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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

1992

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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<sup>-3</sup> in the early drainage, well above the WHO limit of 10 g N m<sup>-3</sup>, but dropped to around 2 g N m<sup>-3</sup> 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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## 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.	Corers 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.	1989 Spring .....	125
6.2.2.2.	1990 Drainage season .....	125
6.2.2.3.	1991 Drainage season .....	128
6.2.3.	Nitrate .....	130
6.2.3.1.	1989 Spring .....	130
6.2.3.2.	1990 Drainage season .....	130
6.2.3.3.	1991 Drainage season .....	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.	Applied solutes .....	136
6.3.1.2.	Resident solutes .....	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.	Rainfall input .....	151
7.3.1.2.	Herbage uptake .....	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

<b>REFERENCES</b> .....	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  $500 \text{ g Br m}^{-3}$  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
<b>CHAPTER 5</b>		
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 season . . . . . 171

- Fig. 8.3. Measured (■) and predicted, using analytical (---) and numerical solutions (—), nitrate concentrations for paddock A for the 1990 drainage season. (a) assumes the plant N uptake is as nitrate and (b) assumes plant uptake is half as nitrate and half as ammonium . . . 173
- Fig. 8.4. Measured (■) and predicted, using analytical (---) and numerical solutions (—), nitrate concentrations for paddock B for the 1990 drainage season. (a) assumes the plant uptake is as nitrate and (b) assumes plant uptake is half as nitrate and half as ammonium . . . 174
- Fig. 8.5. Measured (■) and predicted, using analytical (---) and numerical (—) solutions, nitrate concentrations for paddocks A (a) and B (b) for the 1991 drainage season . . . 178

## 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)
- $x_i$  =  $i$ th 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

$\alpha$	= a rate coefficient ( $T^{-1}$ )
$\epsilon$	= gas-filled porosity
$\mu$	= mean of a distribution
$\rho_b$	= bulk density ( $M L^{-3}$ )
$\rho_s$	= particle density ( $M L^{-3}$ )
$\theta$	= volumetric water content ( $L^3 L^{-3}$ )
$\theta_f$	= volumetric moisture content of the soil at 'field capacity'
$\theta_m$	= a mobile water content
$\theta_{im}$	= an immobile water content
$\theta_{st}$	= transport volume fraction
$\Phi$	= a source (or sink) term for solute ( $M L^{-3} T^{-1}$ )
$\sigma^2$	= variance of a distribution

# CHAPTER 1

## INTRODUCTION AND REVIEW OF LITERATURE

### 1.1. INTRODUCTION

Movement of water and solutes through soil has been a subject of interest for more than a century. The study of solute movement has been intensified in the past two decades. Attempts have been made to predict the movement of water and solutes under different conditions. Movement of solutes from the root zone is called leaching.

Solutes or plant nutrients are added to soils from different sources. For example, nitrogen (N) is added to soils through biological fixation, fertilizer addition, atmospheric input and animal returns. N added through these sources is liable to be leached in the form of nitrate (White, 1988). Leaching not only depletes the available soil N for plant uptake, thereby limiting the potential plant and animal production, but also contaminates surface and underground water, thereby affecting water quality or endangering the aquatic environment by eutrophication. The European Community has imposed a limit of 50 mg l<sup>-1</sup> for nitrate, equivalent to 11.3 mg l<sup>-1</sup> NO<sub>3</sub>-N, in potable water (Council of the European Communities, 1980). Thus a study on nitrate leaching becomes important from the environmental as well as the economic point of view.

Because the increase in nitrate concentrations in water has coincided with an increase in the use of nitrogen fertilizers, it is often assumed to that these fertilizers have been a major contributing factor (Addiscott and Powlson, 1991). But, a major source of groundwater nitrate from agricultural land can originate from mineralization of organic N following cultivation, rather than from the fertilizer itself (Kolenbrander, 1975). So, the study of nitrate leaching from the indigenous soil nitrate source becomes important. Moreover the prediction of solute leaching under field conditions is difficult due to a general lack of satisfactory models of solute movement (Jury 1983; Wagenet, 1983), particularly for the rate or amount of nitrate leaching (Wild and Cameron, 1980; Nielsen *et al.*, 1982; White, 1988). Modelling

nitrate leaching in field soil is made difficult for the following reasons (White, 1988): (1) inputs of water and N are spatially and temporally variable; (2) microbial transformation and plant uptake of N during and between leaching events can change the pool of nitrate available for leaching; and (3) heterogeneity of the soil's physical properties can cause spatial variability in water movement.

So the overall aim of this study was to measure and model the movement of nitrate in natural soil. Because nitrate is biologically reactive, the movement of non-reactive and conservative solutes such as bromide and chloride through soil was also studied. The study was carried out both in the laboratory and in the field.

## 1.2. REVIEW OF LITERATURE ON LEACHING

Reviews on solute leaching, especially nitrate, seem to appear regularly. Recently Wild and Cameron (1980), Nielsen *et al.* (1982), Cameron and Scotter (1986), Keeney (1986) and White (1988) have carried out in depth reviews of the measurement and modelling of nitrate leaching. In this review the methods of measuring, and the factors affecting, solute leaching are discussed. There is a small section on the sources and transformation processes of N. Subsequently the principles and philosophy of various models used for predicting solute leaching are briefly discussed.

### 1.2.1. Sources and transformation processes of N

Undisturbed soils under vegetation have average N reserves of 5000 kg N/ha (Cameron, 1992). Most of this (over 90 %) is held as insoluble organic N present in decomposed organic matter. Organic nitrogen in the soil is relatively immobile, and is inaccessible for either plant uptake or leaching. Microbes convert it to ammonium and then to the mobile nitrate form, not necessarily when crops need it, but when conditions suit. At any one time only about 1-2 % of the total N content in soils is present in a plant available form (Woodmansee *et al.*, 1981; Cameron, 1992). In New Zealand, biological fixation provides most of the N for pastures, and it has been estimated that approximately 1 million tonnes of N annually is added to soil through this source (Syers, 1982; Bolan *et al.*, 1991).

#### 1.2.1.1. *Mineralization*

Nitrogen mineralization is a process by which organic N is converted into mineral N. Firstly, organic N is converted into ammonium ions by a process called ammonification. Ammonium in soils is also added to soil through the application and hydrolysis of certain type of nitrogen fertilizers. Ammonium ions are subsequently oxidized via nitrite to nitrate, and this process is called nitrification. The reactions are generally mediated in soil by the activities of two small groups of chemoautotrophic bacteria, *Nitrosomonas* and *Nitrobacter*.

#### 1.2.1.2. *Immobilization*

Immobilization is a process in which mineral N is converted into organic N, i.e. the reverse of mineralization. Whether net mineralization or immobilization occurs in a soil depends on its carbon to nitrogen ratio. When the C:N ratio is high (>20-25) net immobilization results.

### 1.2.2. Processes involving N losses

Mineral N can be lost from the soil solution by the processes of denitrification, volatilization, and leaching. It can also be removed by the processes of immobilization and plant uptake.

#### 1.2.2.1. *Ammonia volatilization*

Ammonia volatilization is a process by which ammonium is converted into free ammonia gas which is released into the atmosphere (Freney *et al.*, 1983). The quantities of ammonia lost are highly variable depending on factors such as rate, type and method of fertilizer application, soil pH, and environmental factors including temperature, moisture, and wind (Black *et al.*, 1985). Losses through ammonia volatilization of fertilizer N applied to the surface of grassland or bare soil often appear to be in the range of 0 to 25 % (Black *et al.*, 1985).

#### 1.2.2.2. *Denitrification*

Denitrification is a process by which nitrate is biochemically reduced under anaerobic conditions, the products being nitrous oxide and dinitrogen gas. These gases can be lost from the soil into the atmosphere (Firestone, 1982). The rate of denitrification in

soil depends on the nitrate concentration, oxygen diffusion rate, the availability of carbon substrate, temperature, and pH. Colbourn and Dowdell (1984) generalized that direct and indirect estimates of losses of  $N_2$  and  $N_2O$  from soils range from 0 to 7 % of fertilizer N applied on grassland soils. Denitrification may occur in specific locations in soil, such as within an aggregate, and does not necessarily require the complete profile to be anaerobic (Cameron, 1992).

Denitrification is undesirable because a valuable plant nutrient is lost. But with increasing concern about nitrate losses to natural waters, denitrification plays a more favourable role of preventing nitrate losses into surface waters and aquifers (Addiscott *et al.*, 1991). The desirability of denitrification depends, however, on the nature of the final product formed. Dinitrogen gas,  $N_2$ , is no problem because it makes up 79 % of the atmosphere in any case, but nitrous oxide is implicated in two major environmental problems, climate change and the depletion of the ozone layer. The rate of denitrification is likely to be greater in wet clay soils and this can further reduce the apparent leaching loss (Kolenbrander, 1972; Gambrell *et al.*, 1975).

### 1.2.2.3. *Leaching*

As mentioned in an earlier section, organic N is relatively immobile in soil. Ammonium N is positively charged, and is generally retained on soil colloids by adsorption and also within the interlamella regions of 2:1 mixed layer minerals. Thus it is relatively immobile and to some extent it is protected from leaching. Nitrogen is leached mainly as nitrate (White, 1988). Nitrate in solution is a negatively-charged ion, and thus repelled from cation exchange sites. The vulnerability of nitrate to leaching is related to the availability of nitrate in the soil solution. Leaching of nitrate is one of the main pathways for N loss from pastures (Steele and Vallis, 1988; White, 1988), and thus is the focus of this study.

### 1.2.3. **Methods of measuring solute leaching**

To estimate the amount of nitrate leaching, two variables, the quantity of water participating in leaching and the flux-averaged nitrate concentration in that water, must be known (White, 1988; Bergstrom and Johansson, 1991). Accurate measurement of these two variables is difficult due to spatial and temporal variability

(White, 1985). Nitrate concentrations in drainage water can be measured directly from lysimeters and mole-pipe drained systems, or estimated indirectly from soil sampling or porous cup sampling. Since all these methods are used in this study, it is appropriate to discuss briefly each one of them.

#### **1.2.3.1. Indirect methods (*soil sampling and porous cup sampling*)**

Soil sampling is a cheap and easy method in which soil samples are taken with a corer to the desired depth. The soil samples are then extracted with water or electrolyte solution and the nitrate concentration in the extractant is measured. This method has been widely used to find the nitrate concentrations in the soil solution (e.g. Mohammed *et al.*, 1984; Field *et al.*, 1985). Sampling at regular intervals provides information on changes in the amount of nitrate in the soil. These changes do not necessarily arise from leaching. They may also be due to plant uptake and microbial transformations in the soil. Thus sampling does not explicitly tell us how much is leached or at what concentrations nitrate moved.

The principle of the suction cup ("artificial root") was first described by Briggs and McCall (1904). Wagner (1962) described its modern equivalent. Suction cups are constructed of hydrophilic materials with fine pores. When suction is applied to the sampling system, water flows from the soil into the suction cup. Recent reviews of this method are given by Litaor (1988), Grossmann and Udluft (1991). Porous cups are relatively cheap and fairly easy to use. Their installation is relatively simple and causes very little disturbance to the soil profile. They allow continuous sampling during any period and at several different depths in a soil profile. The cup can draw water from large distances - up to about 0.6 m (Van der Ploeg and Beese, 1977).

The disadvantages of suction cups are that the soil solution is drawn from a wide variety of pores not all of which may contribute to the flow. Reproducibility of either the volumes of water extracted or the nitrate concentrations measured are not very satisfactory. The reasons for this could be due to the intrinsic variability of the cups themselves, slight differences in installation, and variability in the soil (Wood, 1973). Also, the rate at which the cups fill can affect the nitrate concentration that they measure - and add to the problem of reproducibility (Hansen and Harris, 1975).

A problem associated with both soil sampling and porous cup sampling is the spatial variability in nitrate concentrations (Nielsen *et al.*, 1979; Cameron and Wild, 1984; MacDuff and White, 1984; White *et al.*, 1987), and thus these methods require a large number of replicate measurements. Also it may be difficult to obtain deep samples especially on stony soils. Estimating the leaching losses with an indirect method, e.g. from the concentration of leachate collected from suction devices or soil samples and a water balance can lead to substantial errors, as is shown later in the thesis.

#### 1.2.3.2. Direct methods (*lysimeters and mole-tile drainage systems*)

A lysimeter is a system in which the soil volume is well defined, usually soil is enclosed in a casing. The lysimeter, like a porous ceramic cup, is quite simple in concept but not particularly easy to use. In lysimeters because the soil volume is precisely defined, inputs and outputs of water and solutes can be easily measured. The first lysimeter with undisturbed soil was constructed by Lawes and Gilbert in 1870 (Lawes *et al.*, 1882). They showed the importance of the structure of the undisturbed soil on water and solute movement, and questioned the relevance of using filled-in lysimeters to learn about water and solute movement through natural soil. Barbee and Brown (1986) used porous cups and lysimeters to evaluate chloride concentrations in three differing soils: a loamy sand, a moderately-structured silt loam and a strongly-structured clay soil. They found no significant difference between applied chloride concentrations measured in the water samples from the two measuring techniques in sandy soils. They found differences in other soils. A problem that can be associated with lysimeters is edge-flow. Cameron *et al.* (1990) provided a technique to stop this edge-flow by injecting vaseline between the edge of the soil core and the soil.

A mole-pipe drained system has a big advantage in monitoring solute leaching because of the relevance of such experiments to normal agriculture, that is, solute leaching is studied at a scale comparable to the normal field scale of agricultural operations. The area of soil from which the water and solute originate is well defined. The spatial variability of solute and water movement is integrated over the field. A problem is that the drains may not intercept all the percolating water and

therefore do not properly measure the amount of leaching that occurs over a whole field (Thomas and Barfield, 1974).

#### **1.2.4. Factors affecting solute leaching**

Some of the important factors which influence solute leaching directly or indirectly are climatic conditions, soil properties, fertilizers and land management.

##### **1.2.4.1. Climatic conditions**

As mentioned earlier the amount of leaching depends on the downward movement of water. Such movement occurs when rainfall is greater than evaporation and when soil is relatively wet during autumn, winter and spring (Alison, 1968; McLean, 1977; Cameron *et al.*, 1978). The leaching pattern depends to some extent on rainfall intensity (Wild and Cameron, 1980; Milburn *et al.*, 1990). In autumn rainfall plays an important role of increasing the soil water content and thus drainage is generally minimal (Williams, 1975). Chloride in soil increases over summer due to a lack of leaching. When the soil rewets a flush of N mineralization occurs (Birch 1958, White *et al.*, 1983, Cameron and Haynes, 1986), increasing the pool of resident nitrate, particularly in the surface layer where more organic matter is found. This results in high chloride and nitrate concentrations in the drainage in the first flows in autumn and early winter, and a subsequent concentration decline (Harris *et al.*, 1984; Haigh and White, 1986). This pattern is often most marked if the previous summer has been unusually hot and dry (Williams 1976; Garwood and Tyson, 1977; Foster and Walling, 1978). By late spring or early summer, leaching becomes negligible as plant growth accelerates and evapotranspiration generally exceeds rainfall. Exceptions do occur when heavy spring rain falls on land that has recently been fertilized (Macduff and White, 1984).

Temperature affects the rate of N mineralization of organic matter. Thus, as temperature rises the nitrate content in soil often increases which affects nitrate leaching. Temperature also affects plant growth rates and hence the capacity of plants to absorb water, and chloride and nitrate from the soil.

#### 1.2.4.2. *Properties of soil*

The important soil physical properties involved in nitrate leaching are the hydraulic conductivity and water storage capacity of a soil, which are directly related to its texture and structure. The texture of the soil, that is the relative proportions of sand, silt and clay, changes vertically in a field soil. This 'variability' is one of the complicating factors in measuring leaching. The volumetric water content above which water moves freely under the influence of gravity ("field capacity") is generally greater in clay soils than sandy soils. In general, the amount of nitrate leached is more in sandy soils than in clay soils (Kolenbrander, 1969; Cooke, 1976; Sommerfeldt *et al.*, 1982).

Depending on the soil's structure, some of the rain water entering the soil, particularly during storms, may move rapidly from the A horizon by pathways between aggregates which bypass much of the soil in the B horizon (Scotter, 1978; Smettem *et al.*, 1983; White *et al.*, 1983). This affects the rate of solute leaching. When solute is held within soil aggregates it will be protected from leaching when bypass flow occurs (Cunningham and Cooke, 1958; Wild, 1972; Thomas and Phillips, 1979). However if fertilizer has been recently applied, or if soil solute is held on the outside of aggregates, bypassing flow causes it to leach faster than it would by uniform displacement (Addiscott and Cox, 1976; Barraclough *et al.*, 1983). Solute within aggregates is relatively protected from leaching during individual events, but between events some of it diffuses to the aggregate exteriors whence it can be leached. It has been shown that only a part of the soil water is apparently effective in solute transport during individual rainfall events (Smettem *et al.*, 1983; Scotter *et al.*, 1984; White *et al.*, 1984, 1986; White, 1987).

Most temperate agricultural soils carry an overall negatively charged surface. Nitrate, being a negatively charged ion, is forced away from the clay surface. Negative adsorption and the exclusion of nitrate from very fine pores in soils of this kind may cause a nitrate pulse to move slightly faster than the accompanying water (Cameron and Wild, 1982), but the effect is usually insignificant compared to the bypassing effect created by the soil's structure (White *et al.*, 1984; Dyson and White, 1987). Many tropical soils tend to be acidic and often have an overall positive

charge on the clay, particularly in the subsoil low in organic matter. In such soils, therefore, the nitrate is attracted to the clay and experiments show that the nitrate is to some extent held back against being washed out (e.g. Wong *et al.*, 1987).

Substantial leaching losses of nitrate can occur from unfertilized bare fallow soils (Lowe, 1973; Guiot, 1981). Under cultivated situations, Dowdell *et al.* (1984) found a more significant loss of nitrate from the mineralization of organic matter than from applied fertilizers. They estimated less than 10 % of the applied fertilizer was lost by leaching.

#### 1.2.4.3. *Fertilizers*

Nitrogen fertilizer usually contains nitrogen in one of three forms, ammonium, nitrate or urea. Of these the commonest, on a world basis, is urea. Studies have shown that nitrate leaching losses increased when fertilizer was applied at rates above the optimum for crop production (Burwell *et al.*, 1976; Baker and Johnson, 1981). The amount and type of N fertilizer used can have a major influence on the amount of nitrate available for leaching (Pratt *et al.*, 1967). Addition of fertilizer N may tend to stimulate mineralization of soil organic N and thus lead to enhanced leaching of native soil nitrate called a 'priming effect' (Jenkinson, 1983). Also past applications of fertilizer N which have become incorporated into the organic N fraction may become a source of nitrate for leaching when mineralized (Mackenzie and Viets, 1974). Haigh and White (1986) estimated that up to 43 % of one year's application of fertilizer N was apparently leached under grazing. As expected, the proportion of fertilizer N that is leached is inversely related to the recovery of N by the plants (Webster and Dowdell, 1984).

#### 1.2.4.4. *Soil management*

Soil use and land management play an important role in determining the extent of nitrate leaching. Vegetation helps in taking up the available nitrate from the soil solution and thus reducing nitrate leaching. Perennial crops such as trees and grass are generally more effective in this way than annual crops. Water draining from forests usually contains little nitrate because most of the nitrogen is cycled from the soil to the trees and then back to the soil in leaf-fall in a closed cycle. Grass absorbs

nitrogen whenever mineralization occurs and grassland is potentially a less leaky system than arable farming. However a substantial amount of nitrate leaches when forest is cleared or grassland is ploughed. Ploughing of old grassland accelerates nitrate leaching because of the increased rate of mineralization of organic N (Cooke, 1976; Foster *et al.*, 1982). Grassland often responds to higher rates of fertilizer N than other crops (Morrison *et al.*, 1980).

Field and Ball (1978) found that grass species in New Zealand pastures are usually under N stress and appear to absorb N from the upper layers of the soil almost as fast as it becomes available from mineralization, except during drought. The leaching losses of N from pastures have been considered to be small because of the ability of the grass to utilize large amounts of N. However, recent studies (Wild and Cameron, 1980; Ryden *et al.*, 1984; Haigh and White, 1986) have shown that large leaching losses of N (25%-40% of the N input) can occur from intensively managed grazed pastures. The main problem with grazed grassland systems is that they use nitrogen very inefficiently. Cut grass uses nitrogen efficiently because the nitrogen it contains is removed from the field and because it continues to regrow after each cut almost all the year round. The grazed system leaks more nitrate because on average more than 80 % of all nitrogen consumed by the animal is returned to the soil in urine and dung in which the organic N is readily mineralized. The main effect of grazing seems to be the concentration of soluble N in small volumes of soil under urine patches, and the local concentration of mineral N greatly exceeds plant uptake capacity. Leaching losses can be relatively large (up to 90 kg N/ha/yr) on intensely managed pastures where high fertilizer rates are combined with high stocking rates (Steele *et al.*, 1984; Ryden *et al.*, 1984). The effect of grazing animals on leaching losses has been well demonstrated (Ball and Ryden, 1984; Steele, 1984).

