

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

**A COMPARISON OF THE FATE OF ELEMENTAL SULPHUR AND SULPHATE SULPHUR
BASED FERTILIZERS IN PASTURE SOILS**

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

Sathien Phimsarn

1991

Soil Science

Massey University Library
Thesis Copyright Form

Title of thesis: "A Comparison Of The Fate Of
Elemental Sulphur And Sulphate
Sulphur Based Fertilizers In Pasture Soils

- (1) (a) ~~I give permission for my thesis to be made available to readers in Massey University Library under conditions determined by the Librarian.~~
- (b) I do not wish my thesis to be made available to readers without my written consent for 3 months.
- (2) (a) ~~I agree that my thesis, or a copy, may be sent to another institution under conditions determined by the Librarian.~~
- (b) I do not wish my thesis, or a copy, to be sent to another institution without my written consent for 3 months.
- (3) (a) ~~I agree that my thesis may be copied for Library use.~~
- (b) I do not wish my thesis to be copied for Library use for 3 months.

Signed

Sathien Phimsarn
Sathien Phimsarn

Date

Nov 20, 1991

The copyright of this thesis belongs to the author. Readers must sign their name in the space below to show that they recognise this. They are asked to add their permanent address.

NAME AND ADDRESS

DATE

ABSTRACT

Nitrogen fixation by legumes has a particular requirement for adequate soil sulphur status. Sulphur (S) is a mobile nutrient and is easily leached from aquatic soil environments, therefore regular topdressing with S fertilizer is required to maintain legume vigor and pasture production in most New Zealand pasture soils. Escalating fertilizer costs have focused attention on the efficiency of use of S fertilizers, particularly superphosphate (SSP) and alternative elemental S (S^0) based fertilizers less liable to leaching loss in this aquatic environment.

Field and glasshouse trials, using the resident clover/ryegrass sward on undisturbed soil cores (150 mm diameter, 100 mm depth), were undertaken to determine the comparative short-term fate of SSP and different particle sizes of S^0 . Methods for manufacturing radioactively labelled (^{35}S) fertilizers were developed. In addition, the effect of sheep dung on the short-term immobilization of soil and fertilizer S was also investigated. A simple computer simulation model explaining the observed transformation of soil sulphur and ^{35}S labelled fertilizer was developed.

Initially, the effect of sheep dung on the short-term immobilization of soil and fertilizer S was investigated. Very small amounts (about 2-5%) of plant (clover/ryegrass pasture) S and P, within 100 mm of the area surrounding the dung pellet, were derived from the dung. Under the experimental conditions that prevailed, dung S behaved as a slow release S form causing neither greater immobilization of soil or fertilizer S nor mineralization of soil organic S. It was concluded that the impact of dung return on short-term (< one year) S fertilizer fate need not be considered.

An initial field trial comparing the fate of microfine S^0 (< 0.010 mm) relative to sulphate-based SSP was undertaken on Tokomaru silt loam, a New Zealand yellow-grey earth (Fragiaqualf). The microfine S^0 oxidized within 30 days of application but initially (up to 60 days) was slightly less effective than SSP in terms of plant uptake. Over longer periods of time (150 days) their performances were comparable. Final cumulative plant uptake at 150 days accounted for 13.6% of microfine S^0 and 16.3% of the SSP-sulphate.

The major transformation of ^{35}S from microfine S^0 and ^{35}S labelled gypsum in SSP to soil organic ^{35}S forms occurred in the first 30 days after application. The organic ^{35}S activity formed from $^{35}S^0$ was twice that formed from sulphate-based fertilizer and was mainly carbon-

bonded ^{35}S in the top 33 mm of the pasture soil profile. The amount of organic ^{35}S remaining as carbon-bonded ^{35}S decreased with soil depth and the reverse occurred for the ester-sulphate ^{35}S . By 150 days, greater activity from the microfine $^{35}\text{S}^0$ remained in the soil organic S fraction than from the sulphate- ^{35}S fertilizer, indicating that more soil organic S reserves may be formed through the use of fine S^0 fertilizer than from the sulphate-based fertilizer. This also indicated the advantage of using S^0 in minimizing the S leaching losses in this aquic environment.

An inverse dilution technique using an isotope injector developed at Massey University to uniformly label undisturbed soil cores with carrier-free $^{35}\text{SO}_4^-$ solution was used to measure the impact of S^0 and sulphate-based fertilizers on the fate of soil S. Results were consistent with the labelled fertilizer technique and both techniques indicated rapid incorporation of ^{35}S into soil organic S and that the carbon-bonded S formed was likely to be a subsequent source of mineralized S available to plants.

Soil samples from the preliminary field study were used to evaluate soil preparation and extraction techniques. Soil sampling and preparation techniques were evaluated on the basis that an extract sampling the plant available S pool in soil should have the same ^{35}S specific activity as plant growing on that soil. The average ^{35}S specific activity in a calcium dihydrogen phosphate (CaP-S) (0.04 M) extract from a freeze-dried sample of the top 60 mm of a pasture soil was most closely related to the ^{35}S specific activity of plants growing on that soil. CaP-S extracts from field-moist soil or 0.01 M CaCl_2 extracts from field-moist or freeze-dried soils had higher specific activities than plants. It was concluded that plants were able to extract soil S from soils which was not exchangeable with added $^{35}\text{SO}_4^-$ fertilizers during either the field experiment or extraction with 0.01 M CaCl_2 .

The second series of field and glasshouse trials were conducted to investigate the fate of ^{35}S labelled SSP, gypsum and S^0 of varying particle sizes (<0.150 mm, 0.150-0.250 mm and 0.250-0.500 mm, in granulated and non-granulated forms) in two pasture soils contrasting in mineralogy and fertility status. Under glasshouse conditions, 50 mm of simulated rainfall was applied to each of the undisturbed soil cores during the first 56 days after fertilizer application. For the remainder of the period, cores were watered from below using a saucer. Field cores remained subject to the local climate. Both the rate of oxidation in soil and the efficiency of plant use of S^0 was improved by decreasing its particle size. Relative to soluble SO_4^- -S applied as gypsum or SSP, the plant utilization of *oxidized* S^0 was similar.

Granulation of finer S^0 with or without finely ground phosphate rock had little effect on the

long-term (180 days) oxidation rate or the efficiency with which, after oxidation, finely ground S^0 was taken up plants.

