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**A STUDY OF THE LEACHING OF NON-REACTIVE SOLUTES AND NITRATE
UNDER LABORATORY AND FIELD CONDITIONS**

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

Gujjaiah Nanjaiah MAGESAN
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DEDICATION

This thesis is dedicated to my late parents,
G. Nanjaiah and G.N. Raniammal,
who have never been to school.

ABSTRACT

Leaching of solutes such as nitrate from soil to surface water and groundwater is of environmental and economic concern. Leaching experiments were conducted both in the laboratory using large intact soil cores (230 mm diameter; 250 mm depth) and in the field using a mole-pipe drained Tokomaru silt loam soil under pasture.

In the laboratory experiments 'tracers' (tritium, bromide or chloride) were applied as pulse or step-change inputs to the soil surface during steady flow. A transfer function model, based on a probability density function (pdf), which characterised solute travel between inlet and outlet surfaces in terms of cumulative drainage, was used to predict solute movement. Using tracer model parameters, leaching of indigenous chloride was reasonably predicted, but the leaching of indigenous nitrate could not be modelled satisfactorily. This was apparently due to the dynamic nature and spatial variability of the biological transformations to which nitrate is subject in soil.

In the field experiment solid sodium bromide and urea were applied in autumn 1990 to adjacent drained paddocks, each 0.125 ha in area. Soil, suction-cup and drainage samples were collected regularly during the drainage seasons of 1990 and 1991. The average amounts of drainage collected were 250 mm in 1990 and 320 mm in 1991, but the average amounts of nitrate leached were 47 and 20 kg N/ha, respectively. The results indicate the importance of source-strength for nitrate in N leaching loss. The nitrate-N concentration was around 35 g N m^{-3} in the early drainage, well above the WHO limit of 10 g N m^{-3} , but dropped to around 2 g N m^{-3} later in the drainage season. About 8 % of the applied N, but 52 % of the applied bromide, was leached during the 1990 drainage season. This shows the important effect that biological reactions such as immobilization can have in reducing nitrate leaching.

Comparisons were made between solute concentrations of suction-cup solution, soil extracted solution, and the drainage. For non-reactive solutes such as bromide (an applied solute) and chloride (an indigenous solute) the suction cup data provided better estimates of the solute concentration in the drainage than did the soil solution data. For nitrate, neither of these two measurements could estimate accurately solute concentrations in the drainage.

The solute leaching data obtained in the field were modelled using transfer functions. The bromide and chloride data were used to calculate the pdf of solute travel times. For chloride, an exponential pdf fitted the data slightly better than a lognormal pdf, despite it having only one rather than two fitted parameters. The chloride pdf appeared to be similar for both 1990 and 1991. For bromide, the inferred pdf conformed to a log-normal distribution and was quite different from the pdf derived from the chloride data. It seems that assuming a pulse (Dirac delta) flux input for a surface-applied solid fertilizer is not valid, and that this is the reason for the discrepancy between the pdfs obtained using the bromide and chloride data. When the pdf derived from the chloride data was used to model nitrate leaching, the result was generally disappointing.

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TABLE OF CONTENTS

ABSTRACT	iii
ACKNOWLEDGEMENTS	v
TABLE OF CONTENTS	vii
LIST OF TABLES	xiv
LIST OF FIGURES	xvi
LIST OF PLATES	xxiii
LIST OF SYMBOLS	xxiv

