorus and sulphur in superphosphate. p. 384-388. In Proc. XI Int. Grassld. Cong.

——————— (1971).
Reaction of surface-applied superphosphate with soil. II. Movement of the P and S into the soil. Aust. J. Soil Res. 9: 95-106.

Williams, C.H. and C.H. Donald (1954).
Fertility and productivity of a podzolic soil as influenced by subterranean clover and superphosphate. Aust. J. Agric. Res. 5: 664-687.

Williams, C.H. and A. Steinbergs (1959).
Soil sulphur fractions as chemical indices of available sulphur in some Australian soils. Aust. J. Agric. Res. 10: 340-352.

Williams, W.A., C.M. McKell and J.N. Reppert (1964).
Sulphur fertilisation of an annual range soil during years of below average rainfall. J. Rge. Mgmt. 17: 1-4.