### **1.3. MODELLING SOLUTE LEACHING : Principles and philosophy**

Models are simplified descriptions of reality. They enable the most important aspects to be identified, studied, simulated, and ultimately predicted in advance (Addiscott *et al.*, 1991). Models are being increasingly used as management tools to predict the fate of agricultural chemicals, toxic wastes and salinity in soil.

Many models of solute leaching have been developed over the years, some simple and some complicated. The simplicity or complexity of a model often depends on whether it is constructed from a management or research perspective. In general, the quantity of required input data, depth of consideration of basic processes, and sensitivity, of simulations of a research oriented model are greater than a management oriented model. Several reviews have been written recently on solute transport models (e.g. Addiscott and Wagenet, 1985; Brusseau and Rao, 1990; Jury *et al.*, 1991, Jury and Flühler, 1992).

Models can be put into several categories (Addiscott and Wagenet, 1985; Jury and Nielsen, 1987). Addiscott and Wagenet (1985) distinguish between *functional* and *mechanistic* models, and between *deterministic* and *stochastic* models. Functional models aim to give a reasonably good general description of the leaching process and its results without going into great detail. Mechanistic models, on the other hand, try to incorporate the best possible description of the process in the leaching mechanism. A deterministic model presumes that for a given set of events there is a unique definable outcome, but a stochastic model presumes the outcome to be uncertain and is structured to account for this uncertainty. Jury and Nielsen (1987) classify the modelling approaches into two groups, *process* models and *stochastic* models. Process models develop a description of transport based on mass conservation and flux laws, leading to differential equations to predict values of the water and solute variables as functions of position and time. In contrast, stochastic models describe the variables as random functions, which depend on the distribution of values of the soil properties which determine their movement. Rather than predict values of concentration as a function of position and time, stochastic models predict concentration averages and variances, and are used to calculate the probability of having a concentration of solute at a given depth or time.

There are many solute transport models available but not all models are discussed here. A brief introduction of functional models is given. Then process models and stochastic models are described. Finally the models developed for a mole-tile drained field are discussed.

### 1.3.1. Functional models of solute transport

Functional models are based on the observed quantitative relationships among variables, and they are less mechanistic (Addiscott and Wagenet, 1985). A useful functional model was developed by Burns (1974). It can be visualized as a vertical series of stirred containers each of which overflows into the one below. Water added to the top one is assumed to mix instantaneously with water and solute already there before an equivalent volume overflows. These containers represent layers in the soil and the volume held in each of them corresponds to the volumetric moisture content of the soil at 'field capacity',  $\theta_f$ . Burns (1975) developed another useful leaching equation,

$$f = \left( \frac{P}{P + \theta_f} \right)^h \quad (1.1)$$

where  $f$  is the fraction of solute that is washed below a depth  $h$  cm by the percolation of  $P$  cm of rain. This equation applies to a surface-applied solute. If the solute is initially distributed through the soil to the depth  $h$ , then  $h$  in the equation is replaced by  $h/2$ .

Neither of the approaches suggested by Burns takes account of mobile and immobile water in the soil, and they are likely to perform best on sandy or other relatively unstructured soils. Addiscott (1977) and Addiscott and Whitmore (1991) developed a model similar to the Burns model (1974), but incorporated mobile and immobile water in each layer. Rain or irrigation causes flow through the soil in the mobile water. After each flow event, solute moves between the mobile and immobile water to equalize the concentrations between the two zones. The Burns and Addiscott models can be very useful for management purposes.

### 1.3.2. Piston flow model of solute transport

This is a simplified model, and it assumes water and solutes move through soil only by convection, or mass-flow. In this model, the incoming water or solution replaces the water initially present in the soil, or in other words, it pushes it ahead without mixing with it. This is only approximated if the soil is completely uniform in pore

size, which means practically never. Jury (1975) calculated solute travel times and effluent concentrations using a mathematical model to characterise the curved water flow pathways to a tile drain, coupled with a piston flow model to calculate the solute movement. Rao *et al.* (1976) found the piston flow model to give a good estimate of the position of the solute front in sandy soils but not, of course, its spread. However Wild and Babiker (1976) found that this model tended to overestimate nitrate movement and suggested that the model ignored the effects of soil aggregates. Although this model predicts the position of the front of the displacing solution, it gives no estimate of how much this front is spread out.

### 1.3.3. Convection-dispersion equation for solute transport

The convection-dispersion equation (CDE) is the classic mechanistic approach to modelling the transport of solute through the soil by water. This model assumes that water and solutes move through the soil by two processes, convection and dispersion. Dispersion means that the solute becomes dispersed, or spread out, within the flow. There are two reasons for dispersion happening. One is that water flows more rapidly in some pores than others, so that the solute is carried forward faster in some places than others. This may be due to variation in pore water velocities in soil due to different sizes of pores, and/or different pathlengths of water movement (tortuosity). The other reason is diffusion, the "natural tendency" of a solute to spread itself uniformly throughout the whole volume of water in which it finds itself. Diffusion occurs whether or not the water is flowing. Even in columns of repacked soil dispersion is observed.

If the water flow is at a steady-state, then the solute movement can be described by the CDE as (Nielsen and Biggar, 1962; Jury *et al.*, 1976; Wagenet, 1983; Cameron and Scotter, 1986)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} \quad (1.2)$$

where  $C$  is the flux-averaged solute concentration ( $M L^{-3}$ ),  $D$  is a parameter called the diffusion-dispersion coefficient ( $L^2 T^{-1}$ ),  $V$  is the mean pore water velocity ( $L T^{-1}$ ) which is equivalent to Darcy flux density over volumetric water content,  $z$  is the depth ( $L$ ) and  $t$  is the time ( $T$ ).

If the solute is adsorbed, or subject to gain or loss during transport, additional terms can be included in the CDE to describe such processes, giving

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial s}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} \pm \Phi \quad (1.3)$$

where  $\theta$  is volumetric water content ( $L^3 L^{-3}$ ),  $\rho$  is the bulk density ( $M L^{-3}$ ),  $s$  is the amount adsorbed per unit mass ( $M M^{-1}$ ) and  $\Phi$  represents a source (or sink) term for solute ( $M L^{-3} T^{-1}$ ).

The CDE can be solved analytically for certain boundary and initial conditions (Kirkham and Powers, 1972) and also numerically (De Smidt and Wierenga, 1978; van Genuchten and Alves, 1982). Numerical solutions are flexible in accommodating a range of initial and boundary conditions for water and solute.

#### 1.3.4. Mobile-immobile model of solute transport

In a structured soil, however, water containing solutes does not move at the same velocity due to the presence of a range of soil pore sizes. Preferential flow through macropores (Scotter, 1978; White, 1985) occurs in structured soils. Solutes move faster through macropores and slower through micropores. To incorporate the effect of preferential flow of solute, a model known as the "mobile-immobile" water model was developed (Coats and Smith, 1956; van Genuchten and Wierenga, 1976; Addiscott, 1977; Scotter *et al.*, 1991). In this model the total water content ( $\theta$ ) is divided into two notional water contents: a mobile water content  $\theta_m$  and an immobile water content  $\theta_{im}$ . The solute is transported by a convection-dispersion process in the mobile region, and also exchanges with solute in the immobile region by a diffusion process. Although this model has been used successfully (Nkedi-Kizza *et al.*, 1983), as a simulation model it has a drawback. Its parameters generally cannot be measured independently and can only be obtained by curve fitting outflow data using simultaneous optimization (Jury *et al.*, 1991). Also there are difficulties in defining the mobile and immobile phases. Clothier *et al.* (1992) have proposed a promising method to measure the mobile phase using a disc permeameter. The mobile-immobile model equation is

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = D_m \frac{\partial^2 C_m}{\partial z^2} - q_m \frac{\partial C_m}{\partial z} \quad (1.4)$$

where  $q_m$  is water flux density in the mobile volume ( $L T^{-1}$ ). The rate of mass transfer between the mobile and immobile region is expressed in the model as

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (1.5)$$

where  $\alpha$  is a rate coefficient ( $T^{-1}$ ). Equation (1.5) states that the rate of change of solute concentration in the immobile region is proportional to the difference in concentration between the two regions.

Recently, Tillman *et al.* (1991) used the mobile-immobile model of solute transport under transient field conditions. They coupled a mobile-immobile variant of the convection-dispersion equation with a description of the transient water flow and root water extraction. They used this model successfully to describe the main features of the non-reactive solute (bromide) movement under different regimes of water application. They inferred that if a slug of liquid nitrogen fertilizer was applied to a relatively dry topsoil, it will be much less prone to subsequent leaching than if applied to wet soil. On the other hand, if it is desired to get a non-sorbed fertilizer down into the subsoil as quickly as possible, it should be applied to moist soil and followed immediately by irrigation. Their model ignored spatial variability in both the water and solute fluxes. They argued that for unsaturated flow under conditions with a spatially uniform flux at the surface, one would expect the variability to be much less compared to the leaching under ponding conditions.

There is generally wide spatial variability in soil physical and chemical properties within a field (Biggar, 1978; Nielsen *et al.*, 1979; Cameron and Wild, 1984; Macduff and White, 1984). The spatial and temporal variability of field soils makes difficulties in using the above models. The recognition of the variability of soil properties has led to the use of stochastic models for prediction of solute movement in field soils, or at least the inclusion of stochastic parameters in deterministic models (Nielsen *et al.*, 1986).

### 1.3.5. Transfer function model of solute transport

Transfer functions provide an interesting alternative approach, which may be entirely non-mechanistic in form. They have been applied to industrial processes by Dankwaerts (1953) and hydrological processes by Ericksson (1971). Jury (1982) developed a transfer function model (TFM) for soil which does not require the restrictive assumptions of the CDE. The simplest description of the downward movement of solute is the travel time, the time the solute takes to move from the soil surface to a specified depth. If the application rate of the surface applied solution is steady, then the "time" form of the equation can be expressed in the "drainage" form. The simplicity of the model makes it useful as a management tool for solute movement (Addiscott and Wagenet, 1985). TFMs show promise for simulating the leaching of both surface-applied and indigenous soil solutes under both laboratory and field conditions (White *et al.*, 1992). These models have been successfully applied in the laboratory for both applied solutes (White, 1985; White *et al.*, 1984; 1986; Dyson and White, 1987; Khan and Jury, 1990; White and Magesan, 1991) and resident solutes (Magesan *et al.*, 1990; 1991; White and Magesan, 1991; White *et al.*, 1992) and also applied to field conditions (Jury *et al.*, 1982; White *et al.*, 1986; 1987; Butters *et al.*, 1989; White and Heng, 1990).

The "net applied water" form of the transfer function model is (Jury and Roth, 1991)

$$C_{ex}(I) = \int_0^I f(I-I') C_{ent}(I') dI' \quad (1.6)$$

where  $f(I)$  is the net applied water probability density function (pdf) which has dimensions ( $L^{-1}$ ), and is the fundamental solute transport property;  $f(I) \Delta I$  is the probability that solute added at  $z = 0$  (soil surface) when  $I = 0$  will exit at  $z = L$  between  $I$  and  $I + \Delta I$  net applied water.  $C_{ent}$  and  $C_{ex}$  are the flux concentrations of nonreactive solutes ( $M L^{-3}$ ) at the entrance and exit surfaces, respectively.

#### 1.3.5.1. Measurement of transfer function parameters

A detailed discussion of the measurement of transfer function parameters is given by Jury and Roth (1990). Here the methods are given in a simplified manner. Two standard types of experiment that can be performed to obtain  $f(I)$  under laboratory

and field conditions are: (1) a narrow-pulse input (a Dirac delta input in the flux concentration), and (2) a solute front input (a step change in input flux concentration).

A distinction between volume-averaged concentrations and flux-averaged concentrations needs to be made here. Volume-averaged concentration is the concentration of soil solution obtained by extracting a volume of soil. Flux-averaged concentration is the effective concentration of the moving water in the soil. Suction-cup samples and drainage samples represent (possibly different) flux-averaged concentrations.

In a narrow-pulse input experiment, a concentration pulse of mass  $M_o$  ( $M L^{-2}$ ) is applied at an instant to the soil surface at  $I = 0$ . In laboratory experiments it is usually applied in solution form. Solid fertilizer applied to the soil surface in the field is often assumed to be a pulse input (more discussion concerning this is given in Chapter 7). The average outflow flux concentration  $C_{ex}(I)$  is then measured at the exit surface as a function of  $I$ . For soil cores,  $C_{ex}(I)$  is the effluent concentration (e.g. White and Magesan, 1991). For mole-tile drained fields,  $C_{ex}(I)$  is the mole-pipe drainage concentration (e.g. White, 1987). For large fields that drain freely, the outflow concentration is often estimated from the average of a set of solution samplers at  $z = L$  (Butters *et al.*, 1989). For a Dirac delta input added to the entrance surface,

$$f(I) = M_o^{-1} C_{ex}(I) \quad . \quad (1.7)$$

For a conservative solute the mass  $M_o$  ( $M L^{-2}$ ) need not be measured at the input surface. It can be calculated from the mass recovered as (Jury, 1982):

$$M_o = \int_0^{\infty} C_{ex}(I') dI' \quad . \quad (1.8)$$

For solute front inputs, where a flux concentration  $C_o$  is added to the inlet end at  $I = 0$ ,  $f(I)$  is equal to (Jury, 1987):

$$f(I) = C_o^{-1} \frac{dC_{ex}(I)}{d(I)} \quad (1.9)$$

Once  $f(I)$  has been obtained, the transport volume fraction  $\theta_{st}$  can be calculated from either the median or mean  $I$  water input displacement (White *et al.*, 1986), as is shown in Chapter 4.

A lognormal probability density function (pdf) is often found for one dimensional flow through large, intact cores (White *et al.*, 1984, White and Magesan, 1991). The pdf for such flow is given by (Jury *et al.*, 1986; Dyson and White, 1987),

$$f(I) = \frac{\exp[-(\ln I - \mu)^2/2\sigma^2]}{\sqrt{2\pi}\sigma I} \quad (1.10)$$

where  $\mu$  is the mean of the distribution of  $\ln I$  and  $\sigma^2$  its variance.

Jury *et al.* (1991) mentioned that any linear solute transport model that obeys the solute conservation equation can be represented as a transfer function. The piston flow model and CDE can be represented as transfer function equations in the form of (1.6) (Jury and Roth, 1990). The pdf of the CDE is known as a Fickian pdf (Jury and Sposito, 1985) and is

$$f(I) = \frac{L \exp[-(L - VI)^2/4DI]}{2\sqrt{\pi DI^3}} \quad (1.11)$$

### 1.3.6. Solute transport models for mole-pipe drained fields

Most of the models available at present to describe field situations are one-dimensional. Scotter *et al.* (1991) developed two models for the leaching of a non-reactive solute to a mole drain. Because the field study of solute leaching in this present study was carried out using a mole-pipe drainage system, a brief review on these two models is given here. The first model was research-oriented and thus it required many model inputs such as rainfall intensity and basic soil hydraulic data. In fact, this model was developed from another model which described the soil water flow to a mole drain (Scotter *et al.*, 1990). The second model was simpler and was management-oriented. It required only a few inputs.

The first model of Scotter *et al.* (1991) may be classified as a mechanistic model (Addiscott and Wagenet, 1985) or process model (Jury and Nielsen, 1987). It simplifies two-dimensional water and solute flow to a mole drain by dividing the soil between the mid-mole plane and the mole into notional compartments. Also soil depth is divided into two horizontal layers, a thin surface layer and a thicker lower layer. It assumes that the solute movement occurring between compartments is by convection and mechanical dispersion. To take preferential flow into account, the soil water and solute in any compartment is assumed to be divided into mobile and immobile phases, with diffusion tending to equalize the concentration between them. Nearly all the flow in saturated structured soils takes place through the macropores. An explicit finite difference solution to the water and solute mass-balance and flux equations was used in this model.

The second model of Scotter *et al.* (1991) can be classified as functional (Addiscott and Wagenet, 1985). It is simple both in concept and in the mathematical equations. The required inputs are daily rainfall and evaporation rates. It is assumed that the soil solution behaves as if it were a well-mixed system (Raats, 1978b). A soil system is said to be effectively well-mixed, when the solute concentration in the drain flow is the same as the average soil solution concentration in the soil below the water table. The equations used for prediction of leaching losses of solute can be easily solved using a spreadsheet.

These two models can be extended to the leaching of a reactive solute. Because of the number of model inputs and its sophistication, the first model was able to simulate leaching under different situations, such as immediately after fertilizer application and during bypass flow induced by prolonged heavy rain. The second model, however, could not simulate these situations because of its simplicity.

White (1987) and Heng (1991) have developed transfer function models for mole-pipe drained field situations. These models will be discussed in Chapter 7.

#### 1.4. PURPOSE AND STRUCTURE OF THIS STUDY

Although some information about the purpose of this study was given earlier in this chapter, this section gives further discussion on the purpose of this study and why this study was conducted in the laboratory using large undisturbed soil cores and in mole-pipe drained fields of Tokomaru silt loam soil. The structure of this study is also described.

In the past many leaching studies have been carried out in the laboratory, usually using disturbed soil (e.g. Bolan *et al.*, 1986). Moreover, small columns of soil were used. Solute transport in natural undisturbed soil cores is different to that in disturbed, repacked soil columns due to the pore systems (macropores and micropores). Moreover, the parameters estimated from disturbed soil columns do not represent the natural soil. Ritchie *et al.* (1972) suggested that the effects of discontinuities in conducting pores caused by the core walls can be reduced by using large cylindrical soil cores. Biggar and Nielsen (1967), and Scotter (1978) suggested that leaching soil at water contents below saturation could produce more efficient leaching of salts from the soil profile. So in this study large undisturbed soil cores were leached under largely unsaturated steady-state flow conditions.

Most of the leaching studies carried out on mole-pipe drained fields, either in Tokomaru silt loam soil (Turner *et al.*, 1976; Sharpley and Syers, 1979; Mohammad *et al.*, 1984; Scotter and Kanchanasut, 1981; White and Heng, 1990; Scotter *et al.*, 1991; Heng *et al.*, 1992) or overseas studies on different soil (Haigh and White, 1986; White, 1987) have emphasized the leaching of externally applied fertilizer. But none of these studies gives much detail on the leaching of indigenous solutes, especially nitrate. So the objective of this field study was mainly to study the leaching of indigenous nitrate. Because nitrate undergoes biological transformations, the leaching of indigenous chloride, which is a conservative solute, was also studied. Chloride has been shown to be a good tracer of nitrate movement (Wetselaar, 1962) and the two ions to have comparable rates of leaching in field conditions (Cameron and Wild, 1982).

Sodium bromide was applied externally as a tracer because bromide and nitrate have been found to move similarly through soil (Smith and Davis, 1974). Bromide has also been widely used as a tracer to study the movement of non-reactive solutes in laboratory experiments (Clothier, 1984; Clothier and Elrick, 1985; Clothier *et al.*, 1988; Scotter and Tillman, 1992; White *et al.*, 1992) and in field experiments (Jury *et al.*, 1982; Smith *et al.*, 1984; Brasino, 1986; Butters *et al.*, 1989). Bromide ions are preferred because of their negligible background concentration in most soils, and because they can be easily analyzed.

The methods and materials of the experiments conducted are explained in Chapter 2. In Chapter 3 the results of laboratory experiments are given, and the data are modelled using a transfer function model in Chapter 4.

Results of the field experiments are given in Chapters 5 and 6. In Chapter 5, soil, suction cup and herbage results are given. Also the flux-averaged and volume-averaged concentrations of solutes in the soil are compared. In Chapter 6 leaching results and solute mass balances are given.

In Chapter 7 the leaching results of chloride and bromide are modelled using analytical solutions of the transfer function model. Different parametric forms of the pdfs are compared. Since the analytical solution of the TFM could not be extended to nitrate because of the biological transformations it underwent, a numerical solution of the TFM is developed in Chapter 8. A general discussion and conclusions are given in Chapter 9.

**CHAPTER 2**  
**MATERIALS AND METHODS**  
**FOR LABORATORY AND FIELD EXPERIMENTS**

**2.1. INTRODUCTION**

As mentioned in Chapter 1, experiments were carried out in the laboratory as well as in the field to measure the leaching losses of indigenous nitrate from the soil. Because nitrate undergoes biological transformations, the leaching of indigenous chloride, which is a conservative solute, was also studied. In the experiments to be described, externally applied tracers were used to investigate the movement of water and indigenous solutes. Some experiments carried out in the laboratory were in two parts. In the first part, tritiated water was used to leach indigenous solutes from columns of undisturbed soil. In the second part, water containing either bromide, chloride or nitrate was used to leach from the soil the tritium which had been applied in the first part of the experiment. For the field experiment in 1990 solid NaBr (200 kg Br/ha) was applied on 29 May 1990 to one paddock as a tracer. Urea was applied at the same time to an adjoining paddock.