CHAPTER 1. INTRODUCTION AND LITERATURE REVIEW

1.1. INTRODUCTION	1
1.2. REVIEW OF LITERATURE ON LEACHING	2
1.2.1. Sources and transformation processes of N	2
1.2.1.1. <i>Mineralization</i>	3
1.2.1.2. <i>Immobilization</i>	3
1.2.2. Processes involving N losses	3
1.2.2.1. <i>Ammonia volatilization</i>	3
1.2.2.2. <i>Denitrification</i>	3
1.2.2.3. <i>Leaching</i>	4
1.2.3. Methods of measuring solute leaching	4
1.2.3.1. <i>Indirect methods (soil sampling and porous cup sampling)</i>	5
1.2.3.2. <i>Direct methods (lysimeters and mole-pipe drainage system)</i>	6
1.2.4. Factors affecting solute leaching	7
1.2.4.1. <i>Climatic conditions</i>	7
1.2.4.2. <i>Properties of soils</i>	8
1.2.4.3. <i>Fertilizers</i>	9
✓ 1.2.4.4. <i>Soil management</i>	9
1.3. MODELLING SOLUTE LEACHING: Principles and philosophy	10
1.3.1. Functional models of solute transport	12
1.3.2. Piston flow model of solute transport	12
1.3.3. Convection-dispersion equation for solute transport	13
1.3.4. Mobile-immobile model of solute transport	14
1.3.5. Transfer function model of solute transport	16
1.3.5.1. <i>Measurement of transfer function parameters</i>	16
1.3.6. Solute transport models for mole-pipe drained fields	18
1.4. PURPOSE AND STRUCTURE OF THIS PRESENT STUDY	20

CHAPTER 2. MATERIALS AND METHODS FOR LABORATORY AND FIELD EXPERIMENTS

2.1.	INTRODUCTION	22
2.2.	SITE AND SOIL DESCRIPTION	22
2.3.	LABORATORY EXPERIMENT	25
2.3.1.	Copers used for large core extraction	25
2.3.2.	Core collection	25
2.3.3.	Soil pretreatment	27
2.3.4.	Leaching apparatus	29
2.3.5.	Leaching experiments	31
2.4.	FIELD EXPERIMENT	33
2.4.1.	Field instrumentation	33
2.4.1.1.	<i>Drainage sample collectors</i>	33
2.4.1.2.	<i>Rainfall recorders</i>	35
2.4.1.3.	<i>Suction cup samplers</i>	35
2.4.2.	Fertilizer application	35
2.4.3.	Sample collection	36
2.4.3.1.	<i>Drainage and rainfall</i>	36
2.4.3.2.	<i>Suction cup samples</i>	36
2.4.3.3.	<i>Soil samples</i>	38
2.4.3.4.	<i>Herbage samples</i>	38
2.5.	PHYSICAL AND CHEMICAL ANALYSES	38
2.5.1.	Water content measurements	38
2.5.2.	Preparation of chemical analyses	39
2.5.2.1.	<i>Soil extraction</i>	39
2.5.2.2.	<i>Herbage extraction</i>	39
2.5.3.	Chemical analyses	39
2.5.3.1.	<i>Nitrate</i>	39
2.5.3.2.	<i>Chloride</i>	40
2.5.3.3.	<i>Bromide</i>	40
2.5.3.4.	<i>Tritium</i>	40
2.5.4.	Expression of results	41
2.5.4.1.	<i>Soil solute and drainage concentrations</i>	41
2.5.4.2.	<i>Data transformation</i>	41

CHAPTER 3. RESULTS AND DISCUSSION OF LABORATORY CORE EXPERIMENTS

3.1.	INTRODUCTION	42
3.2.	LIQUID-FILLED PORE VOLUME	42
3.3.	MASS BALANCE OF WATER AND SOLUTES	43
3.3.1.	Water	43
3.3.2.	Nitrate	43
3.3.2.1.	<i>Experiment 1: no pretreatment (cores A and B) ...</i>	44
3.3.2.2.	<i>Experiment 3: with field pretreatment (cores E and F)</i>	44
3.3.3.	Chloride	45
3.3.3.1.	<i>Experiment 1: no pretreatment (cores A and B) ...</i>	45
3.3.3.2.	<i>Experiment 3: with field pretreatment (cores E and F)</i>	45
3.4.	DYE APPLICATION	46
3.5.	SOIL AND LEACHING DATA	49
3.5.1.	Experiment 1: No leaching pretreatment	49
3.5.2.	Experiment 2: Laboratory preleaching	55
3.5.3.	Experiment 3: Pretreatment in the field	55
3.5.3.1.	<i>First phase of the experiment</i>	58
3.5.3.2.	<i>Second phase of the experiment</i>	62
3.6.	CONCLUSIONS	66

