

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.

STUDIES ON THE DYNAMICS OF ORGANIC SULPHUR AND CARBON
IN
PASTORAL AND CROPPING SOILS

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

BHUPINDER-PAL SINGH

2000

ABSTRACT

Soil organic matter (SOM) can be depleted or regenerated by altering land management practices. Soil tests capable of reporting the size of dynamic SOM fractions may be useful for indicating the environmental cost of land use and management practices. Information on the effect of land management practices on soil organic S content and turnover is scarce. This study evaluated the ability of a sequential chemical fractionation procedure to characterise changes in soil S and C organic fractions on a range of pasture and cropping soils with different management histories. The fractionation involved an initial extraction with ion exchange resins followed by dilute (0.1 M NaOH) and concentrated (1 M NaOH) alkali. In addition, recently rhizodeposited ^{14}C (root+exudate derived) produced during a short-term (one week) $^{14}\text{CO}_2$ pulse-labelling study of intact soil cores growing ryegrass/clover pastures, was used to trace the fate of root-derived C in both chemical and density fractionation procedures.

In pasture and cropped topsoils, the major amounts of soil S and C were either extracted in 0.1 M NaOH (49–69% S and 38–48% C) or remained in the alkali-insoluble residual fraction (17–38% S and 46–53% C). These two fractions were more sensitive to change caused by different land use and management practices than the resin and 1 M NaOH fractions. With a large amount of dynamic soil C remaining in the residual fraction it was concluded that increasing strengths of alkali were not capable of sequentially fractionating S and C in SOM into decreasingly labile fractions.

The chemical fractionation allocated recent root and root-released ^{14}C amongst all the fractions. Again, most root ^{14}C appeared in the 0.1 M NaOH and residual fractions. Although small in amount, C of higher specific activity (more recently synthesised root C) was preferentially extracted by resin and 1 M NaOH extracts.

Density separation was not capable of recovering recent root and root-released ^{14}C in a single fraction. Root-derived ^{14}C was distributed between light (mostly fibrous root debris) (42%) and heavy (organics attached to clay and silt) (45%) fractions. The dispersing reagent soluble fraction recovered <13% of the ^{14}C . An anaerobic incubation and various acids and oxidising agents were tried, in order to recover a greater proportion of root and root-released ^{14}C as a single identity. These were not very successful in either

extracting or increasing the alkali solubility of the root C fraction. A 30% H₂O₂ pre-treatment of soil plus roots, or hot 1 M HNO₃ treatment of the residual fraction, were more efficient extractants of the root C fraction and should be investigated further to check their ability to better characterise soil organic S and C fractions with a change in management practices.

The ¹⁴CO₂ pulse labelling study of pasture swards showed a greater allocation of recently photo-assimilated ¹⁴C to the topsoil layer with a greater proportion of ¹⁴C recovered in roots than in the soil. An *in situ* soil solution sampling technique with mini Rhizon Soil Moisture SamplersTM effectively monitored the rapid appearance of a ¹⁴CO₂ pulse in soil water at various depths. A comparison of the ¹⁴CO₂ pulse labelling study under light and dark conditions indicated that, in the light lysimeters, ¹⁴CO₂ photo-assimilation/translocation/rhizosphere respiration was the main pathway for CO₂ generation at various soil depths. In the dark lysimeters, ¹⁴CO₂ diffusion was the main mechanism and ¹⁴C assimilation (either photo-assimilation or assimilation by chemolithotrophs in rhizosphere soil) was small.

The ¹⁴CO₂ activity in soil water from four soil depths of dark and light soil cores, and a CO₂ diffusion model, were used to identify the ¹⁴CO₂ contribution from rhizosphere respiration in the light lysimeters. A model was developed, but the unknown geometry of the air-filled pore space in the undisturbed soil cores made it impossible to precisely calculate the contribution made by root respiration to soil water ¹⁴CO₂ activity.

ACKNOWLEDGEMENTS

I am extremely grateful to:

Dr. Michael J. Hedley for his supervision, encouragement, patience, guidance, and friendship during my study.

Dr. Surinder Saggar for his supervision, valuable suggestions, constructive criticism, and friendship during my study.

Dr. David Scotter for his readiness to help, valuable suggestions, and supervision with the modelling part of this thesis.

Landcare Research, Palmerston North for using tracer laboratory and equipments, Carolyn Hedley for technical assistance and suggestions, and Dr. Graham Shepherd (Landcare Research) and Dr. Glyn Francis (Crop and Food) for soil samples.