In this chapter the experimental site, instrumentation and methods of data collection are described. Field data include rainfall, and analyses of soil, drainage water, herbage and suction cup samples.

**2.2. SITE AND SOIL DESCRIPTION**

The site of the field experiment and the collection of undisturbed cores for the laboratory experiments was the Research Area of the Department of Soil Science, situated about 2 km from the Massey University campus. Figure 2.1 shows a schematic diagram of the experimental site, which consisted of four small adjacent paddocks designated as A, B, C and D. Paddocks A and B were used for the field experiment. The undisturbed soil cores for laboratory leaching experiments were taken from paddocks C and D. The drained area of each paddock was approximately 1250 m<sup>2</sup>.

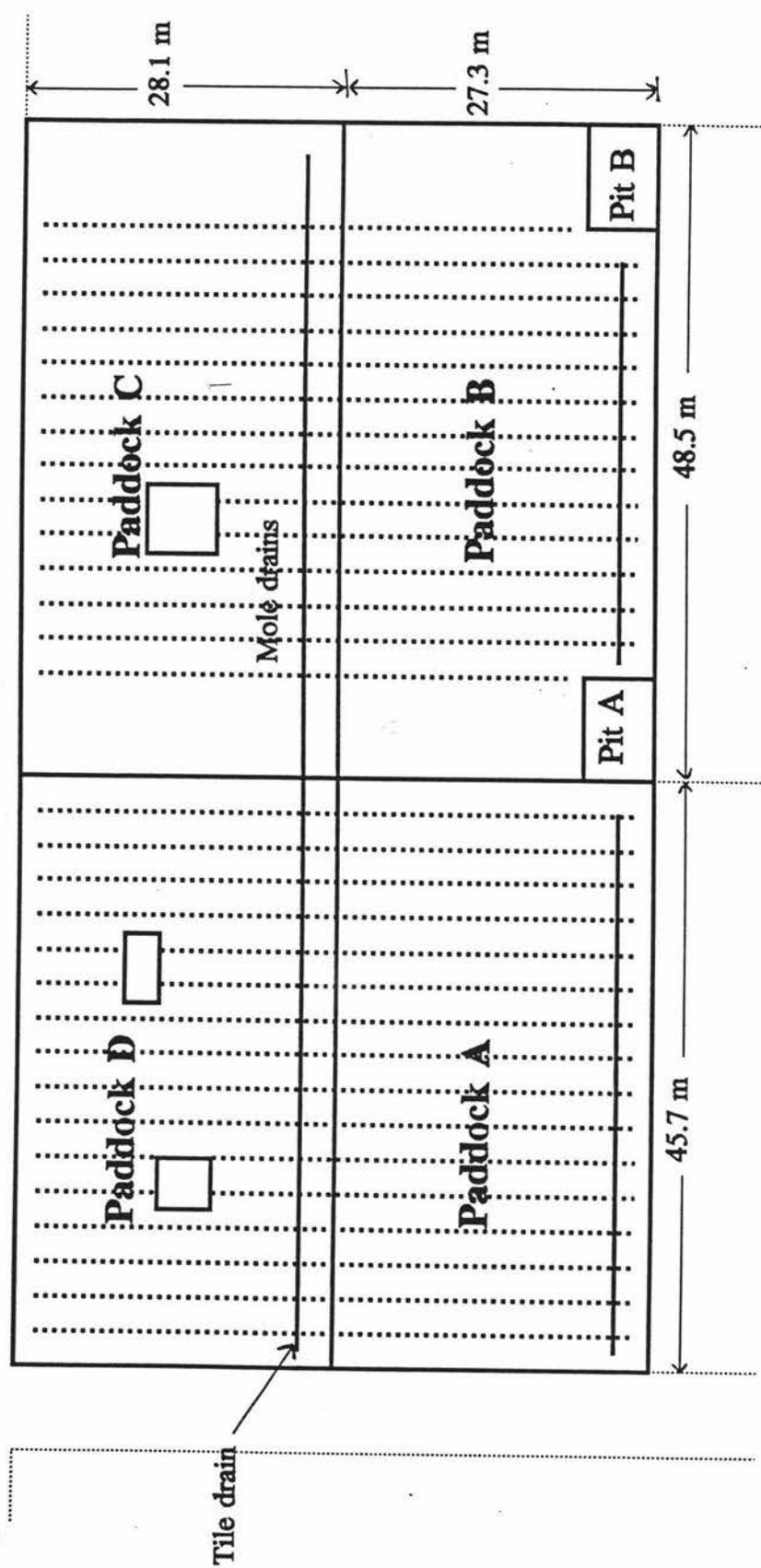


Fig. 2.1 A schematic diagram of the experimental site. Square and rectangular boxes in paddocks C and D are the sites of soil taken for laboratory experiment. Dotted and solid lines represent the moles and pipes respectively

The soil is a Tokomaru silt loam, classified as a Typic Fragiaqualf (Soil Survey Staff, 1975) or as a gleyed Yellow Grey Earth (New Zealand Soil Bureau Staff, 1963). The soil profile has been described elsewhere in detail, with morphological data being presented by Pollok (1975) and physical characteristics by Scotter *et al.* (1979). At the site, the soil consists of a silt loam A horizon extending to approximately 250 mm, a clay loam B horizon between 250 and 780 mm, then a very compact silt loam fragipan C horizon extending from 780 to 1100 mm and underlain by a less compact silt loam (Scotter *et al.*, 1979). A perched watertable normally occurs during winter and spring, due to the low hydraulic conductivity of the subsoil and the fragipan. Mottling in the subsoil, indicative of poor drainage, was observed when large cores were taken for laboratory study. To alleviate the waterlogging conditions the area was mole-pipe drained. Installation of a mole-pipe drainage system is relatively inexpensive and particularly suited to fine textured soils with impermeable subsoils. However, the soil must be stable enough to hold a mole.

The paddocks were moled in 1975 and remoled in 1986. The moles were collapsed along the paddock boundaries to stop the flow of drainage water from one paddock to another. The mole drains, 75 mm in diameter, were pulled at 2 m spacing in the B horizon at approximately 450 mm depth on a gradient of 1 %. The pipe drains, 100 mm in diameter, were installed perpendicular to the moles at approximately 750 mm depth on a minimum gradient of 0.4 %. Backfill above the pipe-drains was the topsoil removed during trenching, which ensured that the low permeability of the subsoil did not affect flow from the moles to the pipe drains. Soil drainage water collected by the mole drains therefore percolated rapidly to the underlying pipe drains. The advantage of the mole-pipe drainage system is that the concentration of solutes in the drainage waters is averaged over the whole paddock, integrating the effects of spatial variability.

The experimental area supported a ryegrass-white clover pasture and was mob-grazed by sheep periodically. Before any fertilizer application, paddocks A and B were each divided into 15 equal compartments to facilitate the spreading of fertilizers and to achieve a uniform distribution.

## 2.3. LABORATORY EXPERIMENT

### 2.3.1. Corers used for large core extraction

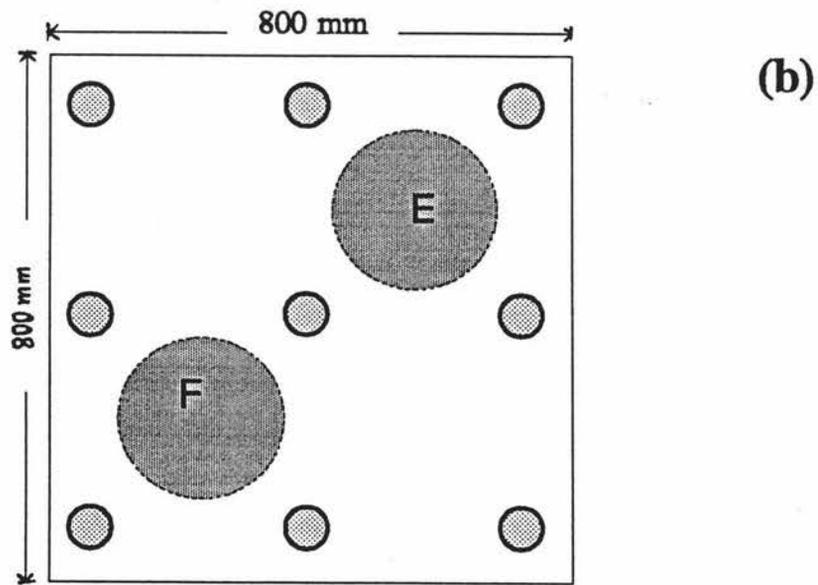
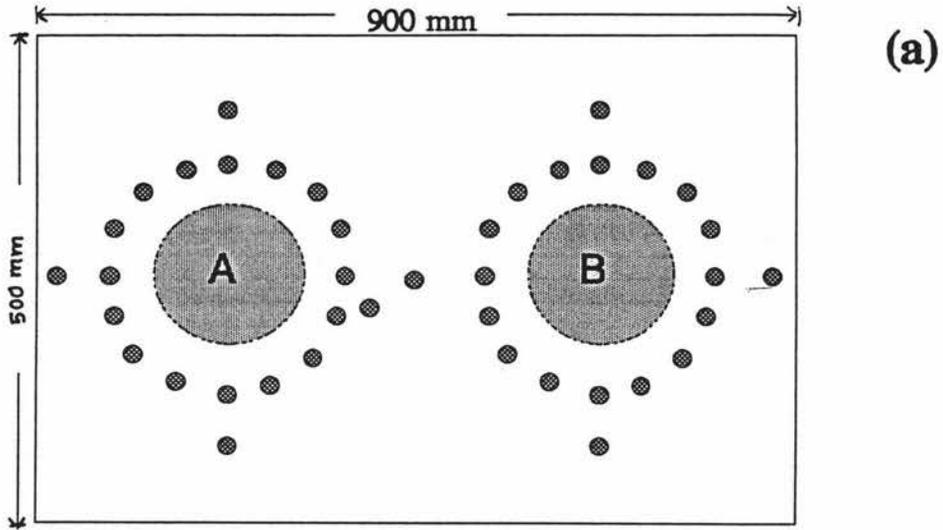
Hollow galvanized steel cylinders, 230 mm in diameter, 250 mm long and 1.4 mm thick were used to collect 'undisturbed' cores of soil. The seams in the cylinders were soldered and smoothed to reduce the possibility of edge-flow. It is considered (Hvorslev, 1949; Aitchison and Lang, 1963 a,b) that for minimum or negligible disturbance of the structure in the sample, the sampler used to extract cores should have as low an area ratio as possible. Area ratio is defined as the ratio of the area of the annulus of displaced soil to the area of the sample at the cutting edge. Certainly it should be  $< 0.15$  and preferably  $< 0.10$  to obtain 'undisturbed' samples. The area ratio used here is about 0.02 so that the corer can be defined as a thin-wall sampler (Loveday, 1974). The soil taken in these corers was used for the laboratory leaching experiments.

### 2.3.2. Core collection

The method used for soil collection was similar to that of Smith *et al.* (1985). The soil cores were taken by driving the corers in to a depth of about 250 mm below the soil surface. A plywood and steel driving head placed on the top of each cylinder was repeatedly tapped with a sledge hammer. After driving a cylinder in to the desired depth, a hole was dug next to the cylinder in such a way that the cylinder could be lifted out easily with little disturbance.

Using a soil corer, small soil cores, 25 mm in diameter and 250 mm long, were taken from around each large 'intact' core. These samples were analysed to estimate the initial concentration of solutes in the soil solution and the moisture content of the soil in the large cores. The small cores were cut into 5 sections (0-50 mm, 50-100 mm, 100-150 mm, 150-200 mm and 200-250 mm). All the soil samples were sealed in plastic bags, and stored at 4 °C until analysed. The intact cores were sealed in double plastic bags and were also stored at 4 °C until used.

Figure 2.2(a) is a schematic diagram of the sampling site for the first experiment. The sampling area was 900 mm x 500 mm. Two large intact cores (A and B), and



**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

twenty small cores around each, were taken. The procedure was as follows. An outline of the sampling site was drawn on a big sheet of paper. This paper was placed on the soil surface where the cores were to be taken. Pointers (match sticks) were inserted into the ground through the paper. Then the paper was removed slowly without disturbing the pointers. Prior the second experiment, four soil cores were taken from an area of 1m x 1m. Two of the cores (C and D) were used in the second experiment whereas the other two cores were used for a preliminary experiment which will be described briefly in section 2.3.4. Note that these cores were taken from the field on an earlier date than the cores for experiment 1. For the third experiment, two soil cores (E and F) were taken from an area of 800 mm x 800 mm, and the schematic diagram of the sampling site is shown in Figure 2.2(b).

The collection of soil cores for first (cores A and B), second (cores C and D) and third (cores E and F) experiments were on 5 July 1989, 10 February 1989 and 5 January 1990, respectively.

### 2.3.3. Soil pretreatment

Cores A and B received no pretreatment and were leached within two weeks of sampling. Pretreatment is defined as creating a uniform distribution of solutes in soil by applying a known concentration of solution. Cores C and D were stored for nearly 22 months at 4 °C before leaching. The volumetric water content decreased from 0.35 to 0.30 m<sup>3</sup> m<sup>-3</sup> during storage. The average soil solution nitrate concentration in the soil increased markedly during storage from 10 g N m<sup>-3</sup> to 180 g N m<sup>-3</sup>. Most of this nitrate was in the top 100 mm depth. The soil solution concentration in the 0-100 mm, 100-200 mm and 200-300 mm layers was 320, 115 and 42 g N m<sup>-3</sup>, respectively. The indigenous solutes present in the soil were leached with two liquid-filled pore volumes (p.v.) of tritiated water as a pretreatment just prior to the leaching experiment (see Section 2.3.5).

For the third experiment, for reasons that will be discussed later, a uniform distribution of chloride was created by pretreatment in the field. The procedure for doing this was as follows. Between 28 October and 1 November 1989, 30 mm per day of 142 g Cl m<sup>-3</sup> (2 mM CaCl<sub>2</sub>) solution was applied by ponding on the soil

surface. The chloride solution was applied to a flat  $0.64 \text{ m}^2$  area. Four metal plates each 800 mm long formed a square border to prevent the ponded water moving outside the sampling area. The chloride concentration in the soil solution before the application of the chloride solution was low ( $\approx 10 \text{ g Cl m}^{-3}$ ).

On 12 December and 13 December 1989, another 150 mm of the same solution was applied by ponding on the soil surface, 90 mm on the first day and 60 mm on the second day. After ponding on 13 December a polythene sheet was spread over the soil surface to minimize evaporation and also to protect the soil from rainfall. Soil sampling was carried out at the site on 15 December 1989. Four soil cores were collected down to a depth of 300 mm from just inside the border with a 25 mm diameter corer. The soil samples were sectioned into six equal depth intervals and analysed for chloride, as described later in Section 2.5.3.2.

The data from the 15 December sampling suggested that although the chloride concentration was fairly uniform at any one depth, the concentration decreased with depth. So another 300 mm of the same solution was applied by spraying instead of ponding. Between 18 December and 22 December 1989, 30 mm per day were sprayed on. Similarly 30 mm per day of the same solution were sprayed on between 24 December and 28 December 1989. On 30 December 1989 the soil was again sampled just inside the border and analyzed for chloride. This sampling showed that a relatively uniform distribution of chloride in the soil had been achieved.

A third and final more detailed soil sampling was carried out just before the large cores were taken on 5 January 1990. Nine small cores were taken at the locations shown in Figure 2.2(b). This soil sampling was the most representative of the pretreated field site, as soil samples were taken from around the large cores and also well inside the border. Two large intact cores (E and F) were also taken from the field on 5 January 1990, from the locations indicated in Figure 2.2(b).

The gravimetric water content determinations and the extraction of the soil samples were done within 2 days of soil sampling. The average volumetric soil water content was  $0.43 \text{ m}^3 \text{ m}^{-3}$ . It was calculated as described in Section 2.5.1.

#### 2.3.4. Leaching apparatus

Before mounting the cores in the leaching apparatus, the following procedures were undertaken: (1) The vegetation was cut as short as possible; (2) The excess soil was removed from the base by gently chipping off aggregates along natural fracture planes to prevent smearing and sealing of conducting pores (Kanchanasut and Scotter, 1981); (3) Acid washed sand (medium fine, laboratory reagent, May and Baker Ltd) was used to cover the soil surface to 10 mm depth, so that the flow from the hypodermic needles would be spread evenly over the core area; (4) A gauze restrainer was attached to the base of each core; and (5) The cores were weighed.

Plate 2.1 shows the apparatus used to leach the intact cores in the laboratory. It consisted of a "dexian" stand to support the cores and a rainfall simulator for the application of solution. The dexian framework was constructed to hold three horizontally mounted chipboard planks. The lower plank was about 400 mm above the bench surface. In this plank two holes 230 mm in diameter (equal to the diameter of the intact cores) were cut. Two large funnels (250 mm diameter) were placed in the holes. The soil columns were supported on the large funnels.

The middle plank was about 250 mm above the lower plank. Two 260 mm diameter holes were cut in it. This plank gave lateral support to the cores, while still allowing them to be moved up and down freely. The upper plank was placed about 100 mm above the soil cores. The rainfall simulator was attached to it.

To construct each rainfall simulator, two plastic tubes with internal diameter 7 mm were formed into a spiral, and the ends of the tubes connected by a 'T' joint. The remaining end of each 'T' joint was connected to a silicon tube which was connected to a peristaltic pump. Nineteen hypodermic needles (vacutainer blood collection needles) were inserted in each spiral in such a way that they were evenly spaced. Plate 2.2 shows the uniform distribution of dye (see Section 2.3.5) on the sand/soil surface, indicating that a uniform application of water was achieved. This was in part because of the 10 mm sand layer placed on the soil surface. The needle outlets were 50-60 mm above the soil surface.



Plate 2.1 Experimental set-up for the intact core leaching experiments

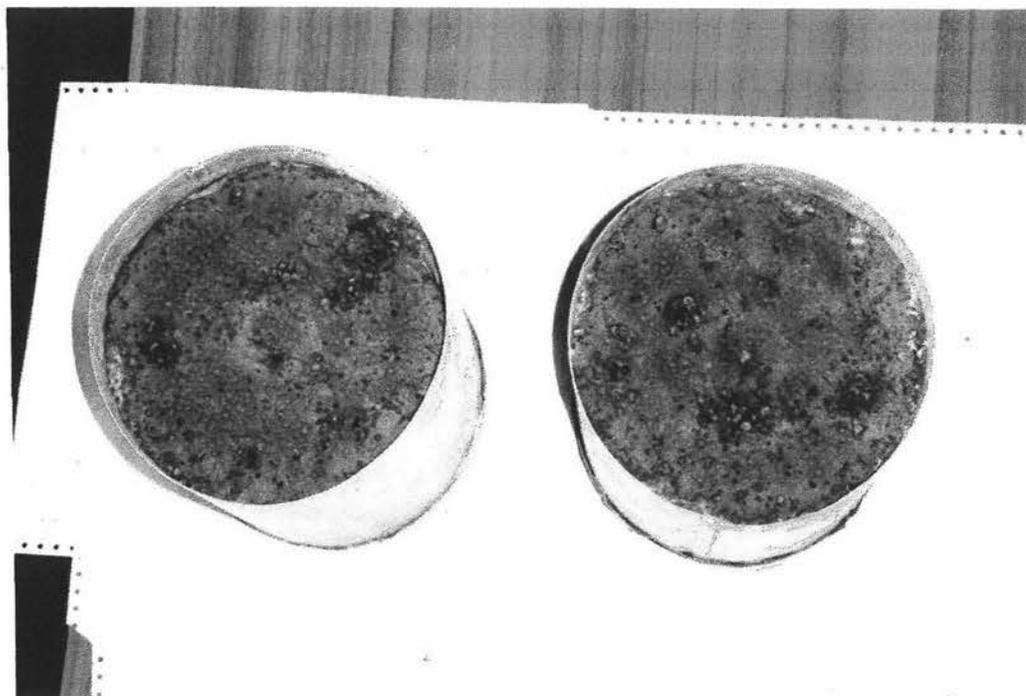


Plate 2.2 Uniform distribution of dye indicating uniform application of tritiated water to the soil surface

During each experiment the two rainfall simulators were supplied by a single peristaltic pump, allowing two cores to be leached simultaneously. A pump rate was chosen that supplied input solution without ponding. Drainage water dripped from the base of the cores and was collected manually.