CHAPTER 4. MODELLING THE MOVEMENT OF NON-REACTIVE SOLUTES THROUGH UNDISTURBED SOIL CORES

4.1.	INTRODUCTION	67
4.2.	THEORY	67
4.3.	ESTIMATION OF MODEL PARAMETERS	70
4.4.	RESULTS AND DISCUSSION	70
4.4.1.	Experiment 1	70
4.4.1.1.	<i>Using tritium BTC to characterize solute pdf ...</i>	70
4.4.1.2.	<i>Modelling resident chloride and nitrate concentrations</i>	70
4.4.2.	Experiment 2	74
4.4.2.1.	<i>Using bromide BTC to characterize solute pdf ...</i>	74
4.4.2.2.	<i>Modelling the leaching of resident tritium ...</i>	76

4.4.3. Experiment 3	78
4.4.3.1. <i>Using tritium and chloride BTCs to characterize solute pdfs</i>	78
4.4.3.2. <i>Modelling the leaching of resident chloride and nitrate</i>	78
4.4.3.3. <i>Modelling the leaching of resident tritium</i>	81
4.4.4. Estimation of model parameters	83
4.4.5. Estimation of the solute transport volume	85
4.5. CONCLUSIONS	85

CHAPTER 5. SOIL, HERBAGE AND METEOROLOGICAL MEASUREMENTS FOR THE FIELD EXPERIMENT

5.1. INTRODUCTION	88
5.2. RAINFALL AND POTENTIAL EVAPOTRANSPIRATION DATA	88
5.3. SOIL MOISTURE DATA	91
5.4. SOLUTE CONCENTRATIONS IN SOIL	91
5.4.1. Bromide	91
5.4.2. Chloride	97
5.4.3. Nitrate-N	101
5.4.4. Ammonium-N	105
5.5. EFFECTS OF SHEEP GRAZING	105
5.5.1. Time effects	105
5.5.2. Depth effects	108
5.6. SUCTION CUP SAMPLING	108
5.6.1. Bromide	110
5.6.2. Chloride	110
5.6.3. Nitrate-N	110
5.7. COMPARISON OF SOLUTE CONCENTRATIONS IN SOIL SOLUTION	113
5.8. HERBAGE PRODUCTION	116
5.9. PLANT UPTAKE	117
5.9.1. Bromide	117
5.9.2. Chloride	117
5.9.3. Nitrogen	120
5.10. CONCLUSIONS	120

CHAPTER 6. LEACHING RESULTS AND MASS BALANCES FOR FIELD EXPERIMENTS

6.1.	INTRODUCTION	122
6.2.	DRAINAGE AND LEACHING RESULTS	122
6.2.1.	Bromide	123
6.2.2.	Chloride	125
6.2.2.1.	<i>1989 Spring</i>	125
6.2.2.2.	<i>1990 Drainage season</i>	125
6.2.2.3.	<i>1991 Drainage season</i>	128
6.2.3.	Nitrate	130
6.2.3.1.	<i>1989 Spring</i>	130
6.2.3.2.	<i>1990 Drainage season</i>	130
6.2.3.3.	<i>1991 Drainage season</i>	134
6.3.	DRAINFLOW RATE AND SOLUTE CONCENTRATIONS	136
6.3.1.	Effects of drainage flow rate on solute concentrations in the drainage	136
6.3.1.1.	<i>Applied solutes</i>	136
6.3.1.2.	<i>Resident solutes</i>	139
6.4.	COMPARISON OF SOLUTE CONCENTRATIONS IN DRAINAGE AND SOIL SOLUTION	139
6.5.	MASS BALANCE OF SOLUTES	143
6.5.1.	Bromide	143
6.5.2.	Chloride and nitrogen	143
6.6.	CONCLUSIONS	145

CHAPTER 7. MODELLING LEACHING OF NON-REACTIVE SOLUTES UNDER FIELD CONDITIONS

7.1.	INTRODUCTION	147
7.2.	THEORY	148
7.3.	BOUNDARY AND INITIAL CONDITIONS	150
7.3.1.	Source-sink term	151
7.3.1.1.	<i>Rainfall input</i>	151
7.3.1.2.	<i>Herbage uptake</i>	151
7.3.1.3.	C_b for bromide and chloride	151
7.4.	RESULTS AND DISCUSSION	151
7.4.1.	Evaluating $f(I)$	151
7.4.2.	The stationarity of $f(I)$	160
7.5.	FRACTIONAL SOLUTE TRANSPORT VOLUME	163
7.6.	CONCLUSIONS	163