Apart from S^0 of large particle size (>0.150 mm) which had not oxidized, the major fate of fertilizer ^{35}S , either under glasshouse or field conditions, was again in soil organic matter mostly formed in the top 33 mm of the soil. Applications of gypsum and SSP caused ^{35}S to move to the 33-100 mm soil depths but there was no additional influence of P on the depth to which SO_4^{2-} was leached.

A preliminary computer simulation model describing the fate of $^{35}SO_4^{2-}$ -S fertilizer was developed. The model provided a very accurate method of predicting plant uptake of S from both SSP fertilized and unfertilized soil cores. The model also indicated that, at any particular soil depth, on average, actual rates of mineralization and immobilization may exceed root uptake of S by 1.5 to 2 fold (mg S turned over per unit of S taken up by plants). The accuracy of the estimated turnover rate could not be validated because the model gave relatively inaccurate predictions of the measured movement and transformations of ^{35}S tracer added to the soil as SSP. There was, however, relative similarity between the observed and predicted proportional distribution of ^{35}S between soil and plant S forms. Such a distribution supported the concept of using root activity as a modifier of mineralization and immobilization rates in order to describe the extent of these processes at different soil depths.

The study has emphasized the greater importance of the surface few millimeters of pasture soil in S transformations, important in the fate of fertilizer and pasture plant nutrition. There appears to be scope in manipulating S^0 particle size to improve the efficiency of the S fertilizer used.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the guidance, understanding, constructive criticism, encouragement, enthusiasm and endless patience of Dr. M. J. Hedley, my chief supervisor.

My gratitude and appreciation is also extended to the following people for their contributions toward the completion of this thesis

Drs. P.E.H. Gregg and S.K. Saggarr for their readiness to help, constructive criticism and valuable discussion.

Mr. R.W. Tillman; Drs. N.S. Bolan; L.K. Heng; D.R. Scotter; W. Chatupote; K. Sakadevan and P. Loganathan for their advice, comments and assistance throughout the research and during the preparation of this manuscript.

Mrs. M. Horne (nee Wallace); Messrs L. Currie; M. Egges; I.A. Painter and M. Bretherton for technical assistance.

Past and present members of the Soil Science Department for their friendship and encouragement.

Fellow postgraduate students, Mr. A. Hammond, Miss K. Hodgson, Mr. D. Tambunan and Mrs C. Hedley for their friendship and proof-reading.

The Thai Ministry of Agriculture and Cooperatives for providing study leave, the New Zealand Overseas Development Aid Programme for financial assistance, the Fertilizer and Lime Research Centre for facilities.

My family, my brothers and sisters for their love and support.

Finally, Suwaree and Nisanart, my wife and my daughter, for their patience, support and encouragement throughout.

TABLE OF CONTENTS

ABSTRACT	ii
ACKNOWLEDGEMENTS.....	v
TABLE OF CONTENTS	vi
LIST OF FIGURES.....	xiii
LIST OF TABLES.....	xvi
LIST OF APPENDICES.....	xix

CHAPTER 1

INTRODUCTION	1
--------------------	---

CHAPTER 2

A REVIEW OF LITERATURE ON ASPECTS OF SULPHUR CYCLING IN GRAZED PASTURE SYSTEM

2.1	INTRODUCTION	4
2.2	NATURE, FORMS AND DISTRIBUTION OF SOIL SULPHUR.....	4
2.2.1	Total sulphur.....	4
2.2.2	Inorganic sulphur.....	5
2.2.2.1	<i>Readily soluble sulphate-S</i>	5
2.2.2.2	<i>Adsorbed sulphate-S</i>	6
2.2.2.3	<i>Other inorganic S forms</i>	10
2.2.3	Organic sulphur	11
2.2.4	Other methods for characterizing soil organic sulphur	13
2.2.5	Microbial sulphur	14
2.3	BIOLOGICAL TRANSFORMATIONS OF S IN SOIL.....	16
2.3.1	Mineralization	18
2.3.2	Immobilization	21
2.4	PLANT REQUIREMENTS	26
2.4.1	Assessing soil sulphur availability	27
2.4.1.1	<i>Plant analyses</i>	28
2.4.1.2	<i>Soil analyses</i>	30
2.4.1.2.1	<i>Depth of sampling and sample preparations</i>	30
2.4.1.2.2	<i>Extractants</i>	32
	<i>a. Readily soluble sulphate-S</i>	33
	<i>b. Adsorbed plus soluble sulphate-S</i>	33
	<i>c. Readily available and adsorbed sulphate and portions of organic S</i>	34
	<i>d. Other methods</i>	34
	<i>e. Use of radioactive ³⁵S</i>	34
2.4.1.2.3	<i>Interpretation of soil tests</i>	35
2.4.2	Fertilizer S requirements	37
2.4.2.1	<i>S recommendation for pastures in New Zealand</i>	37

	2.4.2.2	<i>Form of fertilizers</i>	39
	2.4.2.3	<i>Efficient use of fertilizer S</i>	41
2.5		THE FATE OF FERTILIZER S IN SOIL.....	42
	2.5.1	Oxidation of S ⁰ in soil.....	43
	2.5.2	The fate of sulphate-S	46
	2.5.2.1	<i>Uptake by pasture</i>	47
	2.5.2.2	<i>Leaching losses</i>	49
	2.5.2.3	<i>Immobilization of applied fertilizer sulphur</i>	53
2.6		SULPHUR CYCLING IN GRAZED PASTURES.....	55
	2.6.1	Background	55
	2.6.2	Uptake of S by pasture plants	56
	2.6.3	Return and decomposition of plant litter	57
	2.6.4	Ingestion and excreta return by the grazing animal.....	60
	2.6.4.1	<i>Sulphur in dung and urine</i>	60
	2.6.4.2	<i>Distribution of dung and urine</i>	62
	2.6.4.3	<i>Excreta decomposition</i>	64
2.7		SUMMARY AND CONCLUSIONS	66