During the development of the apparatus a preliminary experiment was conducted with two large cores in which the effluent was collected from the inner and outer areas of each core by means of two concentric funnels. The 10 mm sand layer was not used for this experiment. The ratio of inner to outer areas partitioned was 1 : 0.55. If the water (and solutes) moved uniformly through vertical pathways, then the volume of outflow and the amount of solutes collected from the inner and outer funnels should have had the same ratio of 1 : 0.55. In fact, there was no consistent ratio of volume of effluent collected from the inner and outer funnels. For the first core the ratio increased with time from 1 : 0.18 to 1 : 0.85. For the second core the ratio decreased with time from 1 : 1.55 to 1 : 0.79. The ratio of the amounts of nitrate and chloride leached from the inner and outer funnels followed the same pattern. The observed fluctuation in the relative flow rates could have been due to movement of earthworms during leaching which changed macropore pathways.

As explained in the previous chapter, the reason for using a two funnel system to collect effluent was to detect any edge-flow which might occur between the soil and the corer, but the data did not indicate any consistent effect. Also from the observations of dye flow (see Section 2.3.5) no edge-flow was apparent. Hence in the remaining experiments only one funnel was used to collect the effluent.

### **2.3.5. Leaching experiments**

The large cores were leached initially by applying tritiated water to the soil surface. Each core was irrigated with tritiated water until approximately two p.v. of effluent had been collected. The effluent was collected in volume aliquots gradually increasing from 50 ml to 350 ml as leaching progressed (i.e. the first 10 samples were 50 ml, the next 10 samples were 100 ml and so on). Each leachate sample was divided into two subsamples. To one was added 1 ml of a  $1 \text{ g m}^{-3}$  phenylmercuric acetate solution and the sample stored at  $4 \text{ }^\circ\text{C}$  to preserve the soluble inorganic N

(Klingaman and Nelson, 1976). These samples were later analyzed for nitrate. The other subsample was analyzed for chloride and tritium as described in Section 2.5.3.

For cores A, B, C and D, Nile blue dye (0.05 %) was applied at the conclusion of each experiment. The purpose of applying dye was to:

- (1) Determine whether there was any edge-flow between the cylinder wall and the soil.
- (2) Detect any preferential flow through macropores.
- (3) Determine the effectiveness of the acid-washed sand in spreading evenly the water applied to the surface.

For all cores (A, B, C, D, E and F) subsequent to the last solution application, the cores were allowed to drain freely for several hours and the leachate collected. Then five small cores 25 mm diameter and 250 mm long were taken from each large core. These cores were cut into five sections (0-50 mm, 50-100 mm, 100-150 mm, 150-200 mm and 200-250 mm). The extraction and analysis of these samples were as described for the small soil cores taken in the field (see Section 2.5.3). Then the large cores were weighed, oven-dried at 105 °C for 7 days, and reweighed to calculate the p.v. during leaching.

For cores A and B, tritiated water (4490 cpm/ml) was applied at a rate of 5 mm/hr to the soil surface. Following Prasad *et al.* (1971), 3-amino-1,2,4-triazole ( $56 \text{ g m}^{-3}$ ) was added to the leaching solution to retard nitrification. About two p.v. of effluent were collected.

For cores C and D, which had been stored for nearly 22 months at 4 °C before leaching, laboratory pretreatment involved leaching the indigenous soil nitrate and chloride with tritiated water (4438 cpm/ml) applied at a rate of 4 mm/hr. Immediately after the application of approximately two p.v. of tritiated water a 30 mm 'pulse' input of bromide solution ( $500 \text{ g Br m}^{-3}$ ) was applied, followed by another two p.v. of bromide and tritium free water.

For cores E and F, the experiment was divided into two phases. In the first phase

the cores were leached by the application of tritiated water (4950 cpm/ml), applied at a flux density of 5 mm/hr, until the concentration of tritium in the effluent reached at least 0.96 of that applied. By that time approximately four p.v. of effluent had been collected. In the second phase of the experiment the leaching solution was changed to 3mM CaCl<sub>2</sub> (containing 213 g Cl m<sup>-3</sup>), applied at a flux density of 3 mm/hr, until the relative concentration of chloride approached 1. Relative concentration is defined as the ratio of solute concentration in the effluent to that of applied solution. The flux density was reduced to 3 mm/hr in the second phase of the experiment to avoid ponding. Approximately two p.v. of this solution was applied. At the start of the second phase of the experiment a 20 mm pulse of Ca(NO<sub>3</sub>)<sub>2</sub> solution containing 500 g N m<sup>-3</sup> was applied with the CaCl<sub>2</sub> solution. Terrazole (0.05 %) was used as the nitrification inhibitor in all percolating solutions used in this experiment (Turner and Macgregor, 1978). The reason for changing the nitrification inhibitor was the unavailability of the chemical used earlier.

## 2.4. FIELD EXPERIMENT

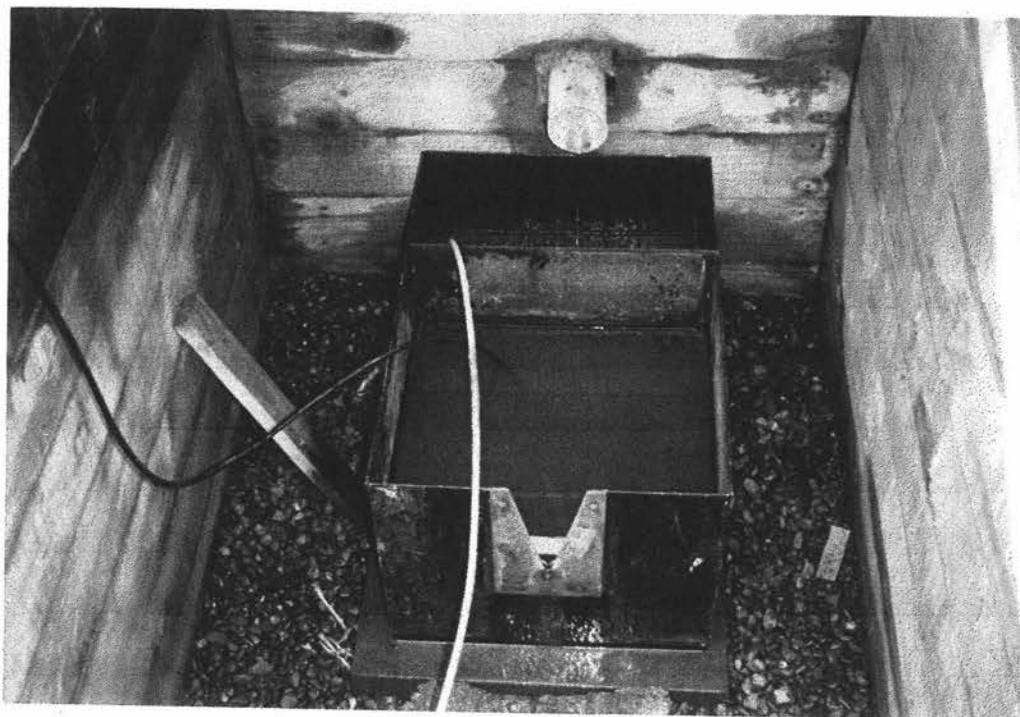
### 2.4.1. Field instrumentation

#### 2.4.1.1. *Drainage sample collectors*

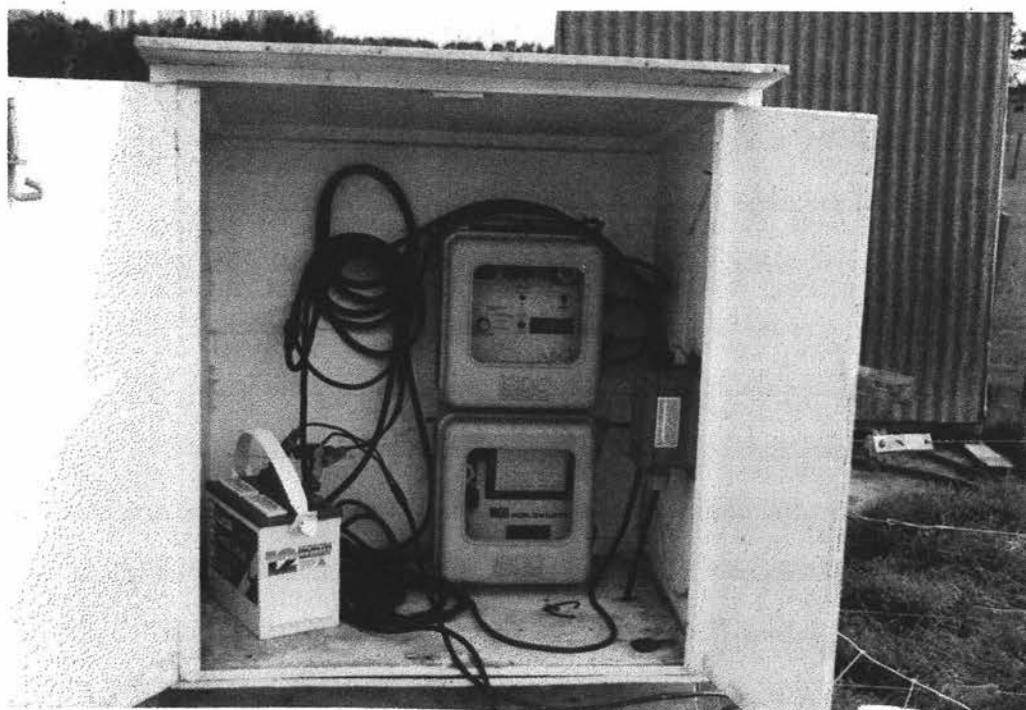
The drainage from the mole drains in each paddock was collected by a single pipe drain. The collected drainage in Paddocks A and B passed through two 30° V-notch weirs installed in pits A and B, respectively (Figure 2.1). Plate 2.3 shows the V-notch weir and the drainage pipe outlet in pit A. These weirs enabled the flow from the two paddocks to be measured. The height of the drainage water through each weir was sensed by a pressure transducer placed on the floor of the weir and connected to a flow meter. Plate 2.4 shows a flow meter and plotter. The flow rate is a function of the height of the water passing through the V-notch weir, given by the following relation

$$Q_w = K_w H_w^{2.5} \quad (2.1)$$

where  $Q_w$  [L<sup>3</sup> T<sup>-1</sup>] is flow rate,  $H_w$  [L] is the height of water from the base of the V-notch, and  $K_w$  is a constant determined by the angle of the V-notch and the units of measurement. The flow meter (ISCO Inc, Model 2300) was calibrated to convert



**Plate 2.3** V-notch weir and a pipe draining in pit A



**Plate 2.4** Flow meter and plotter

water level into the corresponding flow rate. The flow meter displayed flow rates and total flow at the time of observation. To record the flow, a plotter (ISCO Inc, Model 2310) was used. The validity of equation (2.1), and the value of  $K_w$ , had previously been established (Heng, 1991).

Drainage samples were collected using an automatic water sampler (ISCO Inc, Model 2900). It contained twenty-four 500 ml polyethylene bottles. A 100 ml sample of drainage was collected for every 600 litres (equivalent to 0.48 mm) of drainage. However, by the end of June 1991 the drainage volume per 100 ml sample was changed from 600 litres to 1250 litres (equivalent to 1 mm) of drainage. Drainage events were monitored over the drainage season of spring 1989, and winter and spring of 1990 and 1991 (see Chapter 6).

#### **2.4.1.2. *Rainfall recorders***

Rainfall was measured using two rainfall gauges. One recorded continuously and siphoned automatically. This recorded rainfall amounts and intensities. The other was a 250 mm diameter Marquis manual rain gauge. These two instruments were installed about 50 m away from the site. Charts were changed once a week for the continuous recording rain gauge whereas readings were taken daily from the manual rain gauge.

#### **2.4.1.3. *Suction cup samplers***

Suction cup samplers were made with porous ceramic cups (22 mm outside diameter and 80 mm long) joined to PVC tube. They were installed into the paddocks in August 1988 (Heng, 1991). The samplers were inserted at approximately 200 mm and approximately 450 mm (below mole-drain) depths. A total of ten samplers were installed at the 200 mm depth and five at the 450 mm depth in each paddock. One sampler in paddock A and two in paddock B, all at 200 mm depth, were not working properly during 1990.

### **2.4.2. Fertilizer application**

Nitrogen fertilizer in the form of urea (46% N) was applied to the field on 13 September 1989, to enable the effect of spring applied fertilizer on drainage nitrate

concentration to be studied (see Chapter 6). Another important reason was to see whether the pasture response to S fertilizer was limited by N supply (Heng, 1991). Urea was spread on both paddocks A and B at a rate of 50 kg N/ha.

Urea at a rate of 120 kg N/ha was applied on paddock B on 29 May, 1990 (late autumn). Such applications are commonly used to boost winter and early spring pasture growth for high production dairy systems. At the same time, the leaching of indigenous soil nitrate was monitored in paddock A, to which NaBr was applied at the rate of 200 kg Br/ha also on 29 May 1990. As mentioned in Chapter 1, the bromide was used as an externally applied tracer to monitor the movement of water through the soil. It had the advantages of being a mobile solute with physico-chemical properties similar to nitrate, being conservative and not involved in biological transformations, and its presence in the soil and atmosphere is negligible. For these reasons it can be used as an analogue of externally applied nitrate but its mass balance and actual movement through the soil can be easily estimated.

### 2.4.3. Sample collection

Table 2.1. gives the dates of soil, suction cups, herbage sample collection, and also gives grazing details such as number of days and stocking rate.

#### 2.4.3.1. *Drainage and rainfall*

Drainage samples were collected regularly after each rainfall event as described above. Rainfall received during each event was noted and the rain in the raingauge was collected regularly. As for samples collected in laboratory experiments, the drainage and rainfall samples were partitioned into two parts : to one phenyl mercuric acetate (PMA) was added to preserve inorganic nitrogen (Klingaman and Nelson, 1976), and nothing added to the other. The samples were stored in a cold room (4°C) until analysed. The drainage samples were analysed in batches when about 100 to 150 samples had been collected.

#### 2.4.3.2. *Suction cup samples*

The samplers were put under vacuum with a hand-operated pump the day after all major rainfall events, and samples were collected the following day using neoprene

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

Soil	Suction cup	Herbage	Grazing (1 <sup>st</sup> day)	Number of days	Stocking rate
5.4.90		27.4.90			
			2.5.90	7	40
28.5.90	28.5.90				
	15.6.90				
29.6.90	30.6.90	—			
		2.7.90	10.7.90	5	21
	20.7.90				
31.7.90	2.8.90				
	17.8.90				
28.8.90	28.8.90	28.8.90	25.8.90	2	unknown
5.10.90		4.10.90	10.10.90	8	46
		20.11.90			
18.1.91		21.1.91	31.1.91	5	71
		18.3.91			
31.5.91			12.4.91	8	35
11.9.91		11.9.91	16.9.91	8	48
			24.9.91	3	29

tubing attached to a syringe. The extracted solution was analysed for bromide and nitrate for paddock A, and nitrate and chloride for paddock B.

#### **2.4.3.3. Soil samples**

For the experiment conducted in Autumn 1990, soil samples were taken on 5 April to measure the initial concentrations of nitrate, ammonium, chloride and bromide. Paddocks A and B were divided into 15 equal compartments. The soil sampling was carried out at the centre of each compartment. Two samples from each site were taken and pooled together. The soil samples were divided into 6 sections: 0-50 mm, 50-150 mm, 150-250 mm, 250-350 mm, 350-450 mm and 450-600 mm. The last section was from below mole depth (i.e. 450 mm). At the end of the 1990 drainage season once again the soil was sampled below 450 mm to determine the extent of deep percolation of solutes below the mole depth. From paddock A, soil samples were collected to 1 m depth. The samples were cut into 8 sections, i.e. 0-50 mm, 50-150 mm, 150-250 mm, 250-350 mm, 350-450 mm, 450-600 mm, 600-750 mm and 750-1000 mm. The objective of this deep soil sampling was to estimate the deep percolation of bromide ions. Fifteen soil samples from paddock B were collected to a depth of 600 mm at the same time. The soil samples were cut into 6 sections as for the earlier sampling.

#### **2.4.3.4. Herbage samples**

A quadrat of 0.25 m<sup>2</sup> area (0.5m x 0.5m) was randomly thrown and the herbage (aerial parts of all plants) from the area enclosed by the quadrat was cut and packed in a paper bag. The paper bags were weighed beforehand. Four samples were cut from each paddock. Then they were kept in an oven at 55 °C until a constant dry weight was obtained. The herbage was subsampled and ground for analysis.

## **2.5. PHYSICAL AND CHEMICAL ANALYSES**

### **2.5.1. Water content measurements**

Gravimetric water content was measured by drying the soil overnight at 105 °C. Previously published bulk density data (Bramley, 1989; Scotter *et al.*, 1979) were used to convert the gravimetric water contents to volumetric water contents.

## 2.5.2. Preparation for chemical analyses

### 2.5.2.1. *Soil extraction*

To measure bromide, chloride, nitrate and ammonium the soil samples were extracted in the field moist state with 0.05 M  $K_2SO_4$  (equivalent to 5 g oven dry soil solids to 15 ml extractant). The samples were shaken for 1 hour on an end-over-end shaker, centrifuged for 5 minutes at 5000 revolutions per minute, and then filtered through Whatman No. 41 filter paper.

### 2.5.2.2. *Herbage extraction*

#### 2.5.2.2.1. Total nitrogen

A subsample of 0.05 g of dried, finely ground herbage was digested with 4 ml of Kjeldahl mixture (a mixture of concentrated  $H_2SO_4$ ,  $K_2SO_4$  and Se) for four hours at 350 °C (McKenzie and Wallace, 1954). The digest was diluted fifty times and a subsample was used to measure N by autoanalyser (Section 2.5.3.1).

#### 2.5.2.2.2. Bromide and chloride

The method for extraction of herbage samples for bromide and chloride analysis was similar to White and Ayoub (1983). A 0.25 g herbage sample was placed in a conical flask with 60 ml of deionised water and put on a hot plate at a temperature between 85 and 90 °C (simmering) for about 2 h. The mixture was stirred regularly (every 15 minutes). After 2 h, the mixture was cooled and filtered through No. 42 Whatman filter paper into a 100 ml volumetric flask. The filtrate was made up to 100 ml. An aliquot of this filtrate was analysed for bromide and chloride.

## 2.5.3. Chemical analyses

### 2.5.3.1. *Nitrate*

Nitrate was measured colorimetrically using a Technicon Autoanalyzer, Series 2. The method involved initial reduction of  $NO_3^-$  to  $NO_2^-$  by hydrazine/ copper sulphate.  $NO_2^-$  then formed a diazo compound with sulphanilamide which coupled with N-naphthylene diamine dihydrochloride to give a purple azo dye whose absorbance was measured at 520 nm (Downes, 1978).

### 2.5.3.2. *Chloride*

Chloride was analyzed using a Tecator Flow Injection analyzer following the method of Florence and Farrer (1973). The solution was injected into a stream of distilled water and mixed with a reagent consisting of mercury thiocyanate and iron (III) nitrate. Chloride reacts with mercury thiocyanate to form a soluble nonionic compound with mercury. The released thiocyanate ions react in the acid solution with iron (III) to give a red coloured iron (III) thiocyanate complex. The resulting colour was measured photometrically at 463 nm.

### 2.5.3.3. *Bromide*

Bromide in the drainage water and soil extracts was analyzed, after mixing 10 ml of the sample with 0.3 ml of the ionic strength adjuster 5M NaNO<sub>3</sub>, with a bromide selective electrode (Orion solid state bromide electrode) and reference electrode connected to a Orion research model 701/ digital pH meter. The reading was recorded when the number displayed had stabilized, usually after 1 minute. A similar procedure of measurement in soil was used by Abdalla and Lear (1975).

Interference of chloride during the bromide analysis was checked. Three sets of standards of NaBr were prepared: (a) with no Cl added, (b) 20 g Cl m<sup>-3</sup> background and (c) 60 g Cl m<sup>-3</sup> background. The reason for choosing these values was that the concentration of chloride in the drainage in the early part of the drainage season was around 60 g Cl m<sup>-3</sup> and that in the latter part of the season was around 20 g Cl m<sup>-3</sup>. It was interesting to note that there was no or very little interference of chloride ions with the bromide electrode when the bromide concentration in the sample was above 10 g Br m<sup>-3</sup>. Almost all samples had a concentration above 10 g Br m<sup>-3</sup>. The standards with chloride background showed less drift than standards with no chloride background. Soil and drainage samples had a background chloride concentration, so the bromide electrode was calibrated using the standards having 20 g Cl m<sup>-3</sup>.

### 2.5.3.4. *Tritium*

The activity of tritium in the leachate was measured using a Beckman Liquid Scintillation counter after mixing 1 ml of sample with 10 ml scintillation cocktail (Patterson and Greene, 1965).