CHAPTER 8. MODELLING NITRATE LEACHING UNDER FIELD CONDITIONS

8.1.	INTRODUCTION	165
8.2.	THEORY	165
8.3.	MODEL PARAMETER ESTIMATION	167
8.3.1.	Analytical solution to the TFM	169
8.3.2.	Numerical solution to the TFM	172
8.4.	RESULTS AND DISCUSSION	172
8.4.1.	Analytical solution	172
8.4.2.	Numerical solution	177
8.5.	CONCLUSIONS	180

CHAPTER 9. GENERAL DISCUSSION, CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

9.1.	INTRODUCTION	181
9.2.	GENERAL DISCUSSION AND CONCLUSIONS OF LABORATORY EXPERIMENTS	181
9.2.1.	Spatial distribution of soil nitrate and chloride	181
9.2.2.	Effect of long time storage	182
9.2.3.	Preferential flow	182
9.2.4.	Edge flow	183
9.2.5.	Denitrification	183
9.2.6.	Modelling laboratory leaching data	183
9.3.	GENERAL DISCUSSION AND CONCLUSIONS OF FIELD EXPERIMENTS	184
9.3.1.	Deep percolation	184
9.3.2.	Effect of grazing	184
9.3.3.	Drainage and leaching	184
9.3.4.	Suction cup sampling	185
9.3.5.	Comparison of soil solute concentrations	186
9.3.6.	Drainage flow rates and solute concentrations	186
9.3.7.	Modelling field leaching data	187
9.4.	SUGGESTIONS FOR FUTURE RESEARCH WORK	188

REFERENCES	189
APPENDICES	
Appendix 1	205
Appendix 2	207
Appendix 3	209
Appendix 4	210
Appendix 5	212
Appendix 6	214
Appendix 7	216

LIST OF TABLES

CHAPTER 2

Table 2.1	Dates of soil, suction-cup and herbage data collection. Also included is grazing duration and stocking rate	37
-----------	---	----

CHAPTER 3

Table 3.1	Volumetric water content before and during each experiment and liquid filled pore volume for each experiment	42
-----------	--	----

CHAPTER 4

Table 4.1	Model parameters for step-change input solutes	84
-----------	--	----

Table 4.2	Model parameters for pulse input solutes	84
-----------	--	----

Table 4.3	Estimation of the fractional transport volume for step-change input solutes	86
-----------	---	----

Table 4.4	Estimation of the fractional transport volume for pulse input solutes	86
-----------	---	----

CHAPTER 5

Table 5.1	Mean concentration of mineral N and chloride for all samples and concentration of solutes for site 9 in different layers on 28 May 1990	109
-----------	---	-----

Table 5.2	Cumulative herbage production during the 1990 drainage season (kg dry matter/ha)	116
-----------	--	-----

CHAPTER 6

Table 6.1	Average solute concentrations in the drainage at some events of the 1990 drainage season for both paddocks (standard errors are given in the parenthesis)	142
-----------	---	-----

Table 6.2	Predicted and measured leaching losses of solutes during the 1990 drainage season. Prediction was made using average values of solute concentration of upper and lower depths separately	142
Table 6.3	Predicted and measured leaching losses of solutes during the 1990 drainage season. Prediction was made using average values of solute concentration of upper and lower depths .	142
Table 6.4	Bromide recovery (kg Br/ha) for various periods of the 1990 drainage season for paddock A	144
Table 6.5	Chloride and nitrogen mass balance for 1990 (between 29 May and 10 October 1990). The units are kg/ha	144

CHAPTER 7

Table 7.1	Estimation of the fractional transport volume	163
-----------	---	-----

CHAPTER 8

Table 8.1	Measured and predicted leaching losses of nitrate (kg N/ha) for the 1990 and 1991 drainage seasons	179
-----------	--	-----

LIST OF FIGURES

CHAPTER 2

- Fig. 2.1. A schematic diagram of the experimental site. Square and rectangular boxes in paddocks C and D are the sites of soil taken for laboratory experiment. Dotted and solid lines represent the moles and pipes respectively 23