CHAPTER 3 EXPERIMENTAL SITES AND TECHNIQUES

3.1		METHODS FOR RADIOACTIVELY LABELLING FERTILIZER SULPHUR	68
	3.1.1	Introduction.....	68
	3.1.2	Calculating the required ³⁵ S enrichment in fertilizer materials	68
	3.1.3	Labelling S ⁰ fertilizer	69
	3.1.3.1	<i>Labelling microfine S⁰</i>	69
	3.1.3.2	<i>Labelling S⁰ of different particle sizes</i>	69
	3.1.4	Labelling sulphate containing fertilizers.....	70
3.2		EXPERIMENTAL SITES, SOIL AND PLANT PREPARATIONS	70
	3.2.1	Experimental sites	70
	3.2.2	Isolating undisturbed soil cores for field and glasshouse experiments.....	70
	3.2.3	Sample preparations	72
	3.2.3.1	<i>Sheep dung sample preparation</i>	72
	3.2.3.2	<i>Soil sample preparation</i>	72
	3.2.3.3	<i>Herbage sample preparation</i>	72
3.3		CHEMICAL ANALYSES OF SAMPLES	72
	3.3.1	Total S in plant material.....	72
	3.3.1.1	<i>Alkaline hypobromite oxidation method</i>	72
	3.3.1.2	<i>LECO sulphur analyzer</i>	73
	3.3.2	Soluble and extractable S in soil samples (CaCl-S and CaP-S) (Ca(H ₂ PO ₄) ₂ and CaCl ₂ extractable S)	74
	3.3.3	Total S in soil (TT-S)	74
	3.3.4	Total S ⁰ in soil samples (TT-els).....	72
	3.3.5	Organic S (Org-S) in soil samples	75
	3.3.5.1	<i>HI-reducible S (HI-S)</i>	75
	3.3.5.2	<i>Ester-sulphate (Est-S)</i>	75
	3.3.5.3	<i>Carbon-bonded S (Cb-S)</i>	76
	3.3.6	HI-reducible S in digested and extracted samples	76
	3.3.7	Determination of total S in fertilizers.....	76
	3.3.7.1	<i>S⁰ containing fertilizers</i>	76

	3.3.7.2	<i>Sulphate containing fertilizers</i>	77
3.3.8		Radioassay of ^{35}S and ^{32}P	77
	3.3.8.1	<i>Liquid scintillation counting</i>	77
	3.3.8.2	<i>Establishing quench curves</i>	77

CHAPTER 4

EVALUATION OF THE ROLE OF SHEEP DUNG IN THE SHORT TERM IMMOBILIZATION OF SOIL AND FERTILIZER SULPHUR

4.1		INTRODUCTION	79
4.2		EXPERIMENTAL OBJECTIVES	81
4.3		MATERIALS AND METHODS	81
	4.3.1	<i>EXPERIMENT 1, AREA OF PASTURE INFLUENCED BY SHEEP DUNG</i>	81
		4.3.1.1 <i>Design of the experiment</i>	81
		4.3.1.2 <i>Labelling of dung with ^{35}S and ^{32}P</i>	83
		4.3.1.3 <i>Total and extractable S and P in dung</i>	83
	4.3.2	<i>EXPERIMENT 2, EFFECT OF SHEEP DUNG ON GROWTH AND YIELD OF PASTURE</i>	85
		4.3.2.1 <i>Design of the experiment</i>	85
	4.3.3	Chemical Analyses	85
		4.3.3.1 <i>Total S and P in pasture samples</i>	85
		4.3.3.2 <i>Total S and P in dung samples</i>	85
		4.3.3.3 <i>Extractable S in dung samples</i>	86
		4.3.3.4 <i>Exchangeable P in dung samples</i>	86
		4.3.3.5 <i>Radioassay of ^{35}S and ^{32}P activities</i>	87
	4.3.4	Presentation of results (method of calculation)	87
	4.3.5	Statistical analyses	88
4.4		RESULTS	89
	4.4.1	<i>EXPERIMENT 1, AREA OF PASTURE INFLUENCED BY SHEEP DUNG</i>	89
		4.4.1.1 <i>Pasture yield</i>	89
		4.4.1.2 <i>S and P concentrations in and their uptake by pasture</i>	90
		4.4.1.3 <i>Uptake of ^{35}S and ^{32}P by pasture</i>	90
		4.4.1.3.1 <i>Pattern of ^{35}S uptake</i>	90
		4.4.1.3.2 <i>^{35}S specific activity and percent of plant S derived from dung (%SDFD)</i>	90
		4.4.1.3.3 <i>Pattern of ^{32}P uptake</i>	91
		4.4.1.3.4 <i>^{32}P specific activity and percent of plant P derived from dung (%PDFD)</i>	92
	4.4.2	<i>DISCUSSION, EXPERIMENT 1</i>	92
	4.4.3	<i>EXPERIMENT 2, EFFECT OF SHEEP DUNG ON GROWTH AND YIELD OF PASTURE</i>	94
		4.4.3.1 <i>Pasture yield</i>	94
		4.4.3.2 <i>Plant S concentration</i>	94
		4.4.3.3 <i>Plant S uptake</i>	102
	4.4.4	<i>DISCUSSION, EXPERIMENT 2</i>	102
	4.4.5	Area covered by dung and influenced by dung sulphur	105
4.5		CONCLUSIONS	105

CHAPTER 5
EVALUATING FIELD EXPERIMENTATION TECHNIQUES USING ^{35}S LABELLED
FERTILIZERS TO TRACE THE FATE OF SULPHATE AND ELEMENTAL S APPLIED TO
PASTURE SOILS