All past and present staff in the Soil and Earth Sciences group, Bob Toes, Ian Furkert, Anne West and Glenys Wallace for technical assistance, Mike Bretherton for computer related assistance, and secretary Hera Kennedy for her cooperation.

Stephen Trolove for valuable discussion, English suggestions, and friendship, and other fellow postgraduate students, Tin Aye Maung, Afiquir Khan, Jim Moir, Asoka Senereth, Sumanasena, and Saman Bowatte for their friendship and support.

Lyall Domney and Ian Furkert for proof-reading part of this thesis.

The New Zealand Ministry of Foreign Affairs and Trade for granting NZODA-PGS scholarship, and the Punjab Agricultural University, India for allowing study leave.

All past and present Indian and Pakistani friends in Palmerston North, and my landlord Mrs Noelene Domney, for making my stay in New Zealand extremely enjoyable.

My parents, grandmother, brothers, sisters-in-law, brothers-in-law, nephews and nieces for their love, encouragement and support.

Lastly, but most importantly, my wife (Rosy) and our daughters (Harika and Amita), for their continued patience, support, love and encouragement during my study.

TABLE OF CONTENTS

ABSTRACT.....	II
ACKNOWLEDGEMENTS.....	IV
TABLE OF CONTENTS.....	V
LIST OF FIGURES.....	XIII
LIST OF TABLES.....	XVII
LIST OF PLATES.....	XIX
CHAPTER 1 INTRODUCTION	1
CHAPTER 2 LITERATURE REVIEW	4
2.1 CHARACTERISATION OF SOIL ORGANIC MATTER RELATIVE TO ITS TURNOVER AND NUTRIENT AVAILABILITY	4
2.1.1 Chemical characterisation of SOM.....	4
2.1.1.1 <i>Identification of a labile fraction(s)</i>	6
2.1.1.2 <i>Acid hydrolysis</i>	7
2.1.1.3 <i>Oxidation techniques</i>	9
2.1.2 Physical characterisation of SOM.....	10
2.1.2.1 <i>Mechanical disruption</i>	13
2.1.2.2 <i>Sieving</i>	14
2.1.2.3 <i>Sedimentation</i>	14
2.1.2.4 <i>Density separation</i>	15
2.1.3 Chemical characterisation of SOM in physical fractions	17
2.1.4 Nutrients (N, P and S) in soil organic matter.....	19
2.1.4.1 <i>The nature of S in soils and organic S fractionation</i>	19
2.1.5 Tracer use in SOM studies.....	21
2.1.6 The importance of measurable pools in SOM modelling studies.....	23
2.2 CONCLUSIONS.....	26
CHAPTER 3 METHODS FOR ANALYSING SULPHUR AND CARBON IN SOIL AND SOIL EXTRACTS.....	28

3.1	INTRODUCTION.....	28
3.2	METHODS AND MATERIALS	31
3.2.1	A sequential soil S and C fractionation technique.....	31
3.2.2	Analysis of resin extractable S.....	32
3.2.3	Analysis of total S in alkaline extracts.....	32
3.2.3.1	<i>Preparation of standard organic S solutions.....</i>	32
3.2.3.2	<i>In situ production of NaOBr.....</i>	33
3.2.3.3	<i>Tabatabai and Bremner wet oxidation technique with some modifications.....</i>	35
3.2.4	Analysis of total S in soil and residual fraction	36
3.2.5	Analysis of C in different fractions.....	36
3.2.5.1	<i>Chloride (Cl⁻) interference in the resin extract.....</i>	37
3.3	RESULTS AND DISCUSSION.....	38
3.3.1	Calibration of methionine and sulphanilamide organic S standards against standard K ₂ SO ₄ solution	38
3.3.1.1	<i>In situ production of NaOBr.....</i>	38
3.3.1.2	<i>Tabatabai and Bremner wet oxidation technique with some modifications.....</i>	40
3.3.2	A wet digestion procedure for C estimation	41
3.3.2.1	<i>Calibration of neoprene seal against original seal in Kimax tube screw cap.....</i>	41
3.3.2.2	<i>Applicability of the digestion procedure to soil extracts</i>	42
3.3.2.3	<i>Correction in the measured C for chloride interference</i>	43
3.4	CONCLUSIONS.....	43