## 2.5.4. Expression of results

### 2.5.4.1. Soil solute and drainage concentrations

Solute concentrations in the soil are expressed either in terms of  $\text{g m}^{-3}$  soil or  $\text{g m}^{-3}$  soil solution. The advantages of expressing solute concentration in  $\text{g m}^{-3}$  soil are: (1) It is easy to compare the distribution of solute concentration in the soil profile at different times (irrespective of the water content); (2) The concentration of nitrate and ammonium can be plotted on the same graph; and (3) When the depth interval is 100 mm (which applies to all layers except the top layer which is 50 mm) the concentration expressed in  $\text{g m}^{-3}$  soil is equal to  $\text{kg/ha}$ , a mathematical convenience. However when it is desired to compare the soil concentration with the concentration in the solution emerging from the soil, it is necessary to express the soil concentration in  $\text{g m}^{-3}$  soil solution.

The concentrations of the solutions from suction cups and the drainage are expressed in  $\text{g m}^{-3}$  solution.

### 2.5.4.2. Data transformation

Unless otherwise specified all the values have been log transformed to calculate the sample mean ( $m$ ) and the standard deviation ( $s$ ). The maximum likelihood method (Parkin *et al.*, 1988) was used. The equations used were

$$m = \exp\left(\mu + \frac{\sigma^2}{2}\right) \quad (2.2)$$

$$s^2 = m^2[\exp(\sigma^2) - 1] \quad (2.3)$$

where

$$\bar{\mu} = \frac{1}{n} \sum_1^n \ln(x_i) \quad (2.4)$$

$$\sigma^2 = \frac{1}{n-1} \sum_1^n (\ln(x_i) - \bar{\mu})^2 \quad (2.5)$$

and  $x_i$  = the  $i$ th observation,

$n$  = the number of observations in a sample.

## CHAPTER 3

### RESULTS AND DISCUSSION OF THE SOIL CORE EXPERIMENTS

#### 3.1. INTRODUCTION

In this chapter the results obtained from the laboratory experiments outlined in the preceding chapter are presented and discussed.

#### 3.2. LIQUID-FILLED PORE VOLUME

The liquid-filled pore volume of a core (p.v.) is defined as the pore volume filled by liquid during a leaching experiment. The solute transport volume is somewhat loosely defined as the volume of the soil that has interacted with the applied leaching solution. Its upper limit is the liquid filled pore volume.

Table 3.1. gives the volumetric water contents estimated from the small soil cores taken from around each large core, and the liquid-filled pore volumes for all large cores. The depth of water in the large soil cores during leaching is also given. It is found as p.v. divided by the cross-sectional area of the core.

**Table 3.1.** Volumetric water content before and during each experiment and liquid filled pore volume for each experiment

Experiment and core label	Volumetric water content ( $m^3 m^{-3}$ )		Liquid- filled pore volume (ml)	Depth of water present (mm)	
	Before Leaching	During Leaching			
1	A	0.41	0.48	5042	121
	B	0.40	0.48	4939	119
2	C	0.31	0.45	3876	93
	D	0.31	0.44	3659	88
3	E	0.43	0.47	4913	118
	F	0.43	0.46	4951	119

### 3.3. MASS BALANCE OF WATER AND SOLUTES

#### 3.3.1. Water

Any unaccounted for gains or losses of water from the soil cores during leaching were identified from any errors in the mass balance for water. The mass balance error for water was calculated from the equation:

$$\text{Input} - (\text{output} + \text{change in mass of water in core}) = \text{Water unaccounted for.} \quad (3.1)$$

Input is the mass of applied liquid. Output is the mass of effluent collected. The change in mass of water in the core was measured by weighing the cores before and after each leaching experiment.

For cores A and B, 95 % of the applied water was accounted for. The remaining 5 % could have been lost by evaporation. Similarly for cores E and F, 97 % of water was accounted for. The data for cores C and D were not available to compute the mass balance.

The porosity of the soil,  $f$ , can be found as

$$f = (1 - \rho_b / \rho_s) \quad (3.2)$$

where  $\rho_b$  = the bulk density of the soil, and

$\rho_s$  = the particle density.

The mean bulk density of the soil to 250 mm depth was 1.25 Mg m<sup>-3</sup> (Bramley, 1989), and the mean particle density was 2.62 Mg m<sup>-3</sup> (Scotter *et al.*, 1979). Thus the average porosity of the soil was 0.53 m<sup>3</sup> m<sup>-3</sup>. The gas-filled porosity  $\epsilon$  during leaching was calculated as:

$$\epsilon = f - \theta \quad (3.3)$$

and had values ranging from 0.04 to 0.09 m<sup>3</sup> m<sup>-3</sup>.

#### 3.3.2. Nitrate

The initial amount of nitrate in the large cores was estimated from the small cores taken from around each large core. The final concentration of nitrate in the large cores was estimated from the small cores collected from within each large soil core after each leaching experiment.

The mass balance error for nitrate was obtained using the following equation:

(Mass of nitrate in soil before leaching + mass added during leaching) - (mass in the soil after leaching + mass collected in the effluent) = Unaccounted for nitrate (3.4)

For cores A, B, C and D no nitrate was added. Nitrate was added as a pulse to cores E and F.

### 3.3.2.1. *Experiment 1 : no pretreatment (Cores A and B)*

For core A, the estimated amount of nitrate in the soil before leaching was 158 mg. The amount leached was 18 mg. The amount remaining after leaching was 96 mg. Thus 44 mg of nitrate was unaccounted for. For core B, the estimated amount in the soil before leaching was 214 mg, the amount leached was 128 mg and the amount remaining in the soil after leaching was 103 mg. Thus 17 mg more nitrate was recovered than was estimated to be present initially.

The nitrate balance for cores C and D was not carried out because in this experiment nitrate was not dealt with.

### 3.3.2.2. *Experiment 3 : with field pretreatment (Cores E and F)*

The mass balance error for nitrate in core E was calculated as follows:

From the soil sampling around the core, the estimated amount of nitrate in core E before leaching was 21 mg. The amount leached during the first part of the experiment was 4 mg, or 20 % of 21 mg. The amount applied during the pulse input was 432 mg and the amount not leached in the first part of the experiment was 17 mg, giving a total of 449 mg. The amount leached during the second part of the experiment was 291 mg and the amount remaining in the soil at the conclusion of the experiment was 87 mg. So the unaccounted for nitrate-N was 71 mg.

The mass balance error for nitrate in core F was similarly calculated as follows:

The estimated amount of nitrate in core F before leaching was also 21 mg. The amount leached during the first part of the experiment was 4 mg or 20 %. The amount applied during the pulse input was 432 mg, and the amount not leached in the first part of the experiment was 17 mg, giving a total of 449 mg. The amount

leached during second part of the experiment was 278 mg and the amount remaining in the soil was 90 mg. So the unaccounted for nitrate-N was 81 mg.

The unaccounted for nitrate-N could have been lost by denitrification, especially from the surface soil layer. The silica sand, which was applied to the soil surface to help to distribute the applied solution uniformly, could have reduced the oxygen supply thus making the topsoil anaerobic. This, plus a ready supply of nitrate and organic carbon in the topsoil, could have allowed denitrification to occur.

### 3.3.3. Chloride

The method used for the calculation of the mass balance of chloride was similar to the one described above for nitrate.

#### 3.3.3.1. *Experiment 1 : no pretreatment (Cores A and B)*

In the case of chloride, the results are rather unusual. In core A, the estimated amount in the soil before leaching was 43 mg. The amount leached was 71 mg. In core B, the inferred amount of chloride in the soil before leaching was 103 mg. The amount leached was 183. The amount of chloride remaining in the soil after leaching could not be estimated because of the interference of Nile blue dye with chloride measurement.

For cores A and B, the amount of chloride leached was greater than the estimated amount present before leaching. Thus a question arises as to the reliability of estimating solute concentration from the soil samples taken around large intact cores. The reasons for this discrepancy will be discussed later.

#### 3.3.3.2. *Experiment 3 : with field pretreatment (Cores E and F)*

The estimated amount of chloride in core E before leaching was 525 mg. The amount leached during the first part of the experiment was 483 mg. The amount applied during the second part of the experiment was 2749 mg, and the amount not leached in the first part of the experiment was 42 mg, giving a total of 2791 mg. The amount leached during second part of the experiment was 1972 mg. The amount remaining in the soil at the conclusion of the experiment was 722 mg. So

the unaccounted for chloride was 97 mg. As this is only about 4 % of that applied, nearly all the applied and resident chloride was accounted for.

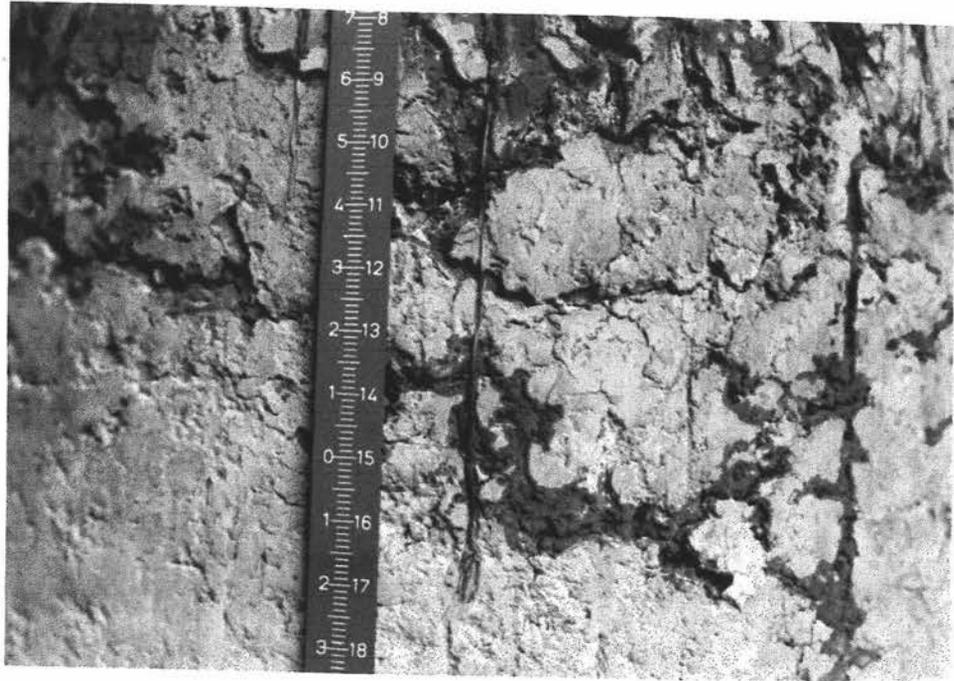
The inferred amount of chloride in core F before leaching was 525 mg. The amount leached during the first part of the experiment was 423 mg. The amount applied during the second part of the experiment was 2749 mg, and the amount not leached in the first part was 102 mg, giving a total of 2851 mg. The amount leached during the second part of the experiment was 2044 mg. The amount remaining in the soil at the conclusion of the experiment was 702 mg. So the unaccounted for chloride was 105 mg, again a satisfactory result.

### 3.4. DYE APPLICATION

Studies using Nile blue dye clearly showed the importance of macropore flow. Plates 3.1, 3.2 and 3.3 show various examples of preferential movement of dye through the soil. The plates show preferential flow occurred through earthworm channels, old root channels, and also through a combination of flow paths, e.g. some old root channels were connected with earthworm channels. Plate 3.1 illustrates this. Similar results were observed by Ritchie *et al.* (1972), Omoti and Wild (1979) and Anderson and Bouma (1973). In general, there was no evidence of edge flow i.e. the movement of dye between the soil and the cylinder walls. However, on one occasion a small stone was pushed ahead of the cutting edge of the cylinder and cut a groove which allowed some edge-flow, as shown in Plate 3.4. Data from this core, which was used for an early trial of the sampling and leaching technology, were rejected.

The dye solution moved into the soil through large pores, such as gaps between roots and the surrounding soil, decayed root channels, worm channels, soil cracks and the incipient fracture planes between structural units. Grass root channels and worm channels appeared to be the major pathways for water intake into the soil profile. Relatively fewer blue-stained roots and worm channels were observed in the subsurface horizon than in the surface horizon.

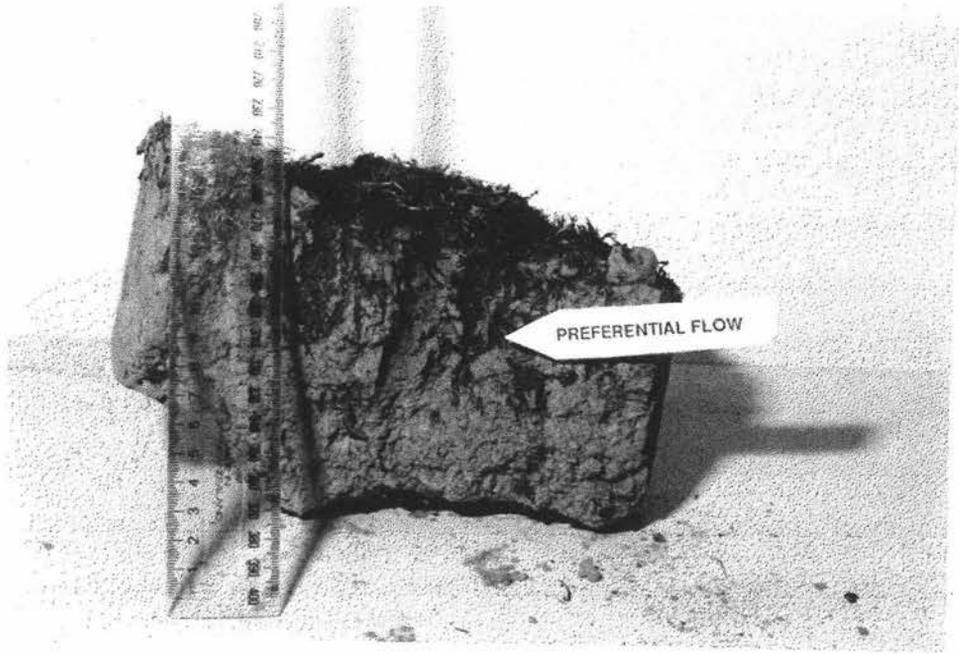
Blue-stained fracture planes, roots and worm channels were observed in vertical



**Plate 3.1** Some root channels connected with earthworm channels



**Plate 3.2** Root channels



**Plate 3.3** Vertical view of dye movement



**Plate 3.4** Edge flow due to a stone which cut a groove during core collection

sections of the soil core. Worm channels did not necessarily have to reach the surface to be effective in conducting water and solutes, provided they were connected with other somewhat smaller conducting channels, planar cracks and/or root channels which did reach the surface. In other words, networks of interconnected pores of different types seemed to provide the preferential flow paths, rather than flow down a single channel.

Some conducting channels were cut off by the core wall, causing blue staining on the side of the soil core, but there was no indication of solution leaking down between the soil and the corer. Due to the very strong adsorption of methylene blue by soil, the colour observed only shows the pathways of highly preferential solute movement.

### 3.5. SOIL AND LEACHING DATA

#### 3.5.1. *Experiment 1: No leaching pretreatment*

Figure 3.1 shows the estimated distribution of nitrate and chloride in the soil solution for cores A and B before leaching on 5 July 1989. No consistent trend of concentration with depth was observed, although nitrate concentration tended to be highest near the surface, and chloride concentration higher at the lower sampling depths.

Figures 3.2 (a) and (b) show the outflow rates as a function of cumulative drainage for cores A and B respectively. After 30 mm of drainage, corresponding to 7 hours for core A and 8 hours for core B, the flow was steady. Figures 3.2 (c) and (d) show the breakthrough curves (BTC) for tritium. A BTC is defined here as a plot of relative concentration as a function of cumulative drainage. The curves are similar for the two cores. A significant amount of tritium was present in the first effluent sample collected from both cores, indicating preferential flow, particularly for core A. For this core the concentration decreased in the next 6 effluent samples, and then increased slowly as leaching progressed. For core B the concentration of tritium decreased for the first three samples, and then increased. This behaviour could be due to swelling during wetting blocking some macropores. The relative concentration from both cores approached 0.9 after approximately two p.v. of drainage.

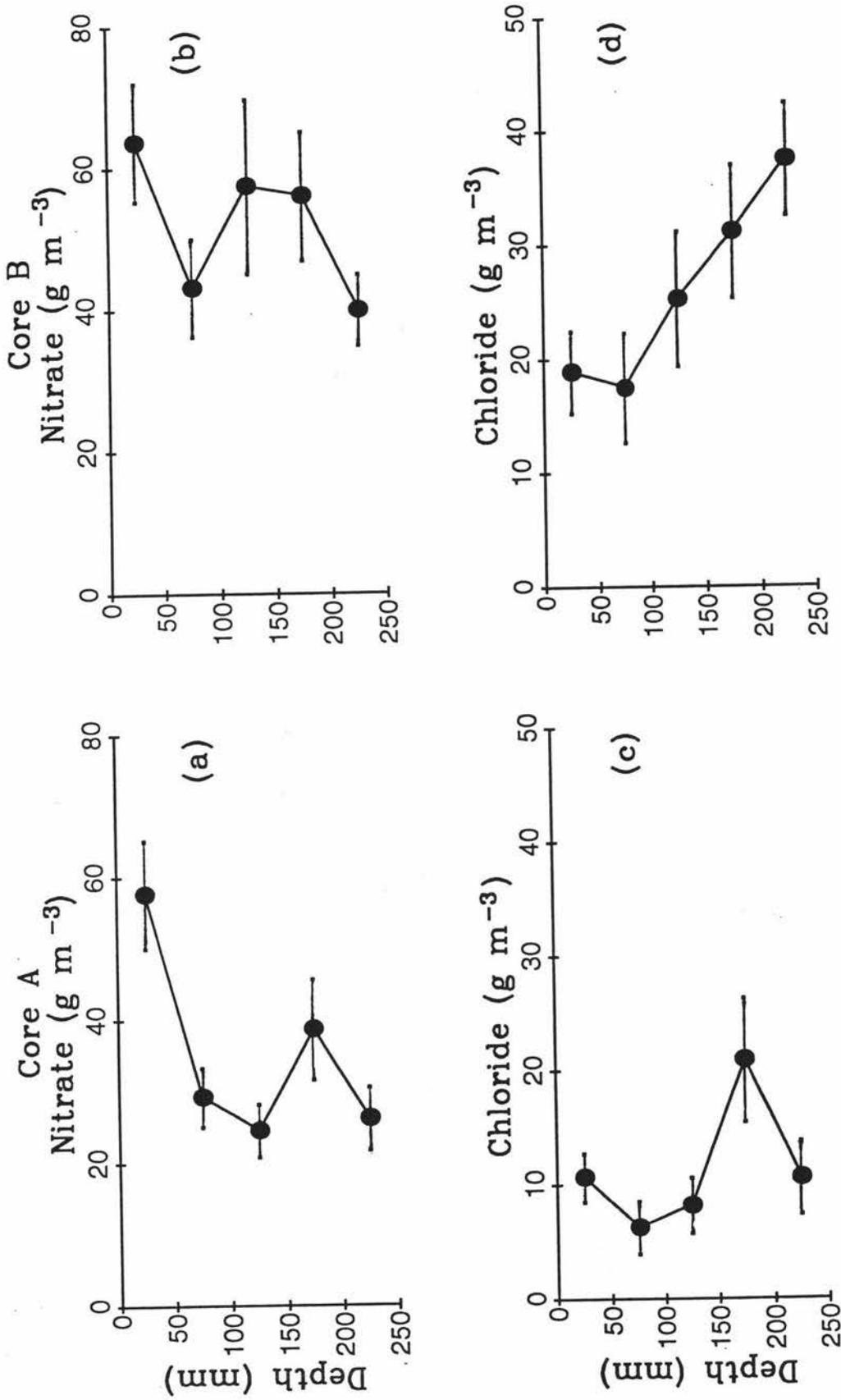


Fig. 3.1. The estimated distribution of nitrate (a and b) and chloride (c and d) in the soil solution for cores A and B before leaching on 5 July 1989