5.1	INTRODUCTION	107
5.2	OBJECTIVES	108
5.3	MATERIALS AND METHODS.....	109
5.3.1	EXPERIMENT 1, ^{35}S LABELLED FERTILIZER.....	109
	5.3.1.1 Preparation of ^{35}S labelled S^0 and SSP	109
	5.3.1.1.1 $^{35}\text{S}^0$ labelled S^0	109
	5.3.1.1.2 $^{35}\text{SO}_4^-$ labelled SSP	109
	5.3.1.2 Trial method.....	110
	5.3.1.3 Sampling and preparation of samples.....	110
5.3.2	EXPERIMENT 2, INVERSE ISOTOPIC DILUTION EXPERIMENT.....	112
	5.3.2.1 Carrier-free ^{35}S preparation and injection technique	112
	5.3.2.2 Trial method.....	112
	5.3.2.3 Sampling and preparation of samples.....	112
5.3.3	Experimental site	113
5.3.4	Chemical analyses	115
5.3.5	Statistical analyses	115
5.4	RESULTS	117
5.4.1	Initial soil S properties and weather conditions during experiments.....	117
5.4.2	EXPERIMENT 1, ^{35}S LABELLED FERTILIZERS.....	117
	5.4.2.1 Accumulated herbage dry matter yield and total S uptake and comparisons between microplot and small plot experiments. 117	
	5.4.2.2 Total recovery of ^{35}S activity in soil and plants	121
	5.4.2.3 Extractable S in soil (CaP-S)	121
	5.4.2.4 Extractable ^{35}S in soil (CaP- ^{35}S)	122
	5.4.2.5 Total organic ^{35}S	124
	5.4.2.6 Carbon bonded and ester sulphate ^{35}S	124
	5.4.2.7 Prediction of the extent of S transformation.....	135
5.4.3	EXPERIMENT 2, INVERSE ISOTOPIC DILUTION	137
	5.4.3.1 Pasture dry matter yield and total sulphur uptake.....	137
	5.4.3.2 Total recovery of ^{35}S in soil and plant	137
	5.4.3.3 Recovery of injected ^{35}S in soil S fractions.....	138
	5.4.3.4 Extractable ^{35}S (CaP-S).....	138
	5.4.3.5 Total organic ^{35}S	140
5.5	DISCUSSION	145
5.5.1	Pasture yield and S uptake	145
5.5.2	Short term fate of the fertilizer sulphur	145
	5.5.2.1 Uptake of ^{35}S labelled fertilizers	145
	5.5.2.2 Recovery of ^{35}S labelled fertilizer in the top 10 cm of soil.....	146
	5.5.2.3 Transformation of ^{35}S in the top 10 cm of soil.....	146
5.5.3	Comparison between labelled fertilizer and inverse dilution techniques	148
5.5.4	The microplot technique (undisturbed soil core).....	148
5.6	CONCLUSIONS	149

CHAPTER 6
THE MEASUREMENT OF PLANT AVAILABLE SOIL SULPHUR

6.1	INTRODUCTION	151
6.2	OBJECTIVES	152
6.3	MATERIALS AND METHODS.....	154
6.3.1	Soil and herbage analyses	154
	6.3.1.1 <i>Extractable S</i>	154
	6.3.1.2 <i>Herbage analyses</i>	154
6.3.2	Statistical analyses.....	155
6.4	RESULTS AND DISCUSSION	156
6.4.1	Effect of soil preparation and extractant.....	156
	6.4.1.1 <i>Effect of soil preparations</i>	156
	6.4.1.1.1 <i>Effect of soil preparation on extractable S</i>	156
	6.4.1.1.2 <i>Effect of soil preparation on extractable ³⁵S activity</i>	157
	6.4.1.2 <i>Effect of extractants</i>	158
	6.4.1.2.1 <i>Effect of extractant on extractable S</i>	158
	6.4.1.2.2 <i>Effect of extractant on extractable ³⁵S activity</i>	158
6.4.2	Specific activity of ³⁵ S in soil extracts and herbage.....	162
6.4.3	Relationships between the specific activity of ³⁵ S in herbage and ³⁵ S in soil extractable S.....	162
6.5	CONCLUSIONS	170

CHAPTER 7
THE INFLUENCE OF FERTILIZER FORM ON THE FATE OF SULPHUR IN SOILS

7.1	INTRODUCTION	171
7.2	OBJECTIVES	172
7.3	MATERIALS AND METHODS.....	172
7.3.1	Soils.....	172
7.3.2	Preparation of soil cores.....	173
7.3.3	Design of the experiments.....	173
7.3.4	Labelling fertilizer S.....	175
	7.3.4.1 <i>Labelling S⁰ containing fertilizers</i>	175
	7.3.4.2 <i>Labelling sulphate containing fertilizers</i>	176
	7.3.4.3 <i>Granulation of S⁰ and S⁰/phosphate rock</i>	176
7.3.5	Experimental conduct.....	178
	7.3.5.1 <i>General</i>	178
	7.3.5.2 <i>Leaching events</i>	178
	7.3.5.3 <i>Soil and herbage sampling</i>	178
7.3.6	Chemical analyses	181
	7.3.6.1 <i>Soil, plant and fertilizer samples</i>	181
	7.3.6.2 <i>Sulphate retention</i>	181
	7.3.6.3 <i>Recovery of added fertilizer ³⁵S⁰ activity from soil cores at day 0</i>	182
7.3.7	Statistical analyses.....	182
7.3.8	Calculation of specific rates (K) of S ⁰ oxidation.....	183

7.4	RESULTS AND DISCUSSION	184
7.4.1	The percentage recovery of $^{35}\text{S}^0$ and %SDFF in pastures as influenced by fertilizer specific activity	184
7.4.2	THE INFLUENCE OF PARTICLE SIZE AND FERTILIZER FORM ON THE FATE OF S^0	186
7.4.2.1	Recovery of ^{35}S in soils and plants	186
7.4.2.2	Plant uptake of S and ^{35}S and percentage of plant S derived from fertilizer (%SDFF)	189
7.4.2.3	Residual $^{35}\text{S}^0$ activity and S^0 (acetone extracts) and extractable S and ^{35}S activity (CaP-S) in soil.....	192
7.4.2.4	Immobilization into soil organic forms	205
7.4.2.5	Movement of ^{35}S down the profile and leaching losses	206
7.4.2.6	Summary.....	218
7.4.3	FATE OF SULPHATE-BASED FERTILIZERS	219
7.4.3.1	Recovery of ^{35}S in soils and plants	219
7.4.3.2	Plant uptake of S and ^{35}S and percentage of plant sulphur derived from fertilizers (%SDFF)	220
7.4.3.3	Immobilization into organic matter	220
7.4.3.4	Movement of ^{35}S down the profile and leaching losses	221
7.4.3.5	Summary.....	222
7.4.4	Comparison of sulphate-based fertilizers and elemental S	223
7.4.5	Comparison of glasshouse and field trials.....	224
7.5	CONCLUSIONS	231