- Fig. 2.2. A schematic diagram of the sampling site for the first experiment (a) and for the third experiment with field pretreatment (b) showing extraction locations for the large and small soil cores 26

CHAPTER 3

- Fig. 3.1. The estimated distribution of nitrate (a and b) and chloride (c and d) in the soil solution for cores A and B before leaching on 5 July 1989 50

- Fig. 3.2. The volume outflow rates (a and b) and the breakthrough curves of tritium (c and d) for cores A and B 51

- Fig. 3.3. The concentration of indigenous nitrate (a and b) and chloride (c and d) in the effluent from cores A and B 53

- Fig. 3.4. The distribution of nitrate (a and b) and tritium (c and d) in the soil solution of cores A and B, respectively, after leaching 54

- Fig. 3.5. The volume outflow rates (a and b) and the breakthrough of bromide (c and d) for cores C and D after the pulse application of 500 g Br m^{-3} in 30 mm of input solution 56

- Fig. 3.6. The breakthrough curve of the tritium which had been applied during the pretreatment (a and b), and the distribution of tritium in the soil after leaching (c and d) 57

- Fig. 3.7. The distribution of nitrate (a and b) and chloride (c and d) in the soil solution after preleaching but before phase one of the leaching experiment, in the soil surrounding large cores E and F 59

Fig. 3.8.	The volume outflow rates (a and b) and the breakthrough curves of the applied tritium (c and d) for cores E and F for the first phase of the experiment	60
Fig. 3.9.	The concentration of nitrate (a and b) and chloride (c and d) in the effluent during the first phase of the experiment for cores E and F	61
Fig. 3.10.	The volume outflow rates (a and b) and breakthrough of nitrate pulse (c and d) for the second phase of the experiment for cores E and F	63
Fig. 3.11.	The breakthrough curve of applied chloride (a and b) and resident tritium (c and d) in the second phase of the experiment for cores E and F	64
Fig. 3.12.	The distribution of nitrate (a and b) and chloride (c and d) in the soil solution after the leaching experiment	65

CHAPTER 4

Fig. 4.1.	Measured (■) and fitted (—) relative concentration of tritium in the effluent for cores A and B	71
Fig. 4.2.	Measured and predicted concentrations of resident chloride (a and b) and nitrate (c and d); measured (■), predicted using the estimated soil solution concentration (—), and predicted assuming C_i as the concentration in first effluent sample (---) for cores A and B	72
Fig. 4.3.	Measured (■) and fitted (—) bromide concentrations (a and b) for cores C and D. Also shown are the measured (■) and resolution of the components of bromide pdf (—) for core C (c and d)	75
Fig. 4.4.	Details for (a) and (b) are given in the text. (c) and (d) show the predicted using parameters derived from the bromide pdf (—) and measured (■) relative concentrations of resident tritium in the drainage from cores C and D	77
Fig. 4.5.	Measured (■) and fitted (—) relative concentration of tritium (a) and (b) in the first part of the experiment; and chloride (c) and (d) in the second part of the experiment for cores E and F	79

Fig. 4.6.	Measured and predicted concentrations of chloride (a) and (b) and nitrate (c) and (d) for cores E and F; measured (■), predicted with the estimated soil solution concentration (—), predicted assuming C_i from the concentration in first effluent (---)	80
Fig. 4.7.	Measured (■) and predicted (—) concentration of tritium (a) and (b) and nitrate (c) and (d) in the effluent during the second part of the experiment. The prediction was carried out with parameters derived from a step input of chloride during the second part of the experiment	82

CHAPTER 5

Fig. 5.1.	Monthly rainfall, together with the long term average, for 1990 and 1991	89
Fig. 5.2.	Penman longterm evapotranspiration data (NZ Meteorological Service)	90
Fig. 5.3.	The mean volumetric water content profiles for the first three soil samplings in 1990 for paddocks A (●) and B (○)	92
Fig. 5.4.	The mean volumetric water content profiles for the last three soil samplings in 1990 for paddocks A (●) and B (○)	93
Fig. 5.5.	The mean volumetric water content profiles for three soil samplings in 1991 for paddocks A (●) and B (○)	94
Fig. 5.6.	The distribution of bromide in the soil profile of paddock A in 1990 for the first three soil samplings after Br application (means and standard errors are shown)	95
Fig. 5.7.	The distribution of bromide in the soil profile of paddock A in 1990 for the last soil sampling after Br application (means and standard errors are shown)	96
Fig. 5.8.	The distribution of chloride in the soil profiles of paddocks A (●) and B (○) in 1990 for the first three soil samplings (means and standard errors are shown)	98