CHAPTER 4 CHEMICAL FRACTIONATION TO CHARACTERISE CHANGES IN SOIL SULPHUR AND CARBON45

4.1	INTRODUCTION.....	45
4.2	MATERIALS AND METHODS	47
4.2.1	Description of field sites	47
4.2.1.1	<i>Mt. Thomas site (fertilised pasture).....</i>	47
4.2.1.2	<i>Kairanga site (short- to long-term cultivation).....</i>	49
4.2.1.3	<i>Wakanui site (short-term pasture cropping).....</i>	49

4.2.2	Preparation of soil samples	49
4.2.3	A sequential soil S and C fractionation technique	49
4.2.4	Analysis of S in different fractions	50
4.2.5	Analysis of C in different fractions	50
4.2.6	Statistics	50
4.3	RESULTS	50
4.3.1	Changes in soil S and C	51
4.3.1.1	<i>Mt. Thomas site (fertilised pasture)</i>	51
4.3.1.2	<i>Kairanga site (short- to long-term cultivation)</i>	54
4.3.1.3	<i>Wakanui site (short-term pasture cropping)</i>	56
4.4	DISCUSSION	58
4.4.1	Organic matter accumulation and depletion	58
4.4.2	Sulphur and carbon fractions sensitive to changes in management practices	59
4.5	SUMMARY	62
CHAPTER 5	PRELIMINARY EVALUATION OF $^{14}\text{CO}_2$ PULSE LABELLING AND SOIL, ROOTS AND SOIL SOLUTION SAMPLING TECHNIQUES TO STUDY THE FATE OF RECENTLY FIXED C IN INTACT SOIL CORES GROWING PREDOMINANTLY RYEGRASS SWARDS	63
5.1	INTRODUCTION	63
5.2	METHODS AND MATERIALS	65
5.2.1	Soil	65
5.2.2	Soil core collection	65
5.2.3	Preparation and placement of RSMS in the soil cores	65
5.2.4	Pulse labelling technique	67
5.2.5	Soil water potential (SWP) measurements at the soil solution sampling depths using RSMS's.	69
5.2.6	Sampling and harvesting	69
5.2.6.1	<i>Soil solution sampling</i>	69
5.2.6.2	<i>Herbage, root and soil sampling and their preparation for analysis</i> ..	70
5.2.7	Analysis	71

5.2.7.1	<i>Basic chemical analysis of soil</i>	71
5.2.7.2	<i>Scintillation cocktail recipe</i>	71
5.2.7.3	<i>¹⁴C in soil solution</i>	71
5.2.8	Total C and ¹⁴ C in shoot, root and soil samples.....	72
5.3	RESULTS AND DISCUSSION.....	72
5.3.1	Soil water potential (SWP) at the root–soil water interface	72
5.3.2	¹⁴ C in atmosphere.....	74
5.3.3	¹⁴ C in soil water	76
5.3.3.1	<i>Nature of ¹⁴C in soil water</i>	78
5.3.3.2	<i>Soil solution ¹⁴CO₂ concentration and root mass distribution</i>	82
5.3.4	¹⁴ C in shoots, roots and soil at harvest.....	83
5.3.4.1	<i>Specific activity and ¹⁴C recovery in plant shoot</i>	83
5.3.4.2	<i>Below ground recovery of ¹⁴C</i>	84
5.4	CONCLUSIONS	87

CHAPTER 6 CHARACTERISATION OF RECENT ROOT AND ROOT-RELEASED CARBON BY SOIL ORGANIC MATTER FRACTIONATION.....89

6.1	INTRODUCTION.....	89
6.2	MATERIALS AND METHODS	91
6.2.1	Soil.....	91
6.2.2	Soil core collection	91
6.2.3	Production of ¹⁴ C labelled rhizodeposited soil C.....	91
6.2.4	Sampling and harvesting.....	92
6.2.4.1	<i>Root and soil sampling and their preparation for analysis</i>	92
6.2.5	Evaluation and modification of SOM fractionation procedures.....	92
6.2.5.1	<i>Chemical fractionation of soil+roots and roots alone (Experiment 1)</i>	92
6.2.5.2	<i>Modifications to the chemical fractionation of soil+roots (Experiment 2)</i>	94
6.2.5.3	<i>Density separation of soil+roots (Experiment 3)</i>	94
6.2.5.4	<i>Density separation of roots, and roots remixed with non–radioactive soil (Experiment 4)</i>	97
6.2.5.5	<i>Chemical fractionation of density fractions (Experiment 5)</i>	98