CHAPTER 8
MODELLING THE FATE OF SULPHUR IN THE SOIL-PLANT SYSTEM
IN GRAZED PASTURE

8.1	INTRODUCTION	232
8.2	MATERIALS AND METHODS.....	234
8.3	MODEL DEVELOPMENT.....	234
8.3.1	Water balance	234
8.3.1.1	Calculating drainage volumes.....	234
8.3.1.2	Estimating actual daily evapotranspiration.....	235
8.3.2	A single sulphate pool for plant uptake, immobilization and leached sulphate.	236
8.3.3	Modelling the fluxes of S between various pools.....	237
8.3.3.1	Predicting the soil solution sulphate concentration	239
8.3.3.2	Accounting for leaching of sulphate	241
8.3.3.2.1	Layered drainage model with mobile and immobile water phases	241
8.3.3.3	Plant uptake of sulphur	244
8.3.3.4	Accounting for immobilization and mineralization of soil organic sulphur	245
8.3.3.5	Executing the model	246
8.4	RESULTS AND DISCUSSION.....	247
8.4.1	Prediction of plant S uptake on unfertilized soil.....	247
8.4.2	Prediction of plant S uptake on superphosphate fertilized soil.....	248

	8.4.2.1	<i>Movement of sulphate from superphosphate into soil</i>	248
	8.4.2.2	<i>Prediction of plant uptake on SSP fertilized plots</i>	250
8.4.3		Prediction of ³⁵ S movement and transformation in undisturbed soil cores.....	251
8.5		CONCLUSION.....	259

CHAPTER 9 SUMMARY

9.1	REVIEW OF LITERATURE	260
9.2	LABELLING TECHNIQUES.....	261
9.3	THE EFFECT OF SHEEP DUNG ON THE SHORT-TERM IMMOBILIZATION OF SOIL AND FERTILIZER S.....	261
9.4	THE FATE OF S FROM S ⁰ AND SSP IN SOIL	262
9.5	MEASUREMENT OF PLANT AVAILABLE SOIL SULPHUR	263
9.6	INFLUENCE OF FERTILIZER FORM ON THE FATE OF S IN SOIL	264
9.7	MODELLING THE SHORT-TERM FATE OF FERTILIZER S IN SOIL	264
9.8	SUGGESTIONS FOR FURTHER RESEARCH.....	265
	BIBLIOGRAPHY.....	267
	APPENDICES	298

LIST OF FIGURES

Figure 2.1	A conceptual flow diagram of the main forms and transformations of sulphur in the soil-plant-animal system (M.J. Hedley, 1990. Lecture notes from Soil Fertility and the Environment, Soil Science Department, Massey University, New Zealand).	17
Figure 2.2	Simplified sulphur cycle showing gains and losses in the CFAS model (Sinclair and Saunders, 1984).....	38
Figure 2.3	Map of New Zealand showing broad climate zones which affect recommended fertilizer S ⁰ particle size ranges (Boswell and Swanney, 1988).....	44
Figure 4.1	A schematic illustration of nutrient transfers in a grazed hill-country pasture (Saggar et al., 1990a).....	82
Figure 4.2	Radioactivity per unit area in harvested pasture at four radial distances (R1, R2, R3 and R4) from radioactively labelled dung applied at three rates (D1, D2 and D3); A = ³² P and B = ³⁵ S at the first (30 days) harvest and C = ³⁵ S at the second harvest (60 days).	95
Figure 4.3	Total percent recovery of ³² P and ³⁵ S in pasture harvested at four radial distances (R1, R2, R3 and R4) from radioactively labelled dung applied at three rates (D1, D2 and D3); A = ³² P and B = ³⁵ S at the first harvest (30 days) and C = ³⁵ S at the second harvest (60 days).	96
Figure 4.4	Percentage of pasture P and S derived from dung at four radial distances (R1, R2, R3 and R4) from dung applied at three rates (D1, D2 and D3); A = %PDFD and B = %SDFD at the first harvest (30 days) and C = %SDFD at the second harvest (60 days) (calculated using specific activity of dung extracts).	97
Figure 4.5	Percentage of pasture P and S derived from dung (%PDFD and %SDFD) at increasing distances from dung (R1, R2, R3 and R4); %SDFD-1 and %PDFD were calculated from the first harvest data (30 days) and %SDFD-2 was calculated from the second harvest data (60 days) (calculated using the specific activity of the (A) exchangeable P and S and (B) the total dung P and S.....	98
Figure 5.1	A cross sectional diagram of the injector system used to inject soil cores with radioisotope in the inverse isotopic dilution experiment (Hedley and Tillman, personal communication).....	114
Figure 5.2	Cumulative plant S uptake (fertilizer plus soil S), amount of plant S cumulatively derived from ³⁵ S labelled fertilizer (SDFD), extractable CaP-S at three soil depths and amount of S applied (microplots).	120
Figure 5.3	Percentage of applied ³⁵ S labelled fertilizer recovered as total soil S in three soil layers and cumulative ³⁵ S uptake by pasture.	126
Figure 5.4	Percentage of applied ³⁵ S present as extractable S (CaP- ³⁵ S) in three soil layers, cumulative plant ³⁵ S uptake and ³⁵ S taken up by pasture at each of five harvests.	127
Figure 5.5	Percentage recovery of ³⁵ S applied as fertilizer in organic S in three soil layers....	128
Figure 5.6	Distributions of ³⁵ S ester sulphate (A) and carbon bonded ³⁵ S (B) in three soil layers (value expressed as percentage of ³⁵ S applied).	129