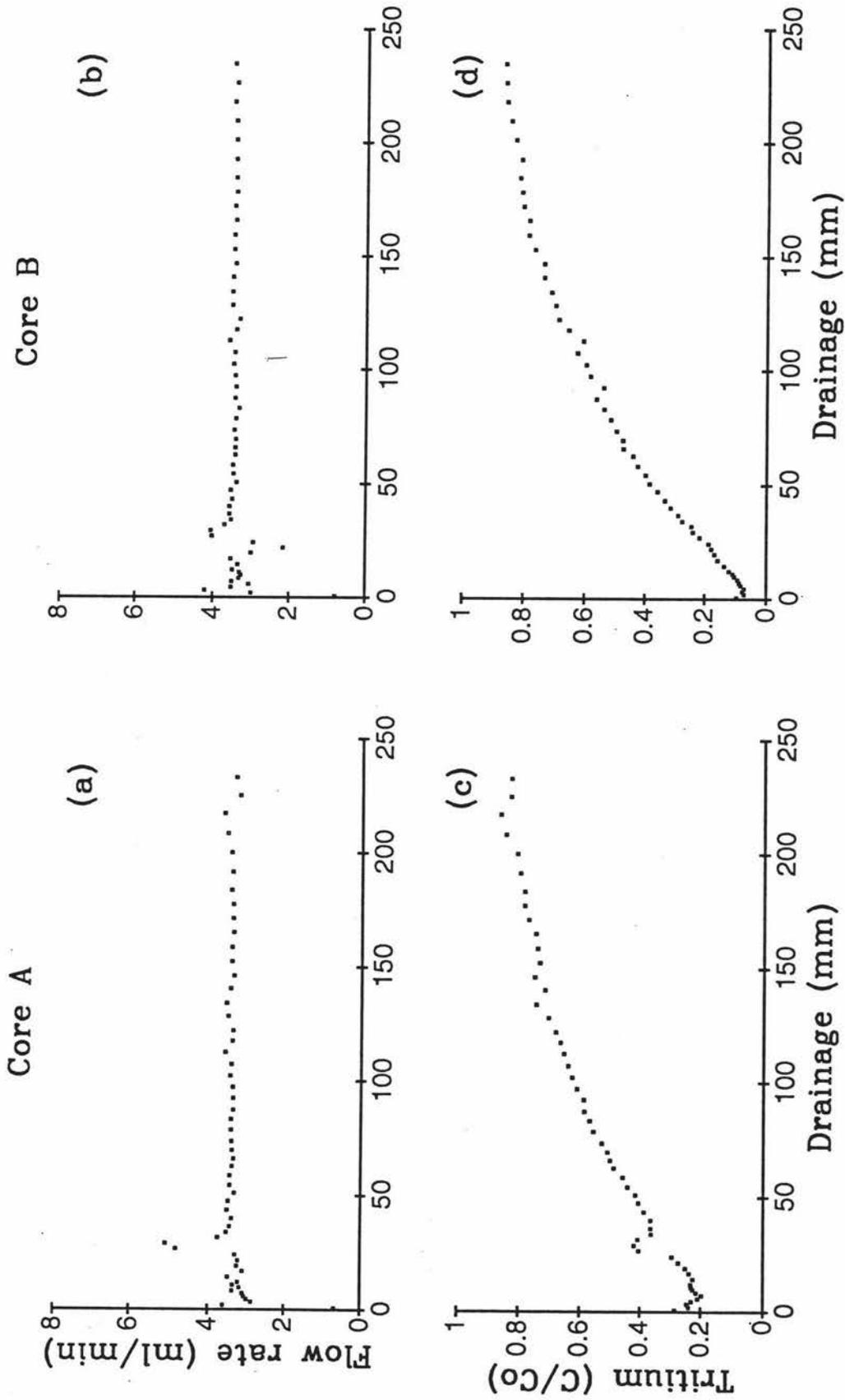


Fig. 3.2. The volume outflow rates (a and b) and the breakthrough curves of tritium (c and d) for cores A and B

Figure 3.3 shows the concentration of indigenous nitrate and chloride leached from cores A and B. Similar curves, showing in general a monotonic decrease in concentration with cumulative drainage, were observed for both cores. However, the concentration of nitrate in the effluent of core B was nearly 10 times higher than that of core A. The results for chloride show a similar discrepancy between cores A and B. The ten-fold difference in nitrate, and five-fold difference in chloride concentration in the effluent from the two cores during leaching, even though the cores were taken only 170 mm apart, is surprising. The most likely explanation is the effect of urine being deposited where core B was taken during the sheep grazing which occurred a few days before the cores were collected.

Figures 3.4 (a) and (b) show the distribution of nitrate in the soil solution of cores A and B, respectively, after leaching. The soil solution concentrations at depth were much higher than those in the final effluent, providing another indication of preferential flow. Figures 3.4 (c) and (d) show the distribution of tritium in the cores after leaching. The distribution is almost uniform with depth, which suggests that by applying more than two p.v. of tritiated water an almost uniform distribution in the soil could be achieved, even though the soil solution concentration is substantially lower than the applied solution, which contained 4490 cpm/ml.

The experiments showed that there was a discrepancy between the concentration of the solutes in the effluent and the inferred concentration of solutes in the soil solution before leaching, as estimated from soil sampling around the core. This discrepancy is probably due to a spatially non-uniform distribution of solutes in the soil before leaching. In other words, the average concentration of solute in the soil samples taken from around the large cores was different to the initial concentration in the cores themselves. One way to avoid this discrepancy is to preleach the solutes in the soil with a tracer. This tracer largely replaces the indigenous soil solutes and creates an almost uniform distribution of the applied solute in the soil solution. So two experiments were designed to study leaching from large cores with a known uniform distribution of solute. In one experiment the preleaching was carried out in the laboratory, and in the other experiment the preleaching was carried out in the field.

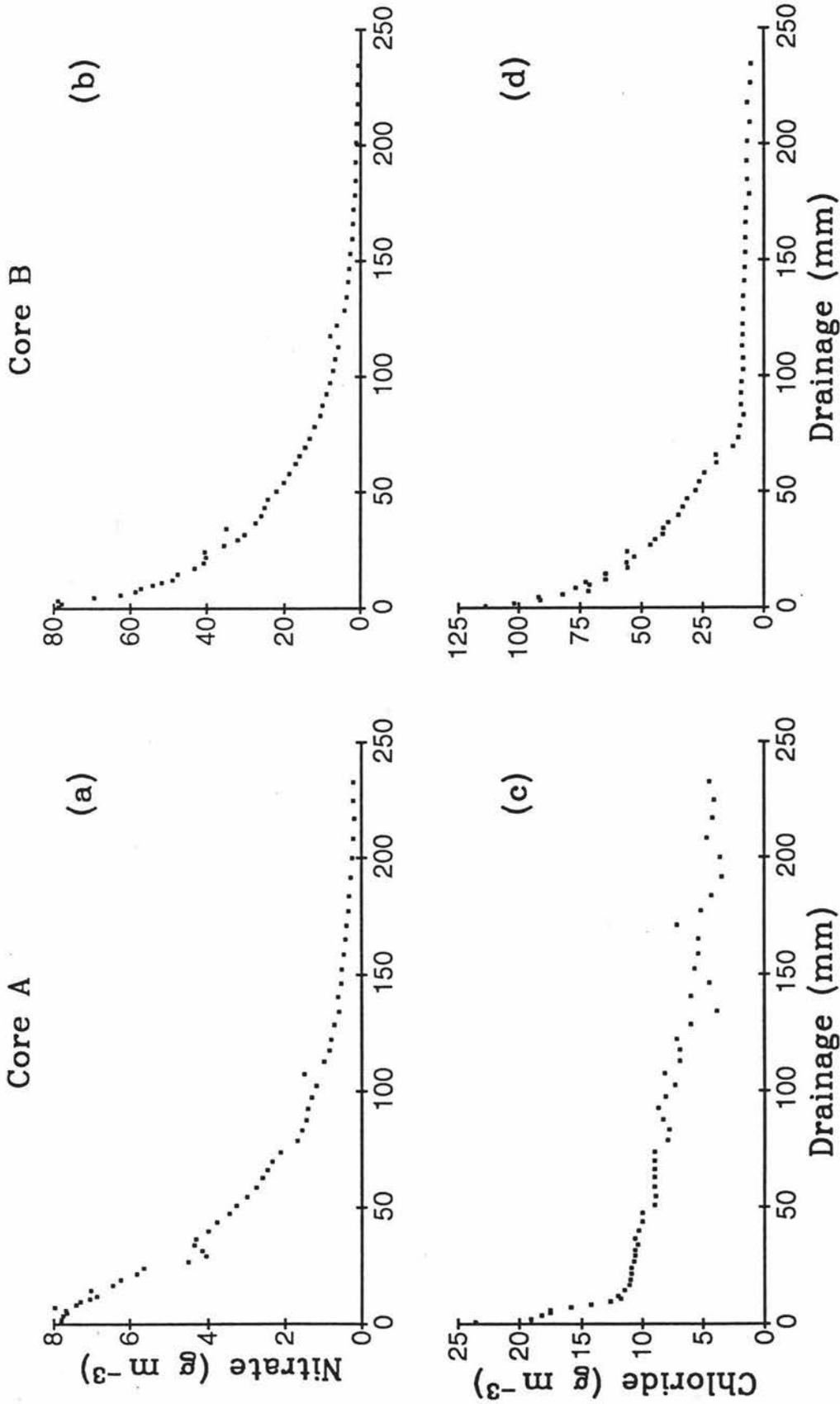


Fig. 3.3. The concentration of indigenous nitrate (a and b) and chloride (c and d) in the effluent from cores A and B

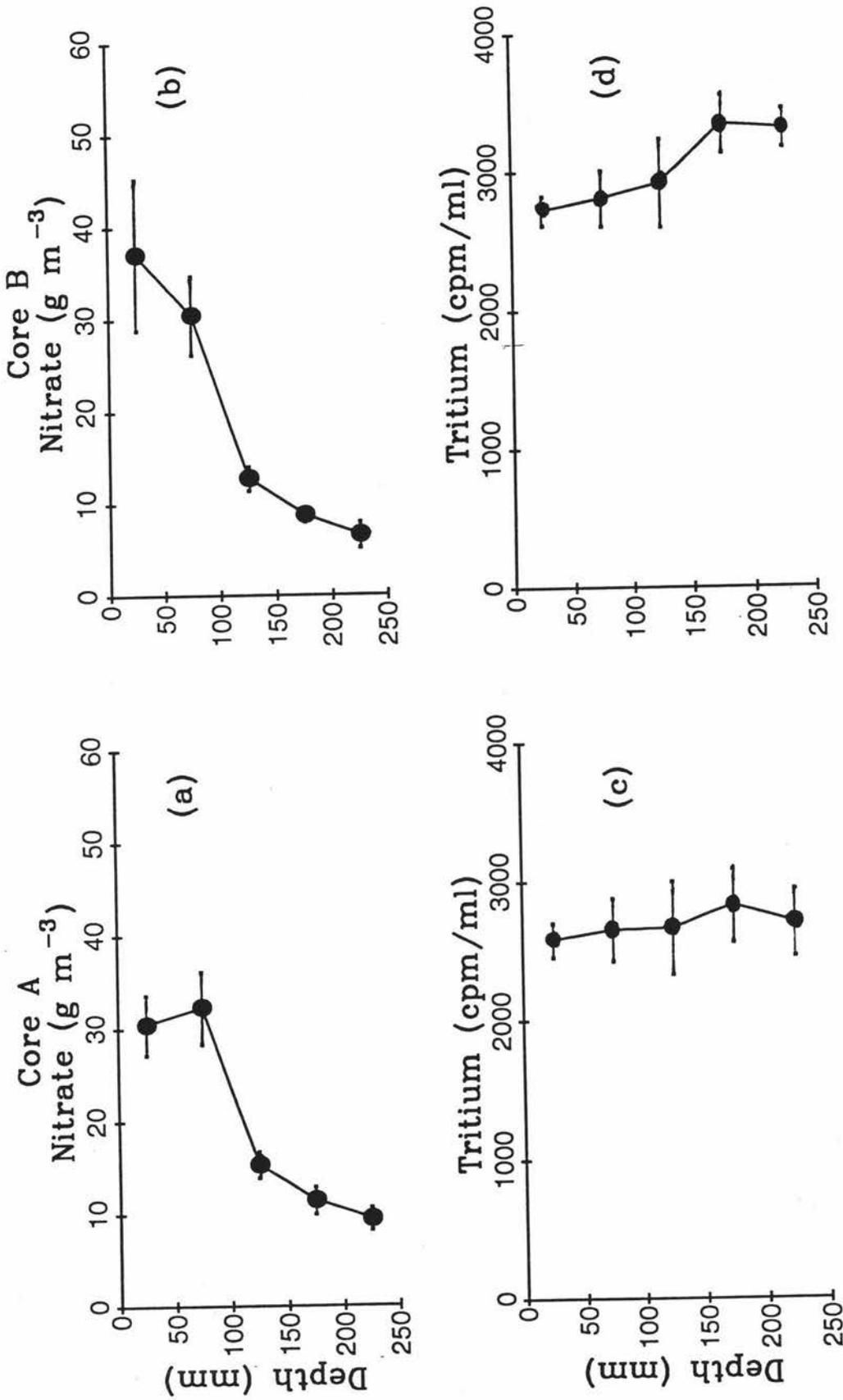


Fig. 3.4. The distribution of nitrate (a and b) and tritium (c and d) in the soil solution of cores A and B, respectively, after leaching

### 3.5.2. *Experiment 2: Laboratory preleaching*

Figures 3.5 (a) and (b) show the outflow rates as a function of cumulative drainage for cores C and D. The flow was reasonably steady for core C but unsteady for core D. The unsteady flow for core D was due to intermittent blockage of needles during leaching. To compensate for the amount not applied during a blockage, the flow rate was subsequently increased for a short time so that the amount applied to both cores was equal. However, the flow was steady during pretreatment with tritiated water.

Figures 3.5 (c) and (d) show the breakthrough of bromide for cores C and D after the pulse application of  $500 \text{ g Br m}^{-3}$  in 30 mm of input solution. The behaviour of the pulse in the two cores was somewhat different. In core C the concentration rose quickly and decreased slowly with a peak concentration of  $180 \text{ g Br m}^{-3}$ , after 25 mm drainage. The concentration was maintained almost constant between 60 mm and 100 mm drainage. In core D the concentration rose more slowly and the peak concentration was  $240 \text{ g Br m}^{-3}$  after 50 mm drainage. The amount of bromide leached from core C and core D was 499 mg and 613 mg, respectively, equivalent to 82 % and 94 % of that applied.

Figures 3.6 (a) and (b) show the leaching of the tritium which had been applied during the pretreatment. In this experiment the initial tritium distribution can be assumed to be fairly uniform, as in the previous experiment it has been shown that an almost uniform distribution of solutes could be attained by applying more than two p.v. of tritiated water. Figures 3.6 (c) and (d) give the distribution of tritium in the soil after leaching.

### 3.5.3. *Experiment 3: Pretreatment in the field*

For the pretreatment, a selected area of soil was regularly irrigated with chloride solution in an attempt to obtain a uniform distribution of soil chloride down to 300 mm depth. Chloride rather than nitrate was used as nitrate can undergo rapid transformations in field soils. Details were given in Chapter 2.

After the pretreatment, two large cores were collected and leached with tritiated water. In the second phase of the experiment, solutes were applied to the surface

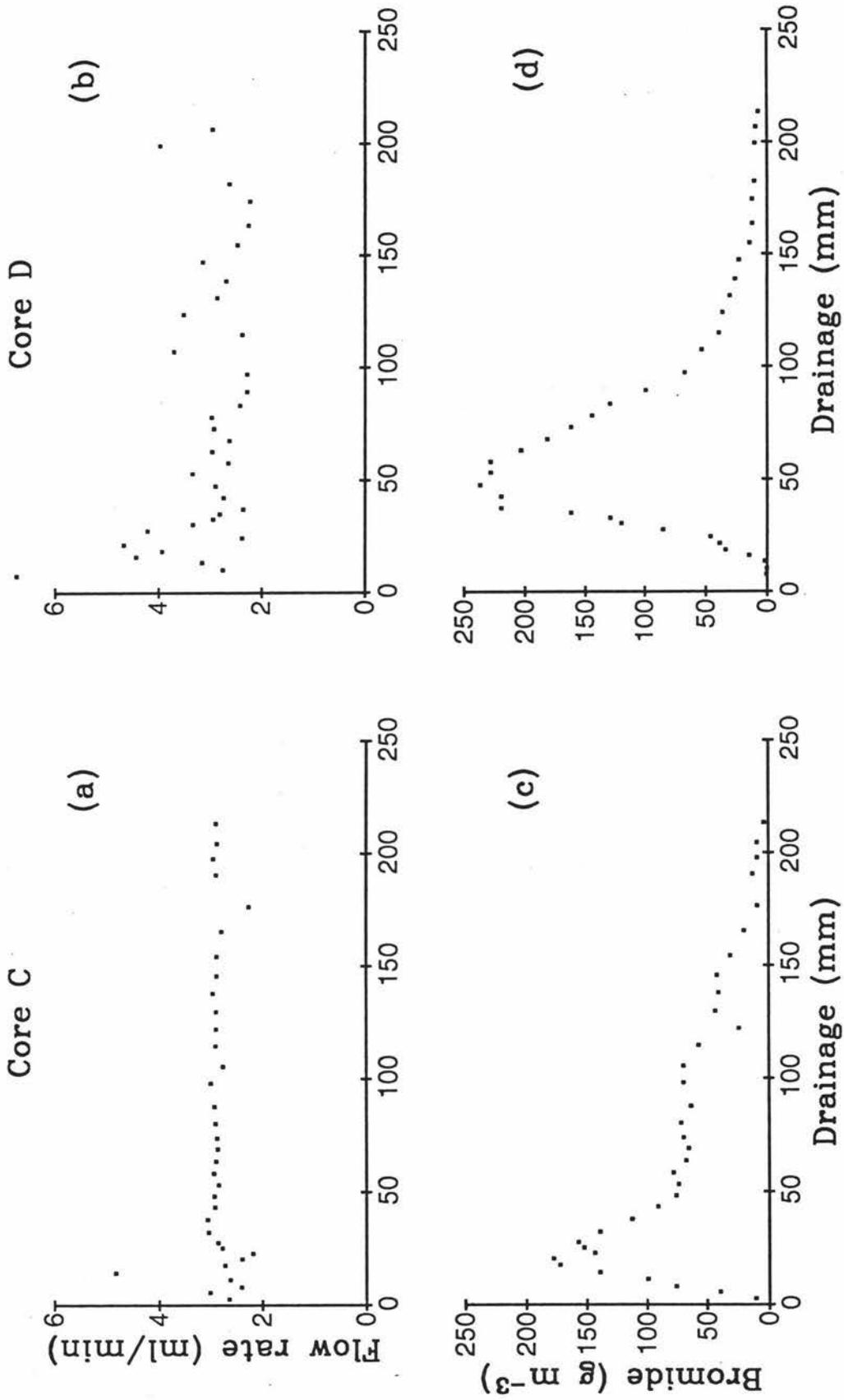


Fig. 3.5. The volume outflow rates (a and b) and the breakthrough of bromide (c and d) for cores C and D after the pulse application of 500 g Br m<sup>-3</sup> in 30 mm of input solution

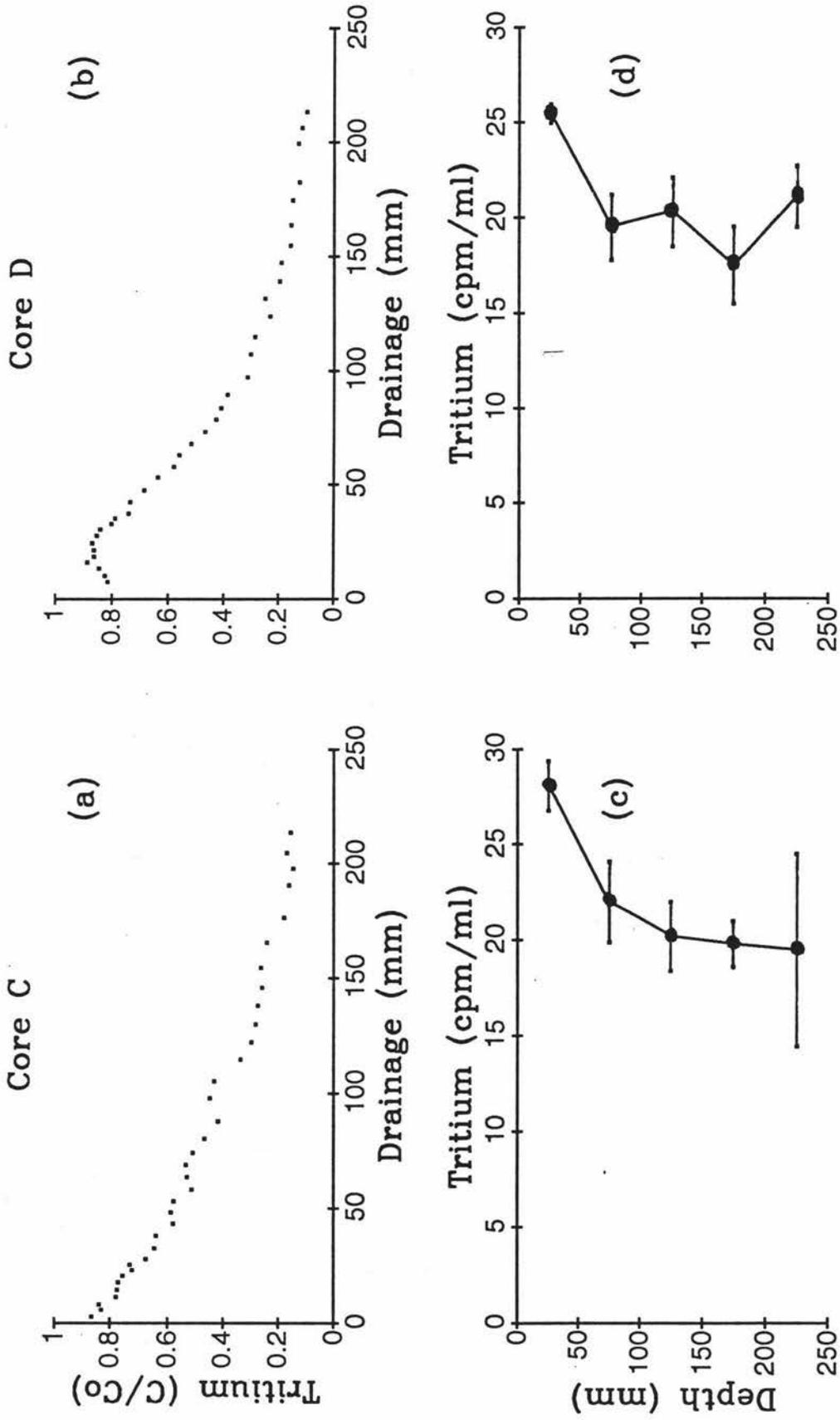


Fig. 3.6. The breakthrough curve of the tritium which had been applied during the pretreatment (a and b), and the distribution of tritium in the soil after leaching (c and d)

both as a step-input (chloride) and as a pulse input (nitrate) and the effluent analyzed. The leaching of the tritium applied during the first phase of the experiment was also observed.