6.2.6	Further attempts to modify the chemical fractionation procedure (Experiments 6 and 7)	98
6.2.6.1	<i>Pre-treatments followed by chemical fractionation of soil+roots (Experiment 6)</i>	98
6.2.6.2	<i>Treatments of the residual fraction of soil+roots (Experiment 7)</i>	101
6.2.7	Analysis	103
6.2.7.1	<i>Total C analysis</i>	103
6.2.7.2	<i>Total ¹⁴C analysis</i>	103
6.2.8	Chloride ion interference in the 5% NaCl extract for total C determination	106
6.3	RESULTS AND DISCUSSION.....	107
6.3.1	Total C and ¹⁴ C activity in samples of soil+roots and roots from different soil depths.....	107
6.3.2	Experiment 1: Chemical fractionation.....	110
6.3.2.1	<i>Chemical fractionation of soil+roots</i>	110
6.3.2.2	<i>Chemical fractionation of roots alone</i>	112
6.3.2.3	<i>Conclusions</i>	114
6.3.3	Experiment 2: Attempts to recover root C in fewer fractions.....	115
6.3.3.1	<i>Part a, acid hydrolysis of soil+roots prior to alkali extraction</i>	115
6.3.3.2	<i>Part b, acid hydrolysis of the alkali-insoluble residual fraction</i>	116
6.3.3.3	<i>Conclusions</i>	117
6.3.4	Experiment 3: Density separation of soil+roots	119
6.3.4.1	<i>Conclusions</i>	124
6.3.5	Experiment 4: Density separation of roots alone, and roots remixed with non-radioactive soil	125
6.3.5.1	<i>Conclusions</i>	126
6.3.6	Experiment 5: Chemical fractionation of density (heavy and light) fractions	127
6.3.6.1	<i>Conclusions</i>	128
6.3.7	Experiments 6 and 7: Further attempts to modify the chemical fractionation procedure.....	129
6.3.7.1	<i>Pre-treatments followed by chemical fractionation of soil+roots (Experiment 6)</i>	129
6.3.7.2	<i>Treatments of the residual fraction of soil+roots (Experiment 7)</i>	134

6.4 GENERAL CONCLUSIONS	136
-------------------------------	-----

CHAPTER 7 A STUDY OF PROCESSES (DIFFUSION AND PHOTO-ASSIMILATION) INVOLVED IN THE TRANSLOCATION OF $^{14}\text{CO}_2$ BELOW GROUND IN PASTORAL SOIL SYSTEM138

7.1 INTRODUCTION.....	138
7.2 METHODS AND MATERIALS	140
7.2.1 Soil.....	140
7.2.2 Soil core collection	141
7.2.3 Preparation and placement of RSMS in the soil cores.....	141
7.2.4 Pulse labelling canopy	141
7.2.4.1 <i>For dark lysimeters</i>	142
7.2.4.2 <i>For light lysimeters</i>	144
7.2.5 $^{14}\text{CO}_2$ generation and injection for pulse labelling.....	144
7.2.5.1 <i>Dark lysimeters</i>	144
7.2.5.2 <i>Light lysimeters</i>	145
7.2.6 Sampling.....	146
7.2.6.1 <i>Air sampling</i>	146
7.2.6.2 <i>Soil solution sampling</i>	146
7.2.6.3 <i>Herbage, soil and root sampling and their preparation for analysis</i>	147
7.2.7 Analysis	148
7.2.7.1 ^{14}C in air samples	148
7.2.7.2 ^{14}C in soil solution	148
7.2.7.3 <i>Total C and ^{14}C in plant and soil samples</i>	149
7.2.8 Methods for estimating possible plant uptake of $\text{H}^{14}\text{CO}_3^-$ by transpiration	149
7.3 RESULTS AND DISCUSSION.....	150
7.3.1 ^{14}C activity in air above the pasture swards.....	150
7.3.2 ^{14}C distribution in plant top herbage, roots and soil at harvest.....	152
7.3.3 ^{14}C activity in soil solution	160
7.3.4 Attempting a ^{14}C balance in lysimeters	164
7.3.5 Factors affecting below ground allocation of ^{14}C	165
7.4 CONCLUSIONS	169