Figure 5.7	Distribution of ^{35}S ester sulphate (A) and carbon-bonded ^{35}S (B) in three soil layers (value expressed as percentage of total ^{35}S remaining in soil core, 0-10 cm).	130
Figure 5.8	Cumulative S (A) and ^{35}S (B) taken up by plants at five harvesting times; observed vs. predicted.....	131
Figure 6.1	Specific activity of ^{35}S in plants and soil extracts (CaCl-S and CaP-S) from superphosphate treated cores at five harvests for three soil depths.	166
Figure 6.2	Relationships between specific activity of ^{35}S in plants and HI-reducible ^{35}S in soil extracts from the <u>top</u> layer; (A) = CaCl-S and (B) = CaP-S.	167
Figure 6.3	Relationships between specific activity of ^{35}S in plants and HI-reducible ^{35}S in soil extracts from the <u>top plus middle</u> layers; (A) = CaCl-S and (B) = CaP-S.....	168
Figure 6.4	Relationships between specific activity of ^{35}S in plants and HI-reducible ^{35}S in soil extracts from the <u>top plus middle and bottom</u> layers; (A) = CaCl-S and (B) = CaP-S.....	169
Figure 7.1	The effect of S^0 particle size on the cumulative S taken up by pasture grown on Ramiha (A) and Tokomaru (B) soils.....	193
Figure 7.2	The effect of granulation of S^0 with or without phosphate rock (SS/PR and SS/gr compared with SS) on the cumulative S taken up by pasture on Ramiha (A) and Tokomaru (B) soils.....	194
Figure 7.3	The effect of S^0 particle size on the cumulative dry matter yield of pasture on Ramiha (A) and Tokomaru (B) soils.	195
Figure 7.4	The effect of granulation of S^0 with or without phosphate rock (SS/PR and SS/gr compared with SS) on the cumulative dry matter yield of pasture on Ramiha (A) and Tokomaru (B) soils.....	196
Figure 7.5	The effect of S^0 particle size on the cumulative percentage ^{35}S uptake by pasture on Ramiha (A) and Tokomaru (B) soils.....	197
Figure 7.6	The effect of granulation of S^0 with or without phosphate rock (SS/PR and SS/gr compared with SS) on the cumulative ^{35}S taken up by pasture on Ramiha (A) and Tokomaru (B) soils.....	198
Figure 7.7	The effect of S^0 particle size on the percentage of cumulative plant S derived from fertilizer (%SDFF) on Ramiha (A) and Tokomaru (B) soils.	200
Figure 7.8	The effect of granulation of S^0 with or without phosphate rock on the percentage of cumulative plant S derived from fertilizer (%SDFF) on Ramiha (A) and Tokomaru (B) soils.....	201
Figure 7.9	The effect of $^{35}\text{S}^0$ particle size on the percentage of oxidized $^{35}\text{S}^0$ cumulatively taken up by pasture on Ramiha (A) and Tokomaru (B) soils.	201
Figure 7.10	The effect of granulation of S^0 with or without phosphate rock on the percentage of oxidized $^{35}\text{S}^0$ cumulatively taken up by pasture (SS/PR and SS/gr compared with SS).	202

Figure 7.11	The effect of S ⁰ particle size on the recovery of extractable ³⁵ S (CaP- ³⁵ S) in soil cores (0-10 cm) in Ramiha (A) and Tokomaru (B) soils.	208
Figure 7.12	The effect of granulation of S ⁰ with or without phosphate rock on the recovery of extractable ³⁵ S (CaP- ³⁵ S) in soil cores (0-10 cm) (SS/PR and SS/gr compared with SS) in Ramiha (A) and Tokomaru (B) soils.....	209
Figure 7.13	Total recoveries of ³⁵ S in three layers of Ramiha soil 180 days after fertilization with two particle sizes of ³⁵ S ⁰	213
Figure 7.14	Total recoveries of ³⁵ S in three soil layers of Tokomaru soils 180 days after fertilization with three particle sizes of ³⁵ S ⁰	214
Figure 7.15	Total recoveries of ³⁵ S in three soil layers of Ramiha soil 180 days after fertilization with fine ³⁵ S ⁰ (SS) granulated with and without phosphate rock.....	215
Figure 7.16	Total recoveries of ³⁵ S in three soil layers of Tokomaru soil 180 days after fertilization with fine ³⁵ S ⁰ (SS) granulated with and without phosphate rock.	216
Figure 7.17	Cumulative dry matter yield (A) and S uptake (B) of pasture on Ramiha and Tokomaru soils; GP and SSP vs. SS.	225
Figure 7.18	Cumulative ³⁵ S uptake (value expressed as percentage of ³⁵ S applied) by pasture (A) and %SDFP (B); ³⁵ S labelled GP and SSP vs. ³⁵ S ⁰ labelled SS.	226
Figure 7.19	Simple relationships between cumulative ³⁵ S uptake (A) (value expressed as percentage of ³⁵ S applied) and S uptake (B) by plants against time (a comparison between sulphate-S and elemental S fertilizers)	227
Figure 8.1	A simple conceptual dynamic sulphur model for grazed pasture	233
Figure 8.2	Hierarchical order of the processes in the S-cycle	238
Figure 8.3	Comparison of predicted and observed plant S uptake on (A) control (unfertilized) and (B) SSP fertilized soil cores (experimental details Chapter 5). The coefficient of determination (R ²) represents the variation in observed data accounted for by the model prediction (PV stands for the less mobile fraction of soil water; 1-α).....	253
Figure 8.4	The measured rainfall and predicted drainage occurring from the top 100 mm of Tokomaru soil during the experiment conducted in Chapter 5. The dotted line shows the disappearance of surface applied superphosphate (30 kg S ha ⁻¹) as it dissolves and moves into soil. The solid line shows the predicted accumulated leaching loss of S from top 100 mm.....	254
Figure 8.5	Comparison of predicted (output every 5 days) and observed amounts of CaP-S in each soil depth in SSP fertilized cores.	255
Figure 8.6	Comparison of predicted and observed percentages of added ³⁵ S recovered in CaP-S fractions from different soil depths.	256
Figure 8.7	Comparison of predicted (output every 5 days) and observed percentage of added ³⁵ S recovered in pasture plants.....	257
Figure 8.8	Comparison of predicted and observed percentage of added ³⁵ S recovered as organic S in different soil depths.....	258