### 3.5.3.1. *First phase of the experiment*

Figure 3.7 shows the distribution of nitrate and chloride in the soil solution after the pretreatment, but before leaching, in the soil surrounding large cores E and F. The nitrate concentration in the soil solution was highest in the 50 - 100 mm layer after preleaching treatment in the field. A possible explanation is that in the top layer the bulk density is lower and the saturated hydraulic conductivity is higher when compared to lower layers. Thus more effective leaching could have been taken place in the top layer. Figures 3.7 (c) and (d) show that the distribution of chloride in the soil solution was almost uniform with depth. The mean estimated concentration of nitrate in the soil solution was  $4.6 \text{ g N m}^{-3}$  and of chloride was  $118.5 \text{ g Cl m}^{-3}$ . This chloride concentration is close to the concentration of the preleaching solution, which contained  $142 \text{ g Cl m}^{-3}$ .

Figures 3.8 (a) and (b) show the outflow rates as a function of cumulative drainage for the first phase of the experiment for cores E and F. The flow was unsteady during the first 27 mm of drainage for core E and 16 mm of drainage for core F. After that outflow was quite steady and the flow rate was almost equal to the inflow rate. Figures 3.8 (c) and (d) show the breakthrough curves of the applied tritium for cores E and F. The tritium data for the two cores were similar. Some tritium was found in the first effluent sample from both cores, but the relative concentration ( $C/C_0$ ) was different; 0.01 for core E and 0.09 for core F. After 2 p.v. of leaching the relative concentration in the effluent reached approximately 0.95 for both cores.

Figure 3.9 shows the nitrate and chloride leached in the first phase of the experiment. The concentration of nitrate in the first 60 mm of drainage from core E was approximately  $1 \text{ g N m}^{-3}$  and after that the concentration steadily dropped, being close to zero after 200 mm of drainage. For core F the initial concentration was higher than that in core E ( $2.4 \text{ g N m}^{-3}$ ), but decreased more steeply with leaching. The estimated mean concentration of nitrate in the soil solution before leaching was

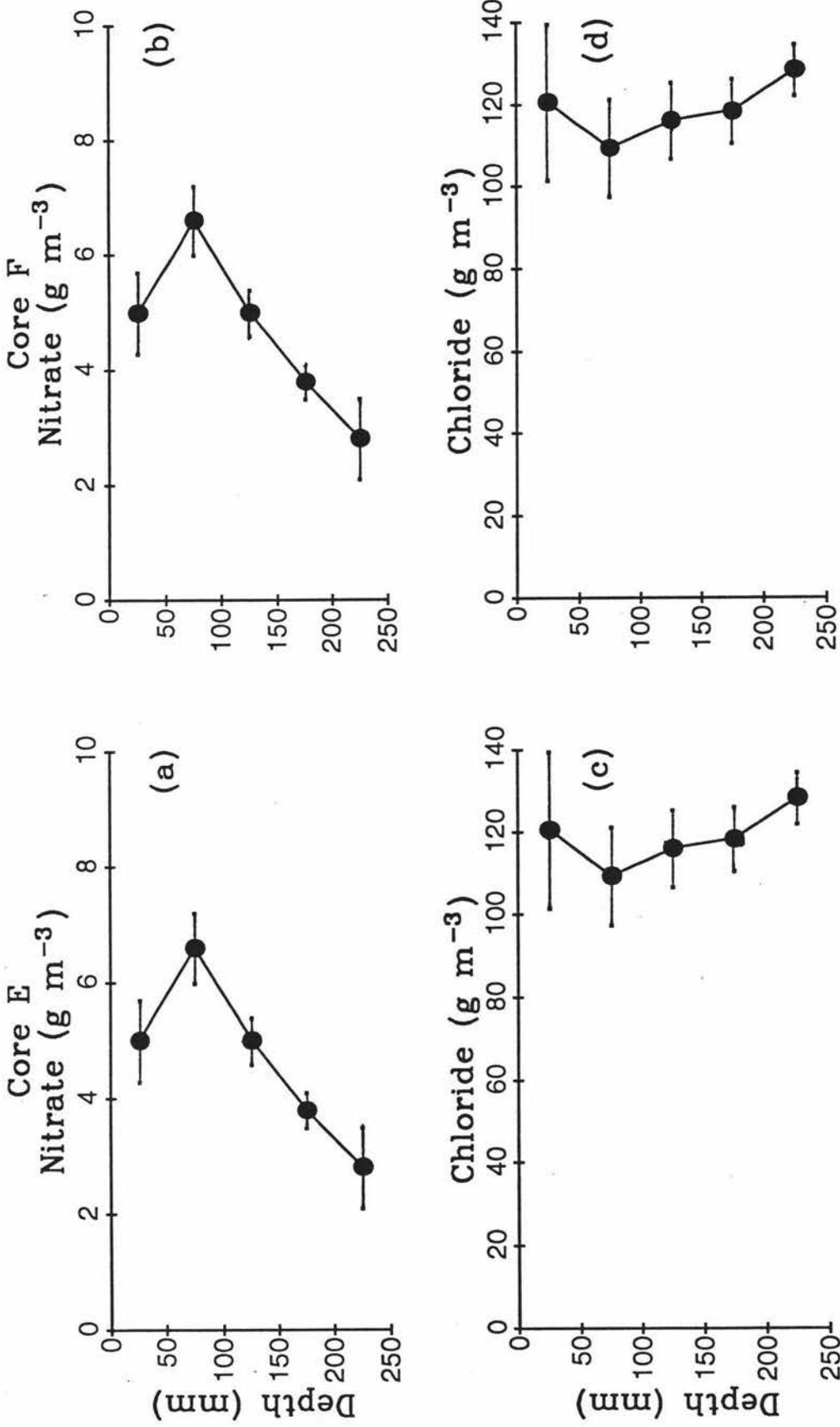


Fig. 3.7. The distribution of nitrate (a and b) and chloride (c and d) in the soil solution after preleaching but before phase one of the leaching experiment, in the soil surrounding large cores E and F

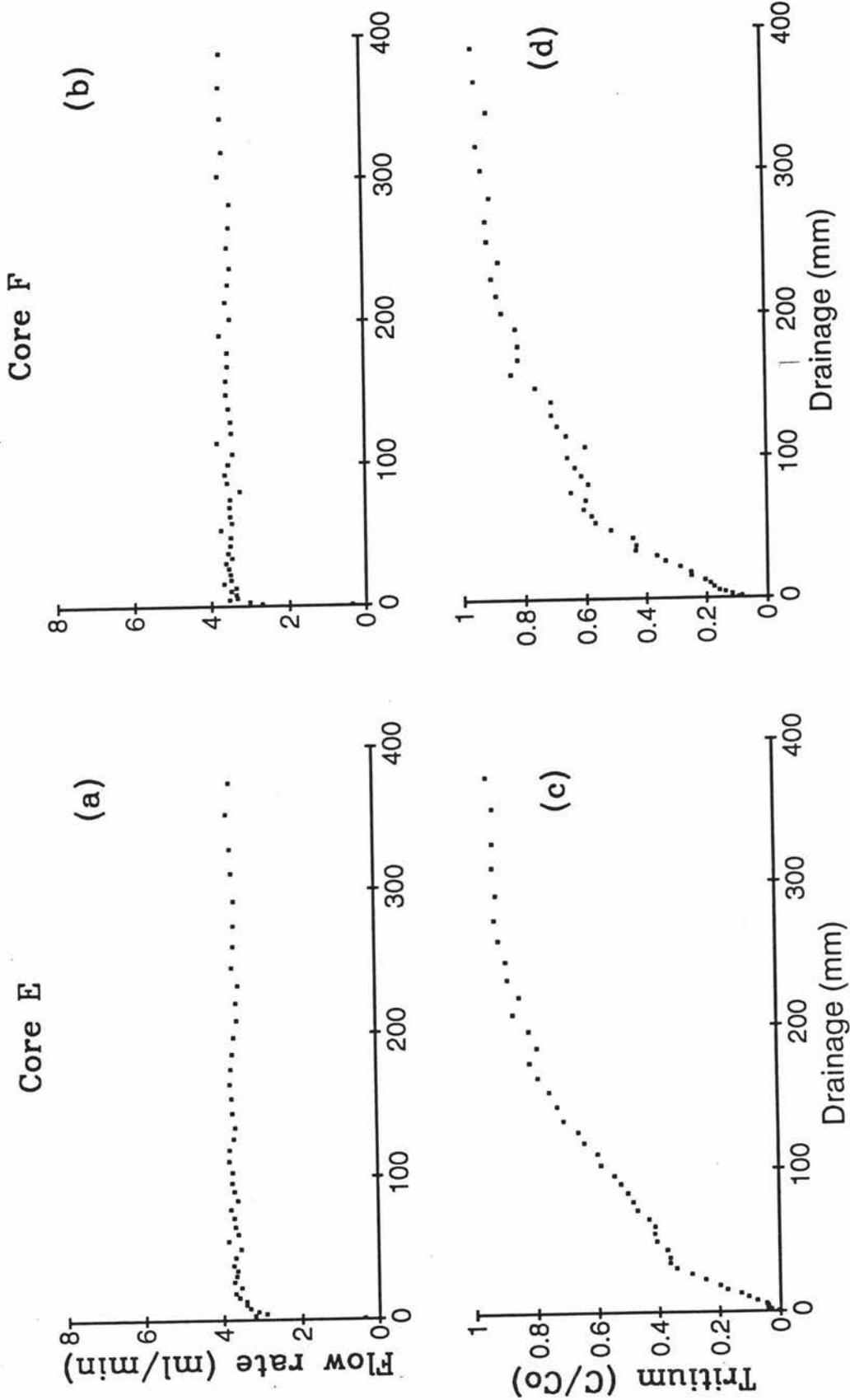


Fig. 3.8. The volume outflow rates (a and b) and the breakthrough curves of the applied tritium (c and d) for cores E and F for the first phase of the experiment

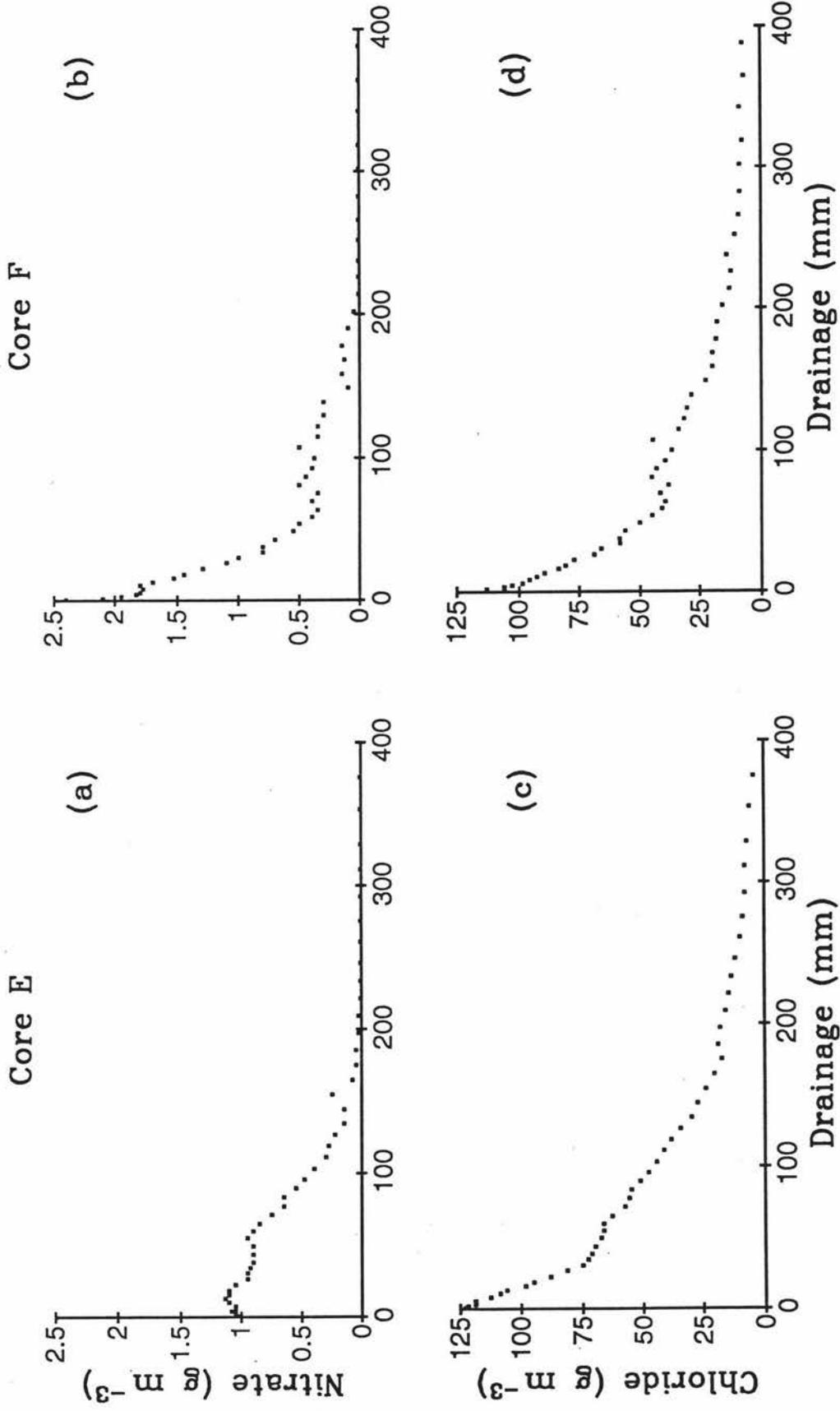


Fig. 3.9. The concentration of nitrate (a and b) and chloride (c and d) in the effluent during the first phase of the experiment for cores E and F

4.6 g N m<sup>-3</sup> for both cores, so the initial leachate concentration was much less than the mean soil solution concentration. The concentrations of chloride in the first effluent from cores E and F were 123 g Cl m<sup>-3</sup> and 106 g Cl m<sup>-3</sup>, respectively. The estimated mean concentration of chloride in the soil solution before leaching was 118.5 g Cl m<sup>-3</sup> in both cores. Thus, whereas the concentration of nitrate in the early effluent did not agree with the mean concentration of nitrate in the soil solution before leaching, the concentration of chloride did. This difference can perhaps be explained as follows. During the pretreatment indigenous solutes in the accessible pore space would have been replaced by the applied chloride. However, nitrate is produced due to slow but constant mineralization during pretreatment. The nitrate present in the effluent is probably the result of diffusion between the mobile and immobile volumes and/or nitrate produced by mineralization.

### 3.5.3.2. *Second phase of the experiment*

Figures 3.10 (a and b) show the outflow rates as a function of cumulative drainage for the second phase of the experiment for cores E and F. The flow was almost steady during the experiment. Figures 3.10 (c and d) show the nitrate breakthrough after the 20 mm pulse application of Ca(NO<sub>3</sub>)<sub>2</sub> solution containing 500 g N m<sup>-3</sup>. The behaviour of the pulse in both the cores was similar. The concentration rose quickly to a peak after approximately 30 mm (0.28 p.v.) of drainage and then decreased slowly, again indicating preferential flow. In core E the peak concentration of nitrate was 80 g N m<sup>-3</sup> whereas in core F, the peak was sharper with a concentration of 103 g N m<sup>-3</sup>. The emergence of peak concentrations before one liquid-filled pore volume of drainage (see Table 3.1) indicates that the water and solutes were flowing through soil macropores, as shown by dye studies (section 3.4).

Figure 3.11 shows the BTC of applied chloride and resident tritium. The concentration of chloride in the step input was 212.7 g Cl m<sup>-3</sup> (3 mM CaCl<sub>2</sub> solution). The relative concentration of chloride approached 0.99 after about 2.3 p.v. of drainage from both cores. As expected the curves for tritium in Fig. 3.11 are approximate mirror images of the chloride curves.

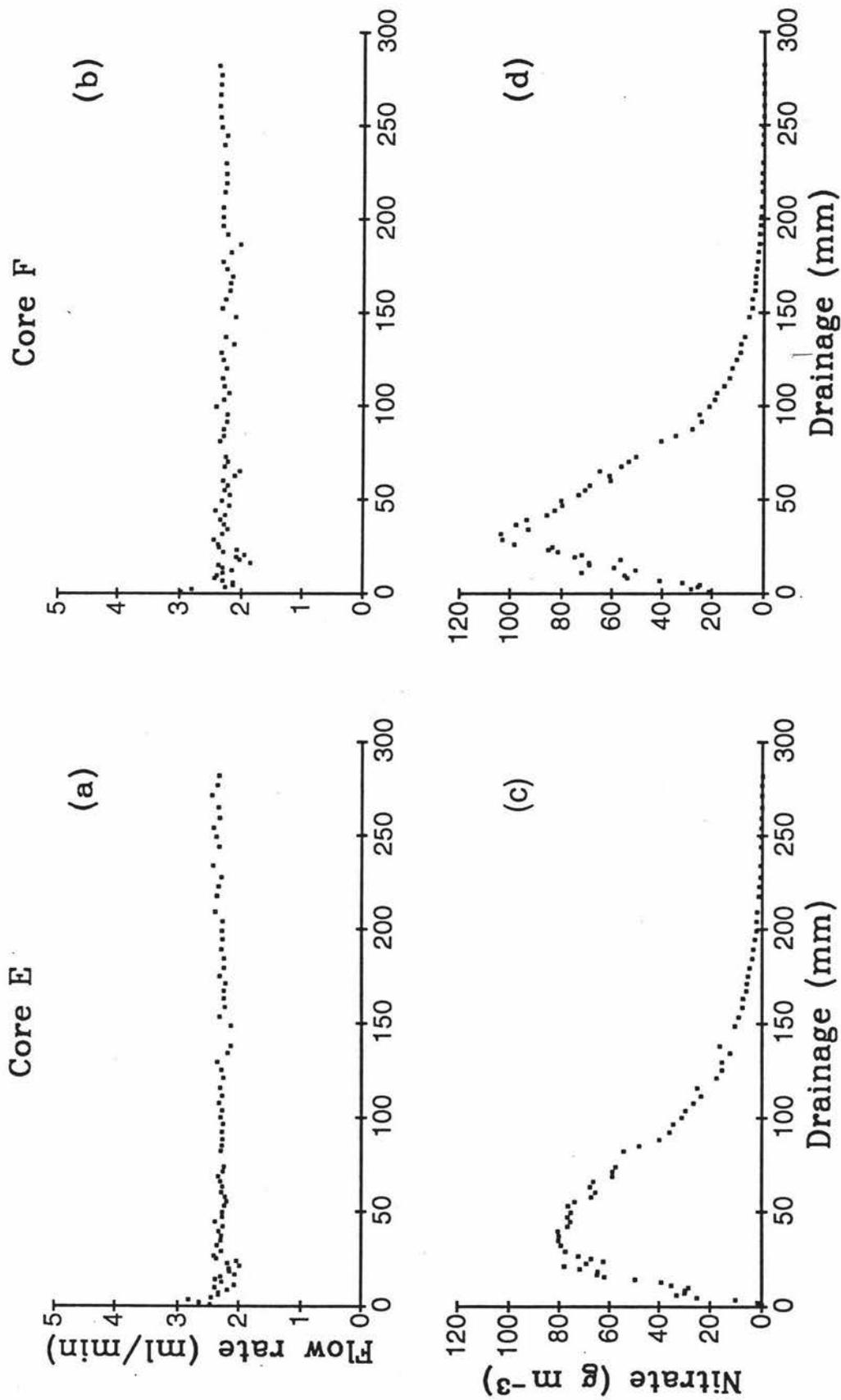


Fig. 3.10. The volume outflow rates (a and b) and breakthrough of nitrate pulse (c and d) for the second phase of the experiment for cores E and F