Fig. 5.9.	The distribution of chloride in the soil profiles of paddocks A (●) and B (○) in 1990 for the last three soil samplings (means and standard errors are shown)	99
Fig. 5.10.	The distribution of chloride in the soil profiles of paddocks A (●) and B (○) in 1991 for all soil samplings (means and standard errors are shown)	100
Fig. 5.11.	The distribution of nitrate in the soil profiles of paddocks A (●) and B (○) in 1990 for the first three soil samplings (means and standard errors are shown)	102
Fig. 5.12.	The distribution of nitrate in the soil profiles of paddocks A (●) and B (○) in 1990 for the last three soil samplings (means and standard errors are shown)	103
Fig. 5.13.	The distribution of nitrate in the soil profiles of paddocks A (●) and B (○) in 1991 for all soil samplings (means and standard errors are shown)	104
Fig. 5.14.	The distribution of ammonium in the soil profiles of paddocks A (●) and B (○) in 1990 for the first three soil samplings (means and standard errors are shown)	106
Fig. 5.15.	The distribution of ammonium in the soil profiles of paddocks A (●) and B (○) in 1990 for the last three soil samplings (means and standard errors are shown)	107
Fig. 5.16.	Bromide and chloride concentrations in suction cup samples at 200 mm depth (●) and 450 mm depth (○) of paddock A and paddock B, respectively (means and standard errors are shown)	111
Fig. 5.17.	Nitrate concentrations in suction cup samples at 200 mm depth (●) and 450 mm depth (○) of paddocks A and B (means and standard deviations are shown)	112
Fig. 5.18.	Relationship between suction cup solution concentration and soil solution concentration for applied bromide (paddock A) and indigenous chloride (paddock B) at 200 mm depth (●) and 450 mm depth (○)	114

Fig. 5.19.	Relationship between suction cup solution concentration and soil solution concentration for nitrate in paddocks A and B at 200 mm depth (●) and 450 mm depth (○)	115
Fig. 5.20.	Bromide and chloride uptake by plants as a function of estimated evapotranspiration for the 1990 drainage season for paddocks A (●) and B (○)	118
Fig. 5.21.	Nitrogen uptake by plants for the 1990 drainage season	119

CHAPTER 6

Fig. 6.1.	Bromide concentration in the drainage water from paddock A collected during the 1990 drainage season	124
Fig. 6.2.	Chloride concentration in the drainage water before and after urea application on 13 September 1989	126
Fig. 6.3.	Chloride concentration in the drainage water collected during the 1990 drainage season	127
Fig. 6.4.	Chloride (+) and nitrate (■) concentration in the drainage water during the 1991 drainage season	129
Fig. 6.5.	Nitrate concentration in the drainage water before and after urea application on 13 September 1989	131
Fig. 6.6.	Nitrate concentration in the drainage water collected during the 1990 drainage season	132
Fig. 6.7.	Applied and indigenous solute chemographs for the 20 June 1990 drainage event	137
Fig. 6.8.	Applied and indigenous solute chemographs for the 14 August 1990 drainage event	138