LIST OF TABLES

Table 2.1	Some standard and alternative S fertilizers in New Zealand (Boswell and Swanney, 1986).....	40
Table 4.1	Mean S and P concentrations, total radioisotope activity and specific activity (SA) of ^{35}S or ^{32}P in dung and extracts of dung (results expressed on dung dry weight).	84
Table 4.2	Pasture dry matter yield as influenced by dung application rates and radial distances of pasture from dung.....	99
Table 4.3	Pasture S and P concentration, S and P uptake of pasture and cumulative S uptake as influenced by dung application and radial distances of pasture from dung.	100
Table 4.4	The percent distribution of ^{35}S and ^{32}P taken up by pasture at different radial distances from ^{35}S and ^{32}P labelled dung applied at various rates.	101
Table 4.5	Pasture dry matter yield (PART A), sulphur concentration (PART B) and total pasture S uptake (PART C) as influenced by dung and fertilizer applications at five harvests.	103
Table 4.6	Calculated percentage of a paddock annually influenced by dung considering camping and noncamping behaviour of sheep.....	104
Table 5.1	Characteristics of ^{35}S labelled fertilizers used in this study.....	111
Table 5.2	Harvesting schedules of herbage from micro-plots at each harvest and number of soil cores destructively sampled.	111
Table 5.3	Chemical properties of sulphur in three soil layers collected before the experiment.	113
Table 5.4	Chemical analyses for soil, plant and fertilizer samples	115
Table 5.5	Cumulative dry matter yield and total pasture S uptake (soil plus fertilizer S) in microplots and small plot experiments during spring-summer seasons (October, 1985 - February, 1986).	119
Table 5.6	The percentage of total ^{35}S labelled fertilizers appearing in soil organic and inorganic ^{35}S fractions recovered from 0-10 cm depth of undisturbed field soil cores at five harvesting times.....	132
Table 5.7	Average extractable ^{35}S (CaP- ^{35}S) expressed as a percentage of total ^{35}S activity <u>applied</u> (PART A) and as a percentage of total ^{35}S <u>remaining</u> (PART B) in three soil layers at five harvests.	133
Table 5.8	Proportion of ^{35}S labelled fertilizers appearing in soil organic and inorganic fractions; amount expressed as percent of total ^{35}S recovered from the 0-10 cm depth of undisturbed soil cores at five harvesting times.	134
Table 5.9	Observed plant S uptake and predicted values using relationships in equation 4 above.	136
Table 5.10	Dry matter yield (DM), total S uptake, cumulative dry matter yield and S uptake and specific activity of ^{35}S in herbage from two harvests.	141

Table 5.11	Mean recovery of ^{35}S from herbage and soils (0-10 cm depth) at two harvests, 30 and 60 days after injection of $^{35}\text{SO}_4^-$ into soil.....	142
Table 5.12	Mean recovery of CaP- ^{35}S and specific activity and total amount of CaP-S in the 0-10 cm soil depth.	143
Table 5.13	Mean recovery of soil ^{35}S organic S fractions from the 0-10 cm soil depth.....	144
Table 6.1	Concentrations of HI-reducible S in CaCl-S (Part A) and CaP-S (Part B) extracts from three soil layers using two soil preparations.	159
Table 6.2	Concentration of HI-reducible ^{35}S in CaCl-S (Part A) and CaP-S (Part B) extracts from three soil layers using two soil preparation techniques.	160
Table 6.3	Concentration of HI-reducible S (Part A) and ^{35}S activity (Part B) in CaCl-S and CaP-S extracts from freeze-dried soils taken from three soil layers.	161
Table 6.4	The specific activity of ^{35}S in CaCl-S and CaP-S extracts of field-moist and freeze-dried soils and plants.	164
Table 6.5	Simple linear relationships, $y=bx$, between specific activity of total ^{35}S in plants (y) and specific activity of ^{35}S in extracts from different soil layers (x).	165
Table 7.1	General properties of the soils used in the studies.	174
Table 7.2	The forms and distribution of soil sulphur ^a in three soil layers collected from field sites before the experiment.....	175
Table 7.3	Characteristics of $^{35}\text{S}^0$ labelled fertilizer used in this study.	177
Table 7.4	Characteristic of $^{35}\text{SO}_4^-$ labelled superphosphate and gypsum used in this study..	177
Table 7.5	Treatments, soil sampling and herbage harvesting schedule for treatments with different particle sizes of elemental sulphur in the glasshouse trial.....	179
Table 7.6	Treatments, soil sampling and herbage harvesting schedule for treatments with different particle sizes, S^0 in the field trials.....	180
Table 7.7	Treatments and soil sampling and herbage harvesting schedule for treatments with ^{35}S labelled gypsum and superphosphate fertilizers in the glasshouse trial.....	180
Table 7.8	Analyses for S and related ^{35}S activities in soil, plant and fertilizer materials.	181
Table 7.9	Effect of fertilizer specific activities on ^{35}S recovery in pastures and percent of plant S derived from fertilizers (%SDFP).	185
Table 7.10	Recovery of labelled ^{35}S fertilizers in pasture, soil and total recovery in <u>Ramiha</u> soil cores in glasshouse and field trials (average of three replications from individual microplots).	187
Table 7.11	Recovery of labelled ^{35}S fertilizers in pasture, soil and total recovery in <u>Tokomaru</u> soil cores in glasshouse and field trials (average of three replications from individual microplots).	188

Table 7.12	Percentage applied $^{35}\text{S}^0$ recovered as residual $^{35}\text{S}^0$ (acetone extracts), in 0-3 cm soil depth (PART A) and extractable ^{35}S (CaP-S) (PART B) in soil cores (0-10 cm) in glasshouse trials and after 180 days in the field trials (average of three replications).....	210
Table 7.13	Percentage applied S^0 recovered as residual S^0 in 0-3 cm layers (PART A) and total amounts of extractable S, CaP-S, (PART B) in soil cores (0-10 cm) in glasshouse trials and after 180 days in the field trials (average of three replications).....	211
Table 7.14	Percentage recovery of total ^{35}S (PART A) and organic ^{35}S (PART B) in soil cores (0-10 cm) at six sampling times in glasshouse trials and after 180 days in the field trials (average of three replications).....	212
Table 7.15	Percentage recovery of ^{35}S in leachates (PART A) and total amounts of sulphur and HI-reducible S (PART B) in leachates at five leaching events in glasshouse trials. .	217
Table 7.16	Total recovery of ^{35}S in soil, plant in two soils resulting from applications of ^{35}S labelled gypsum and superphosphate after 90 days.	228
Table 7.17	Fractions of ^{35}S in soils (% recovery) 90 days after applying ^{35}S labelled gypsum (GP) and superphosphate (SSP).	229
Table 7.18	Distribution (% recovered) of total ^{35}S (TT), organic ^{35}S (Org) and phosphate extractable ^{35}S (CaP-S) in three soil depths of two soils 90 days after application of ^{35}S labelled gypsum (GP) and superphosphate (SSP).	229
Table 7.19	Percentage recovery of ^{35}S labelled fertilizer sulphur in leachates (PART A) and HI-reducible S in leachates (PART B) at five leaching events after ^{35}S labelled gypsum (GP) and superphosphate (SSP) applications.....	230
Table 8.1	Freundlich type equation fitted to laboratory and field measured isotherms.....	240
Table 8.2	The simulated time taken for 30 kg S ha^{-1} to diffuse into Tokomaru silt loam and depth of sulphate movement (radius of outer hemispherical shell from center of granule).....	250