CHAPTER 8 MODELLING $^{14}\text{CO}_2$ DIFFUSION AND ACTIVITY IN THE SOIL SOLUTION OF UNDISTURBED SOIL CORES.....171

8.1	INTRODUCTION	171
8.2	METHODS AND MATERIALS	172
8.2.1	Experimental procedures and analysis.....	172
8.2.2	List of symbols, their definitions and units.....	172
8.3	MODEL DEVELOPMENT	174
8.3.1	Model assumptions	174
8.3.2	Basic transport equations	176
8.3.2.1	<i>Transport equations in the absence of photo-assimilation</i>	177
8.3.2.2	<i>Transport equation in the presence of photo-assimilation</i>	178
8.3.3	Surface boundary conditions for dark and light lysimeters	178
8.3.4	Optimisation of diffusion parameters	179
8.3.5	Simulation of ^{14}C activity in soil water as a function of depth in light lysimeters.....	179
8.3.6	Chemical consideration (dissolution of $^{14}\text{CO}_2$) in the diffusion model.	181
8.4	MODEL OUTPUT AND EVALUATION	185
8.4.1	$^{14}\text{CO}_2$ diffusion in the absence of photo-assimilation	185
8.4.2	$^{14}\text{CO}_2$ diffusion and production in the presence of photo-assimilation.	186
8.5	CONCLUSIONS	189
8.6	PROGRAM MODULES FOR $^{14}\text{CO}_2$ DIFFUSION IN DARK AND LIGHT LYSIMETERS	191
8.6.1	Dark lysimeters	191
8.6.2	Light lysimeters	192

CHAPTER 9 SUMMARY AND CONCLUSIONS, AND IMPLICATIONS FOR FUTURE RESEARCH.....194

9.1	SUMMARY AND CONCLUSIONS.....	194
9.1.1	Literature review.....	194
9.1.2	Standardising analytical procedures for S and C fractions.....	195
9.1.3	Characterisation of changes in S and C fractions	195

9.1.4	Distribution of recently fixed ^{14}C by depth in intact pasture–soil system ...	196
9.1.5	Characterisation of recent root and root–released ^{14}C	197
9.1.6	$^{14}\text{CO}_2$ diffusion and photo–assimilation in pasture–soil system.....	198
9.1.7	Modelling $^{14}\text{CO}_2$ diffusion and activity in intact pasture soils	199
9.2	IMPLICATIONS FOR FUTURE RESEARCH.....	200
REFERENCES	202

LIST OF FIGURES

Figure 2.1: A scheme for the physical fractionation of soil organic matter (after Stevenson and Elliott, 1989).	12
Figure 3.1: A soil S and C sequential fractionation technique	31
Figure 3.2: Relationship between volume (ml) of 0.1 M HCl used during titration of the unused NaOH and concentration of chloride present in the solution to be analysed for total C.....	43
Figure 4.1: Relationship between total soil S and soil C as influenced by different management practices. The total soil S at Wakanui site is the sum of all the S fractions recovered by the sequential fractionation procedure. <i>Treatment codes are given in Table 4.1.</i>	51
Figure 4.2: Changes in amounts of S fractions as total soil S increases from increasing amounts of fertiliser application to the permanent pasture soil (Mt. Thomas) over a six-year period.....	52
Figure 4.3: Effect of S fertiliser application to pasture on different S fractions in the 0–7.5 cm depth of Mt. Thomas soil. <i>Treatment codes are given in Table 4.1. Error Bars: SE of treatment mean.</i>	53
Figure 4.4: Effect of short– to long–term cultivation on different (a) S and (b) C fractions in the 0–10 cm depth of Kairanga soils. <i>Treatment codes are given in Table 4.1. Error Bars: SE of sample mean.</i>	54
Figure 4.5: Comparison of S and C recovered in 0.1 M NaOH and residual fractions from 0–10 cm depth of Kairanga soils. <i>Treatment codes are given in Table 4.1.</i>	56
Figure 4.6: Effect of short–term pasture cropping on different S fractions in the 0–5 cm depth of Wakanui soil. <i>Treatment codes are given in Table 4.1. Error Bars: SE of treatment mean.</i>	57
Figure 5.1: Rhizon soil moisture samplers placed at different depths of undisturbed soil cores growing pasture swards.....	66
Figure 5.2: A rhizon soil moisture sampler (RSMS).....	67
Figure 5.3: Changes in glasshouse temperature ($^{\circ}\text{C}$), PAR ($\mu\text{moles s}^{-1} \text{ m}^{-2}$), and SWP (–cm) at the root–soil interface over time (h) at different soil depths. Pulse labelling was done at time 0 i.e. at 0930 h.....	74