CHAPTER 7

Fig. 7.1.	Bromide (a) and chloride (b) uptake by pasture as a function of drainage for paddocks A(●) and B (○)	152
Fig. 7.2.	Measured (■) and fitted (—) bromide concentrations in the drainage for the 1990 drainage season with (a) lognormal and (b) exponential pdfs	154
Fig. 7.3.	Measured (■) and fitted (—) chloride concentrations in the drainage of paddock A for the 1990 drainage season with (a) lognormal and (b) exponential pdfs	155
Fig. 7.4.	Measured (■) and fitted (—) chloride concentrations in the drainage of paddock B for the 1990 drainage season with (a) lognormal and (b) exponential pdfs	156
Fig. 7.5.	Measured (+ and ■) and fitted (—) chloride concentrations in the drainage of paddocks A and B (data pooled together) for the 1990 drainage season with (a) lognormal and (b) exponential pdfs	157
Fig. 7.6.	Comparison of pdfs of bromide (---) and chloride (—) with (a) lognormal and (b) exponential	158
Fig. 7.7.	Measured (■) and predicted (—) chloride concentrations in the drainage from paddock A for 1991 using 1990 chloride model parameters with (a) lognormal and (b) exponential pdf	161
Fig. 7.8.	Measured (■) and predicted (—) chloride concentrations in the drainage from paddock B for 1991 using 1990 chloride model parameters with (a) lognormal and (b) exponential pdf	162

CHAPTER 8

Fig. 8.1	Schematic diagram of travel pathways used in numerical solution of the Transfer Function Model	168
Fig. 8.2.	Nitrogen uptake as a function of drainage for the 1990 drainage sea.....	169

LIST OF PLATES**CHAPTER 2**

Plate 2.1	Experimental set-up for the intact core leaching experiments	30
Plate 2.2	Uniform distribution of dye indicating uniform application of tritiated water to the soil surface	30
Plate 2.3	V-notch weir and a pipe draining in pit A	34
Plate 2.4	Flow meter and plotter	34

CHAPTER 3

Plate 3.1	Some root channels connected with earthworm channels	47
Plate 3.2	Root channels	47
Plate 3.3	Vertical view of dye movement	48
Plate 3.4	Edge flow due to a stone which cut a groove during core collection	48

LIST OF SYMBOLS

Roman letters

- | | |
|-----------|---|
| f | = fraction of solute that is washed below a depth in cm (Chap 1)
= porosity of the soil (Chap 3) |
| $f(I)$ | = net applied water probability density function (pdf) (L^{-1}) |
| h | = depth cm (L) |
| m | = sample mean (Chap 2) |
| n | = number of observations in a sample. |
| q_m | = water flux density in the mobile volume ($L T^{-1}$) |
| s | = amount adsorbed per unit surface ($M M^{-1}$)

= standard deviation (Chap 2) |
| t | = time (T) |
| x_i | = ith observation, |
| z | = depth (L) |
|
 | |
| C | = flux-averaged solute concentration ($M L^{-3}$) |
| C_a | = Initial uniform soil solution concentration ($M L^{-3}$) |
| C_b | = Source-sink term ($M L^{-3}$) |
| C_{ent} | = flux-averaged solute concentration at the entrance surface ($M L^{-3}$) |
| C_{ex} | = flux-averaged solute concentration at the exit surface ($M L^{-3}$) |
| C_{im} | = solute concentration in the immobile volume ($M L^{-3}$) |
| C_m | = solute concentration in the mobile volume ($M L^{-3}$) |
| C_o | = flux concentration for solute front inputs ($M L^{-3}$) |
| D | = diffusion-dispersion coefficient ($L^2 T^{-1}$) |
| H_w | = height of water from the base of the V-notch weir (L) |

I	= Drainage (L)
I_a	= Mean drainage (L)
I_m	= Median drainage (L)
K_w	= a constant relating to the weir flow calculation
M_o	= a pulse of mass applied to the soil surface at $I = 0$ (M L ⁻²)
M_n	= net mineralization over drainage season (M L ⁻²)
P	= percolation of rain in cm (L)
$P(I)$	= cumulative density function
Q_w	= flow rate in the weir [L ³ T ⁻¹]
V	= mean pore water velocity (L T ⁻¹)

Greek letters

α	= a rate coefficient (T ⁻¹)
ε	= gas-filled porosity
μ	= mean of a distribution
ρ_b	= bulk density (M L ⁻³)
ρ_s	= particle density (M L ⁻³)
θ	= volumetric water content (L ³ L ⁻³)
θ_f	= volumetric moisture content of the soil at 'field capacity'
θ_m	= a mobile water content
θ_{im}	= an immobile water content
θ_{st}	= transport volume fraction
Φ	= a source (or sink) term for solute (M L ⁻³ T ⁻¹)
σ^2	= variance of a distribution