LIST OF APPENDICES

Appendix 3.1	Results from NaOBr digestions of plant material compared with median values published by the International Plant-Analytical Exchange, Wageningen Agricultural University, Netherlands.	298
Appendix 3.2	Calculation for ^{35}S enrichment of fertilizer materials	299
Appendix 3.3	The manufacturing of ^{35}S labelled superphosphate	301
Appendix 4.1	Activities of ^{35}S and ^{32}P in pasture per unit area (square centimetre) as influenced by different application rates of ^{35}S and ^{32}P labelled dung and distances of pasture from dung.	302
Appendix 4.2	Influence of dung application rates and distances of pasture from ^{35}S and ^{32}P labelled dung on the percent recovery of ^{35}S and ^{32}P by pasture.....	303
Appendix 4.3	Specific activity of ^{35}S or ^{32}P in pastures (S.A.) and the percentage of plant S and P derived from dung (%SDFD and %PDFD) calculated using the S.A. of ^{35}S and ^{32}P in the total pool (TP) and extractable pool (EP), CaP-S and Olsen-P, of dung samples.	304
Appendix 4.4	Percentage of plant S (PART A and B) and P (PART C) derived from dung applied at different rates (%SDFD and %PDFD) ^a in pasture at different radial distances away from dung.....	305
Appendix 4.5	Diffusion of sulphate and phosphate in soil.	306
Appendix 4.6	Calculation for area of a paddock influenced by sheep dung.....	307
Appendix 4.7	Weekly rainfall (Rain), drainage water (Drainage), average maximum (Max) and minimum (Min) temperature during the field trial period (June 27, 1985 - August 29, 1985).....	308
Appendix 5.1	Recovery of ^{35}S from ^{35}S labelled gypsum and microfine S^0 fertilizers after application onto the surface of soil cores.	309
Appendix 5.2	Cumulative S uptake by pasture and the percentage and amount of plant S derived from fertilizers (%SDFF) with time.	310
Appendix 5.3	Total CaP-S in three soil layers; CaP-S as percentage of S derived, PART A, from fertilizers (number in parentheses) and PART B, native extractable S and PART C, total extractable S in 0-10 cm depth of soil cores.	311
Appendix 5.4	Cumulative ^{35}S uptake in herbage and total amount of ^{35}S in 0-10 cm soil depth at five harvesting times.....	312
Appendix 5.5	Recovery of total ^{35}S in three layers of soils at five harvest times.	313
Appendix 5.6	Organic ^{35}S expressed as a percentage of total ^{35}S activity applied (PART A) and as a percentage of total ^{35}S remaining (PART B) in three soil layers at five harvests.	314
Appendix 5.7	Carbon-bonded ^{35}S expressed as a percentage of total ^{35}S activity applied (PART A) and as a percentage of total ^{35}S remaining (PART B) in three soil layers at five harvests.....	315

Appendix 5.8	^{35}S Ester sulphate expressed as a percent of total ^{35}S activity <u>applied</u> (PART A) and as a percentage of total ^{35}S <u>remaining</u> (PART B) in three soil layers at 5 harvests.	316
Appendix 5.9	Weekly amount of rainfall (Rain) and drainage water (Drainage), average maximum (Max) and minimum (Min) temperature during the field trial period from October 1985-March 1986.	317
Appendix 6.1	Total S and ^{35}S activity taken up by herbage from ^{35}S labelled superphosphate and microfine S^0 treated plots in five harvests.	318
Appendix 7.1	Cumulative sulphur taken up by pastures (PART A) and cumulative dry matter yield, DM, (PART B) in <u>glasshouse</u> trials (average of seven replications).	319
Appendix 7.2	Cumulative sulphur taken up (PART A) and cumulative dry matter yield, DM, (PART B) of pastures in <u>Field</u> trials; (average of three replications).	320
Appendix 7.3	Sulphur concentration of pastures in glasshouse (PART A) and field (PART B) trials as influenced by different particle size of elemental S.	321
Appendix 7.4	Cumulative percentage of ^{35}S taken up by pastures in glasshouse (PART A) and field (PART B) trials at six sampling times.	322
Appendix 7.5	Percentage of plant S cumulatively derived from fertilizers (%SDFF) in glasshouse (PART A) and field (PART B) trials.	323
Appendix 7.6	Percentage of oxidized elemental $^{35}\text{S}^0$ cumulatively taken up by pastures in glasshouse and field trials; (average of three replications).	324
Appendix 7.7	Percentage recovery of extractable ^{35}S (CaP-S) in three soil layers of Ramiha and Tokomaru soils at six sampling times in glasshouse trials and after 180 days in the field trials (average of three replications).	325
Appendix 7.8	Concentration of soil extractable S (CaP-S) in three layers of <u>Ramiha</u> soil at six sampling times in glasshouse trials and after 180 days in the field trials (average of three replications).	326
Appendix 7.9	Concentration of soil extractable S (CaP-S) in three layers of <u>Tokomaru</u> soil at six sampling times in glasshouse trials and after 180 days in the field trials (average of three replications).	327
Appendix 7.10	Percentage recovery of total ^{35}S in three soil layers in glasshouse trials and after 180 days in the field trials (average of three replications).	328
Appendix 7.11	Sulphur concentration, cumulative sulphur uptake and dry matter yield of pastures on two soils at three samplings in glasshouse trials.	329
Appendix 7.12	Cumulative ^{35}S taken up by pasture and percentage of plant sulphur derived from labelled fertilizers (%SDFF) after application of ^{35}S labelled gypsum and superphosphate in glasshouse trials.	330
Appendix 7.13	Phosphate extractable S concentration and amounts present in three soil depths of two soils 90 days after application of gypsum and superphosphate.	331

Appendix 7.14	Sulphate retention (%) and simple relationships between amounts of adsorbed sulphate (mg S kg^{-1}) and sulphate concentrations in solution (mg S l^{-1}) for three layers of Ramiha and Tokomaru soils.	332
Appendix 7.15	Recovery of $^{35}\text{S}^0$ from two sizes of elemental S at day 0 through NaHCO_3 dry digestion (total ^{35}S) and acetone extraction (total $^{35}\text{S}^0$ activity and S^0) after application onto the surface of soil cores.	333
Appendix 7.16	Weekly rainfall (Rain) and drainage water (Drainage), average maximum (Max) and minimum (Min) temperature during November 1987 - June 1988.	334