- Figure 5.4: ^{14}C activity in soil water extracted from different depths (see legends) below ryegrass/clover swards at different times after injection of a $^{14}\text{CO}_2$ pulse into the atmosphere above ground. *Error Bars: $\pm SE$ of mean of two cores.* 77
- Figure 5.5: Root mass distribution (a), % of injected ^{14}C recovered in soil+roots and roots alone (b), and specific activity ($\text{Bq mg}^{-1}\text{C}$) of soil+roots and roots alone, at different soil depths. The legend points are plotted at the mean depth of various soil slices. *Error Bars: $\pm SE$ of mean of two cores.* 81
- Figure 5.6: Initial ^{14}C activity in soil solution versus root mass distribution at different soil depths. The numbers shown are soil solution sampling depths..... 82
- Figure 5.7: Change in specific activity ($\text{Bq mg}^{-1}\text{C}$) and ^{14}C activity (Bq mg^{-1}) of ryegrass/clover sward shoots at different times after injection of a $^{14}\text{CO}_2$ pulse into the atmosphere above ground. *Error Bars: $\pm SE$ of mean of two cores.* 84
- Figure 6.1: Comparison of ^{14}C counts recovered by ion exchange resin extraction from <2 mm sieved soil (a) with resin in the hydroxide and bicarbonate form and (b) ^{14}C counts recovered from either <2 mm soil or ring-ground soil. Soil samples were taken from different depths below a $^{14}\text{CO}_2$ pulse labelled pasture sward. *Error Bars: SE of mean of two cores.* 93
- Figure 6.2: A range of modifications to the chemical fractionation technique that attempt to recover recently synthesised root carbon by one of four pre-alkali extraction treatments (a, b, c or d) or one of five treatments of the alkali-insoluble residue (e, f, g, h or i)..... 95
- Figure 6.3: A soil organic matter density fractionation procedure followed by chemical fractionation..... 96
- Figure 6.4: Distribution with soil depth of (a) total ^{14}C activity, (b) total C, and (c) specific activity ($\text{Bq }^{14}\text{C mg}^{-1}\text{C}$) in whole soil+roots, roots and soil alone, a week after $^{14}\text{CO}_2$ pulse labelling of a pasture sward. The legend points are plotted at the mean depth of various soil slices. *Error Bars: $\pm SE$ of mean of two cores.* 108
- Figure 6.5: Percent distribution of (a) total ^{14}C activity and (b) total C in different fractions obtained during chemical fractionation of soil+root samples from different soil depths..... 111
- Figure 6.6: The amount of (a) total ^{14}C activity and (b) total C recovered from soil+roots in different chemical fractions, and (c) specific activity of these fractions at different soil depths. The insert in Figure (c) is comparing specific activity of chemical fractions with specific activity of roots at various soil layers. *Error Bars: $\pm SE$ of mean of two cores.*..... 113

- Figure 6.7: Percentage of total ^{14}C activity and total C recovered in acid hydrolysed fractions of (a) whole soil+roots and (b) residual fraction at different soil depths. *Error Bars: SE of mean of two cores*..... 115
- Figure 6.8: Specific activity of the acid hydrolysed fractions from whole soil+roots and residual fraction at different soil depths. *Error Bars: \pm SE of mean of two cores*. ... 117
- Figure 6.9: Percent distribution of (a) total ^{14}C activity and (b) total C in different fractions obtained during density separation of soil+root samples from different soil depths. 120
- Figure 6.10: The amount of (a) total ^{14}C activity and (b) total C recovered from soil+roots in soluble (NaCl) and density (light and heavy) fractions, and (c) specific activity of these fractions at different soil depths. The insert in Figure (c) is comparing specific activity of soluble and density fractions with specific activity of roots at various soil layers. *Error Bars: \pm SE of mean of two cores* 123
- Figure 6.11: Percent distribution of ^{14}C activity, recovered from roots alone and roots remixed with non-radioactive soil, in different density fractions at 2 and 4 cm soil depths. *Error Bars: SE of mean of two cores*. 126
- Figure 6.12: Percentage of (top – a,c) total ^{14}C activity and (bottom – b,d) total C recovered in each chemical fraction of the light and heavy density fractions of soil+root samples from different soil depths. 127
- Figure 6.13: The amount of ^{14}C labelled gases evolved during sampled (i.e. measured between different sampling periods) and full (i.e. measured at the end of incubation) anaerobic incubations of soil+roots. *Error Bars: SE (sampling errors)*. 130
- Figure 7.1: The fitted curves represent the ^{14}C activity (MBq m^{-3}) in the enclosed surface air (surface boundary conditions for the diffusion model) above the pasture swards of both dark and light lysimeters as a function of time after the $^{14}\text{CO}_2$ pulse was first introduced. 150
- Figure 7.2: Percent $^{14}\text{CO}_2$ activity (of the total initial injected activity) at different times (minutes) after injection of $^{14}\text{CO}_2$ pulse above the pasture swards of both light and dark lysimeters..... 151
- Figure 7.3: Change in (a) ^{14}C activity (Bq mg^{-1}) and (b) specific activity ($\text{Bq mg}^{-1}\text{C}$) of pasture shoot at different times after $^{14}\text{CO}_2$ pulse labelling under both dark (symbols only) and light conditions (line plus symbols). 153
- Figure 7.4: Percent distribution by depth of the total ^{14}C recovered below ground at harvest in roots and soil+roots of both (a) dark and (b) light lysimeters. The data points are plotted at mean depth of a soil slice..... 156
- Figure 7.5: ^{14}C activity (Bq mg^{-1}) and specific activity ($\text{Bq mg}^{-1}\text{C}$) of soil+roots and only roots at different soil depths in both (a,b) dark and (c,d) light lysimeters at harvest i.e.

- 30 h after pulse labelling for dark and 190 h after for light lysimeters. The data points are plotted at mean depth of a soil slice..... 158
- Figure 7.6: Specific activity ($\text{Bq mg}^{-1}\text{C}$) of only white roots from both (a) dark and (b) light lysimeters at different soil depths. The data points are plotted at mean depth of a soil slice. 160
- Figure 7.7: ^{14}C activity (MBq m^{-3}) in soil solution from (a) dark1 and (b) dark2 lysimeters at different soil depths (see legends) and times (h) after $^{14}\text{CO}_2$ pulse application to pasture swards..... 161
- Figure 7.8: ^{14}C activity (MBq m^{-3}) in soil solution from (a) light1 and (b) light2 lysimeters at different soil depths (see legends) and times (h) after $^{14}\text{CO}_2$ pulse application to pasture swards..... 163
- Figure 7.9: Root mass (g) at different soil depths in both dark and light lysimeters..... 165
- Figure 7.10: The simulated effect of change in air-filled porosity ($\text{m}^3 \text{m}^{-3}$ of soil) on the oxygen concentration in soil air with depth..... 168
- Figure 8.1: The enlarged conceptual view of the local water and gas geometry adjacent to a RSMS – (a) relatively dry soil with thin water films rapidly reaching equilibrium with the gas phase, and (b) relatively wet soil with large diffusion distances meaning that disequilibrium between the gaseous and dissolved CO_2 is likely..... 175
- Figure 8.2: Log normal function (Equation 8.17) parameter values fitted for different soil depths of both light1 (e,g) and light2 (f,h) lysimeters. 180
- Figure 8.3: The effect of soil pH (≤ 8) on the activities of carbonate species (adapted from Lindsay, 1979) and solubility coefficient of CO_2 in soil solution (K) in equilibrium with two different partial pressure of CO_2 (i.e. 0.021 and 0.0003 atm) in the gas phase. The Δp_{CO_2} indicates the change in log activities of carbonate species (i.e. log of moles per litre) with change in partial pressure of CO_2 from 0.021 to 0.0003 atm and vice versa at different pH values. 184
- Figure 8.4: The measured versus modelled ^{14}C activity (MBq m^{-3}) in soil solution from (a) dark1 and (b) dark2 lysimeters at different soil depths (see against legends and dotted lines) and times (h) after $^{14}\text{CO}_2$ pulse labelling of pasture swards. 185
- Figure 8.5: The measured versus modelled ^{14}C activity (MBq m^{-3}) in soil solution from (a) light1 and (b) light2 lysimeters at different soil depths (see legends) and and times (up to 30 h) after $^{14}\text{CO}_2$ pulse labelling of pasture swards..... 187
- Figure 8.6: The predicted ^{14}C activity ($\text{MBq s}^{-1} \text{m}^{-3}$ soil) of the source/sink term in soil from (a) light1 and (b) light2 lysimeters at different soil depths (see legends) and times (h) after $^{14}\text{CO}_2$ pulse application to pasture swards. 188

LIST OF TABLES

Table 2.1: Comparison of mean residence times of C in theoretical pools of SOM and in soil physical fractions (adapted from Buyanovsky <i>et al.</i> , 1994).	25
Table 3.1: Sulphur recovery from organic S compounds dissolved in alkaline extracting reagents by the NaHCO ₃ fusion technique.	38
Table 3.2: Sulphur recovery by different methods of <i>in situ</i> production of NaOBr.	39
Table 3.3: Sulphur recovery from K ₂ SO ₄ digestion in NaOBr at 160°C.	40
Table 3.4: Sulphur recovery from digests (Method 1) of sulphanilamide dissolved in ethanol or hot water.	40
Table 3.5: Sulphur recovery by two different addition methods of freshly prepared NaOBr.	41
Table 3.6: Calibration of neoprene seal against original seal in the screw cap of the Kimax digestion tube for better C recovery	42
Table 3.7: Carbon recovery from glucose dissolved in different extracting reagents by the dichromate digestion procedure.	42
Table 4.1: Soil classification and treatment description for the Mt. Thomas, Kairanga and Wakanui sites.	48
Table 5.1: Soil pH, total C, N, P and S, and Olsen P values of different depths of Tokomaru silt loam soil.	65
Table 5.2: ¹⁴ C activity in soil solution before and after acidification, and % ¹⁴ C lost upon acidification, at different depths and times after ¹⁴ CO ₂ pulse-labelling. The values of ¹⁴ C counts recovered after acidification (along with standard error values, shown in brackets) are given up to 2 decimal places to show the clear differences between two cores.	79
Table 5.3 Distribution of total injected ¹⁴ C (12.17 MBq) in different components of pasture shoot–root–soil system a week after pulse labelling (i.e. harvest time).	85
Table 6.1: Change in ¹⁴ C counts and counting efficiency with the addition of different amounts of 0.1 M NaOH soil extract.	104
Table 6.2: Percentage of total root ¹⁴ C and root C recovered by the chemical fractionation of roots (from 2 cm soil depth).	114

- Table 6.3: Effect of anaerobic incubation of soil+roots on the recovery of ^{14}C and C, and the specific activity of different fractions with the specific purpose of looking at the fractions used by soil anaerobic microbes during 14 days of incubation period. 131
- Table 6.4: Effect of different H_2O_2 and Na-perborate pre-alkali extraction treatments of soil+roots on the recovery of ^{14}C and C in different chemical fractions, and the specific activity ($\text{Bq mg}^{-1}\text{C}$) of these fractions with the specific purpose of looking at the treatments that reduce the size of the alkali-insoluble residual fraction having a greater proportion of root (structural) C. 133
- Table 6.5: Different treatments of the alkali-insoluble residual fraction of soil+roots to recover a fraction with greater proportions of the recently synthesized root ^{14}C and a high specific activity. 135
- Table 7.1: Distribution of total injected ^{14}C (as MBq and %) in different components of pasture shoot-root-soil system under both dark and light conditions at harvest. 155
- Table 7.2: A comparison of some key properties of soil cores of two ^{14}C pulse labelling studies (present study and study described in Chapter 5) taken from the same pasture field – one is relatively wet than the other. 167
- Table 8.1: List of symbols and parameters used in modelling $^{14}\text{CO}_2$ transport and production in the pasture-soil system. 173

LIST OF PLATES

- Plate 5.1: Dr. Surinder Sagggar carrying out $^{14}\text{CO}_2$ production inside the body of 60–ml syringe fitted with a 3–way stopcock. 68
- Plate 7.1: The $^{14}\text{CO}_2$ pulse labelling system. Dark (A) and light (B) lysimeters placed in sand baths (on the left hand side) and connected to a water bath (on the right hand side). Also showing (C) thermometer for noting glasshouse temperature, (D) quantum sensor for PAR measurements, and (E) 3–way stopcock on the dark bag for sampling and injecting $^{14}\text{CO}_2$ 142
- Plate 7.2: The $^{14}\text{CO}_2$ pulse labelling system, after injection of $^{14}\text{CO}_2$ pulse. Aluminium foil cover is in place over the dark polyethylene bags on ‘dark’ soil cores to control temperature rise inside the bag. 143
- Plate 7.3: Monitoring temperature fluctuations inside of the dark canopy placed over another soil core (i.e. not used for pulse labelling study) in the open environment. . 144
- Plate 7.4: The author sampling of soil solution from one of the light lysimeters by creating vacuum using 1 ml syringe. Transparent polyethylene bag isolates $^{14}\text{CO}_2$ –enriched atmosphere above soil core. 147