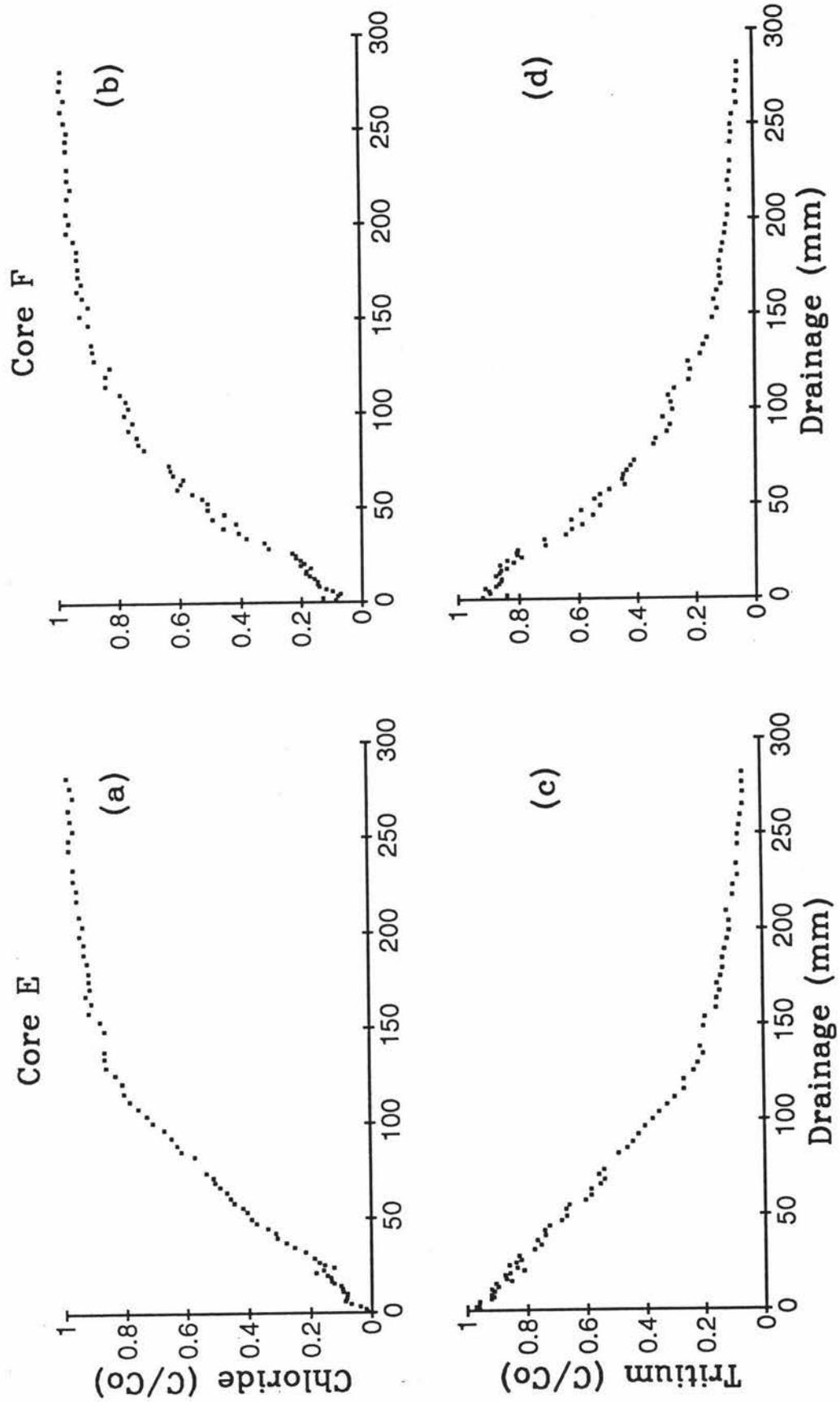


Fig. 3.11. The breakthrough curve of applied chloride (a and b) and resident tritium (c and d) in the second phase of the experiment for cores E and F

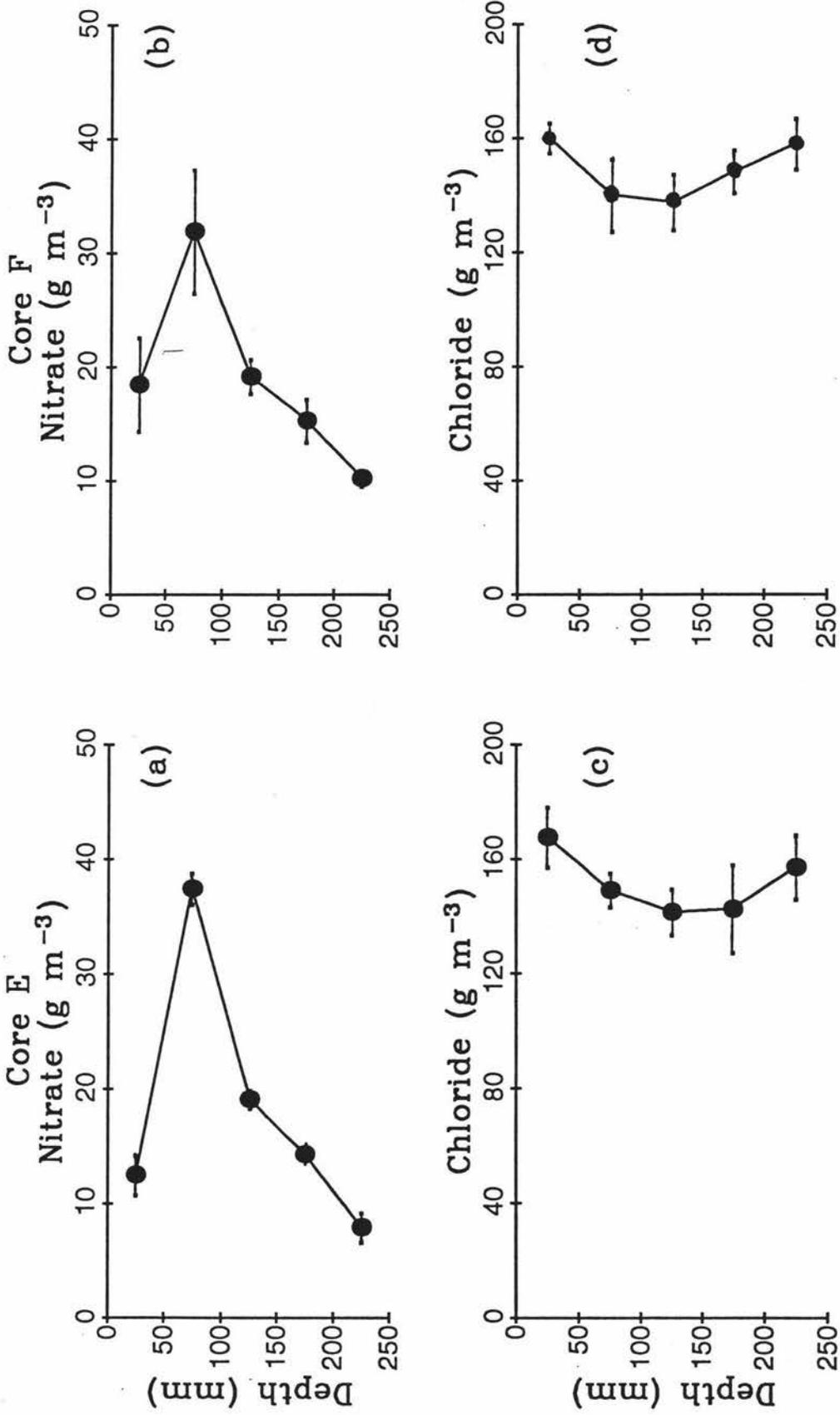


Fig. 3.12. The distribution of nitrate (a and b) and chloride (c and d) in the soil solution after the leaching experiment

Figure 3.12 gives the distribution of nitrate and chloride in the soil solution after the leaching experiment. Note that the concentration of chloride was reasonably uniform with depth, but that the concentration of nitrate is relatively much less uniform. The pattern observed for nitrate in both cores was that the concentration decreased with depth from the second layer onwards, but in the first layer the concentration was lower than in the second layer. This is similar to Figures 3.7 (a) and (b). One possible explanation could be mineralization taking place during the week long experiment where the soil is aerobic and the organic matter content is high. Denitrification Enzyme Activity (DEA) is highest in top 50 mm (J.Luo - unpublished data) and denitrification could have occurred, because of the low oxygen levels there. This would be due to the soil surface being covered with 10 mm of saturated sand, inhibiting air entry through the soil surface (see section 2.3.4).

### 3.6. CONCLUSIONS

Several important conclusions can be drawn from this work. For example :

- (a) Dye studies have indicated that worm holes and root channels were the main preferential pathways for water and solute movement through the soil.
- (b) Estimating the initial solute concentration in the large cores from small soil cores taken from around them was not valid due to spatial variability. The main cause for spatial variability is probably urine and dung spots due to sheep grazing.
- (c) Pretreatment in the laboratory or field can provide a way of obtaining a uniform distribution of resident solute in the soil for leaching experiments. This in fact helps when the leaching process is modelled, as will be shown in Chapter 4.

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

**4.1. INTRODUCTION**

As discussed in chapter 1, for decades soil scientists have treated soil as a uniform porous medium and applied the convection-dispersion equation (CDE) to predict water and solute movement in it (Nielsen and Biggar, 1962). However, the CDE could not be applied successfully to some miscible displacement experiments using natural soil cores due to effect of preferential flow (e.g. Thomas and Phillips, 1979). The transfer function model (TFM) (Jury, 1982; Jury *et al.*, 1986), on the other hand, treats solute transport as a stochastic process, acknowledging that the exact mechanisms governing solute transport may be poorly understood in a heterogenous porous medium such as soil.

In this chapter, the movement of tritium, chloride, nitrate and bromide through undisturbed soil cores described in chapter 3 is modelled using the transfer function approach.

**4.2. THEORY**

The probability  $P(I)$  that a solute applied to the surface of a soil core will exit from the base of the core after cumulative drainage or net infiltration  $I$ , (Jury, 1982; White *et al.*, 1984) is

$$P(I) = \int_0^I f(I) d(I) \quad (4.1)$$

where  $f(I)$  is the probability density function (pdf) of the variable  $I$ . Following Jury *et al.* (1986), under steady-state water flow for a step input of solute that enters a soil core initially only through an entrance surface at the top and disappears permanently only through an exit surface at the bottom, the output concentration can be described

by the equation

$$C_{ex}(I) = \int_0^I f(I-I') C_{ent}(I') dI' \quad (4.2)$$

where  $C_{ex}(I)$  is the concentration at the exit surface after drainage  $I$  (expressed as volume per unit area) and  $C_{ent}(I')$  is the concentration of externally applied solute at the entrance surface after a lesser amount of cumulative drainage  $I'$ .

A lognormal distribution was assumed for the pdf because it has been found to describe solute travel times or velocities in the field (Jury *et al.*, 1982) and in large cores (White *et al.*, 1984), so equation (1.10) applies, that is

$$f(I) = \frac{\exp[-(\ln I - \mu)^2 / 2\sigma^2]}{\sqrt{2\pi}\sigma I} \quad (4.3)$$

where  $\mu$  is the mean of the distribution of  $\ln I$  and  $\sigma^2$  is its variance.

For a step-change in the input concentration from 0 to  $C_o$ , that is for the boundary condition

$$C_{ent} = 0 \quad I \leq 0 \quad ; \quad C_{ent} = C_o \quad I > 0 \quad , \quad (4.4)$$

the solution of (4.2) subject to (4.3) and (4.4) is (Jury, 1982)

$$C_{ex}(I) = \frac{C_o}{2} \left\{ 1 + \operatorname{erf} \left[ \frac{\ln(I) - \mu}{\sqrt{2}\sigma} \right] \right\} . \quad (4.5)$$

Similarly for a square pulse input, with  $C_{ent}$  being  $C_o$  from  $I = 0$  to  $I = \Delta I$ , and otherwise being zero, the output concentration for  $I > \Delta I$  is given by (Jury, 1982)

$$C_{ex} = \frac{C_o}{2} \left\{ \operatorname{erf} \left[ \frac{\ln(I) - \mu}{\sqrt{2}\sigma} \right] - \operatorname{erf} \left[ \frac{\ln(I - \Delta I) - \mu}{\sqrt{2}\sigma} \right] \right\} . \quad (4.6)$$

The leaching of a resident solute initially distributed uniformly throughout the soil is equivalent to a step change in  $C_{ent}$  from  $C_o$  to 0 at  $I \geq 0$ , (White and Magesan, 1991)

and so

$$C_{ex}(I) = \frac{C_i}{2} \left\{ 1 - \operatorname{erf} \left[ \frac{\ln(I) - \mu}{\sqrt{2} \sigma} \right] \right\}. \quad (4.7)$$

In this case,  $C_o$  is replaced by  $C_i$ , the concentration of the resident solute in the accessible soil volume at  $I = 0$ .

White *et al.* (1984) and Jury *et al.* (1986) introduced the concept of an *operationally defined* transport volume,  $\theta_{st}$ . Because of the heterogeneity of the solid surfaces and void spaces in undisturbed soil and the complexity of water movement, especially under non steady-state conditions, the transport volume  $V_{st}$  in any given volume of soil would be irregular in shape and variable in size as water percolates through the soil. Nevertheless, a quantitative description of the probable behaviour of surface-applied tracer ions, once they have entered the transport volume, should be useful for predicting the probable behaviour of resident ions initially in the soil's transport volume. White (1989) initiated the modelling of resident solutes using transfer functions with parameters derived from externally applied solutes; he used chloride as a tracer and nitrate as the resident solute.

$\theta_{st}$  can be calculated from a measure of the centre of location of the solute pdf under particular conditions of measurement, and its value can be used to infer some general conclusions about the nature of solute transport through the soil.  $\theta_{st}$  can be defined using the mean or median travel pathway length. For relatively short observation pathway lengths, the median drainage  $I_m$ , which occurs when  $P(I) = 0.5$ , is preferred to mean drainage (White, 1985; White *et al.*, 1986; Dyson and White, 1987) because it is not affected by the area under the "tail" of the solute breakthrough curve in the same way that the mean is; i.e. the mean value can be affected by a large variance in the drainage distribution. Mean and median pathway lengths were calculated using the model parameters,  $\mu$  and  $\sigma$ , as a function of  $I$  as follows

The mean pathway length	$I_a = \exp(\mu + \sigma^2/2)$	4.8(a)
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The median pathway length	$I_m = \exp(\mu)$	4.8(b)
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Using the mean pathway length,  $\theta_{st} = I_a / L$  4.8(c)

Using the median pathway length,  $\theta_{st} = I_m / L$  4.8(d)

where  $L$  is the length of the core.

### 4.3. ESTIMATION OF MODEL PARAMETERS

A least-squares optimization program (appendix 1 or 2) with either equation (4.5) or (4.6) was used to estimate the model parameters  $\mu$  and  $\sigma$ . These parameters were then used to predict the leaching of resident solutes (appendix 3) using equation (4.7) and also to estimate the solute transport volume.

### 4.4. RESULTS AND DISCUSSION

#### 4.4.1. Experiment 1

##### 4.4.1.1. *Using tritium breakthrough curves to characterize solute pdfs*

In Figure 4.1 the measured tritium data and the fitted curves for cores A and B are plotted against cumulative drainage. The values of  $\mu$  and  $\sigma$  for the best fitted data are also shown in Figure 4.1. The fit to the core A data is not quite as good as the core B data. Note also the shorter median travel time and larger variance for core A, indicating a more skewed pdf.

##### 4.4.1.2. *Modelling resident chloride and nitrate concentrations*

Predicted and measured concentrations are shown for chloride (Fig. 4.2 a and b) and nitrate (Fig. 4.2 c and d) in the effluent from cores A and B, respectively, using the  $\mu$  and  $\sigma$  values derived above. One set of predictions were made using equation (4.7) in which  $C_i$  was the estimated mean concentration in the soil solution initially. In general, these predictions did not agree well with the measured effluent concentrations of nitrate or chloride. A similar discrepancy has been reported in previous studies (White, 1989; White and Magesan, 1991) when the mass rate of nitrate efflux was modelled. A second set of predictions was attempted again using equation (4.7) but with the solute concentration in the first effluent sample from each core substituted for  $C_i$ . These predictions of the effluent concentration were somewhat better for both chloride and nitrate in core A, but not for core B.

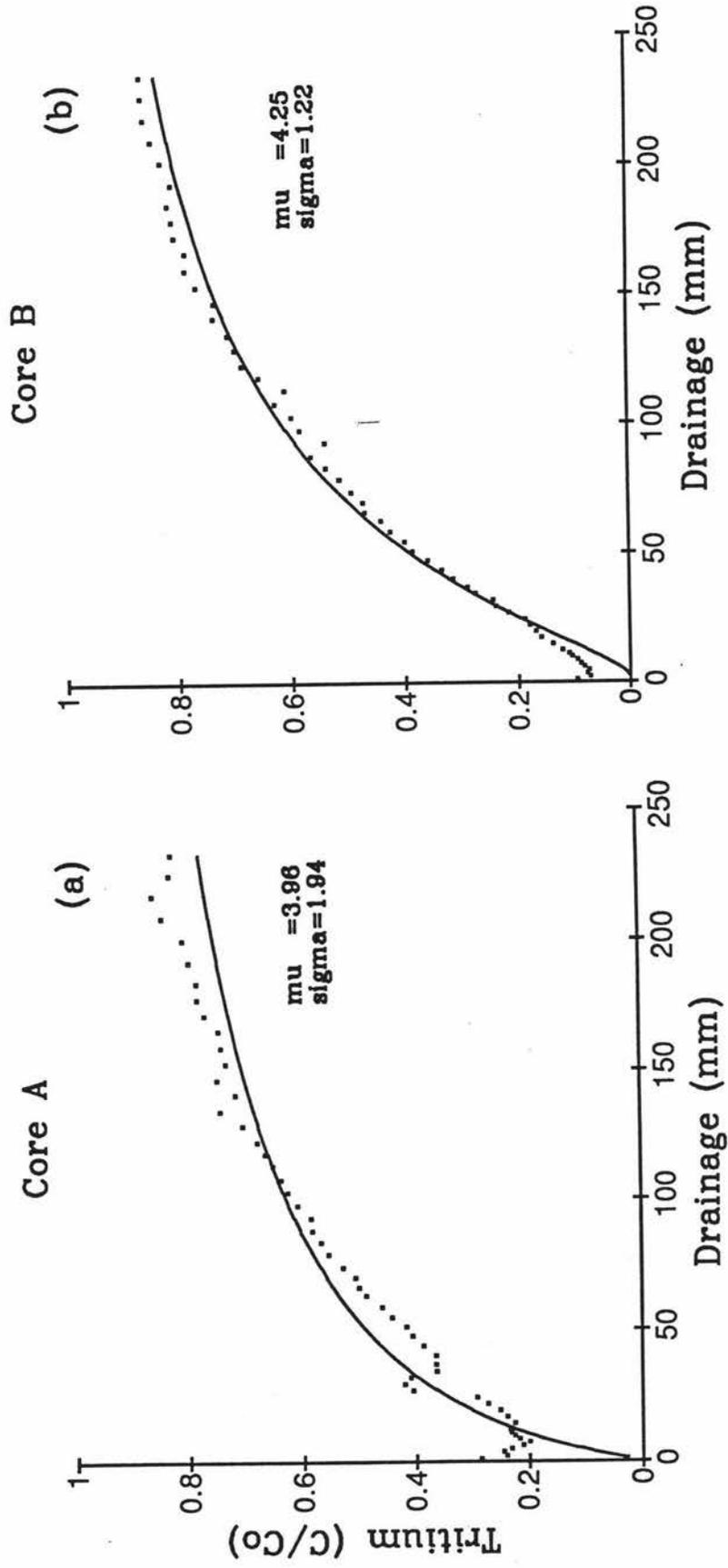


Fig. 4.1. Measured (■) and fitted (—) relative concentration of tritium in the effluent for cores A and B

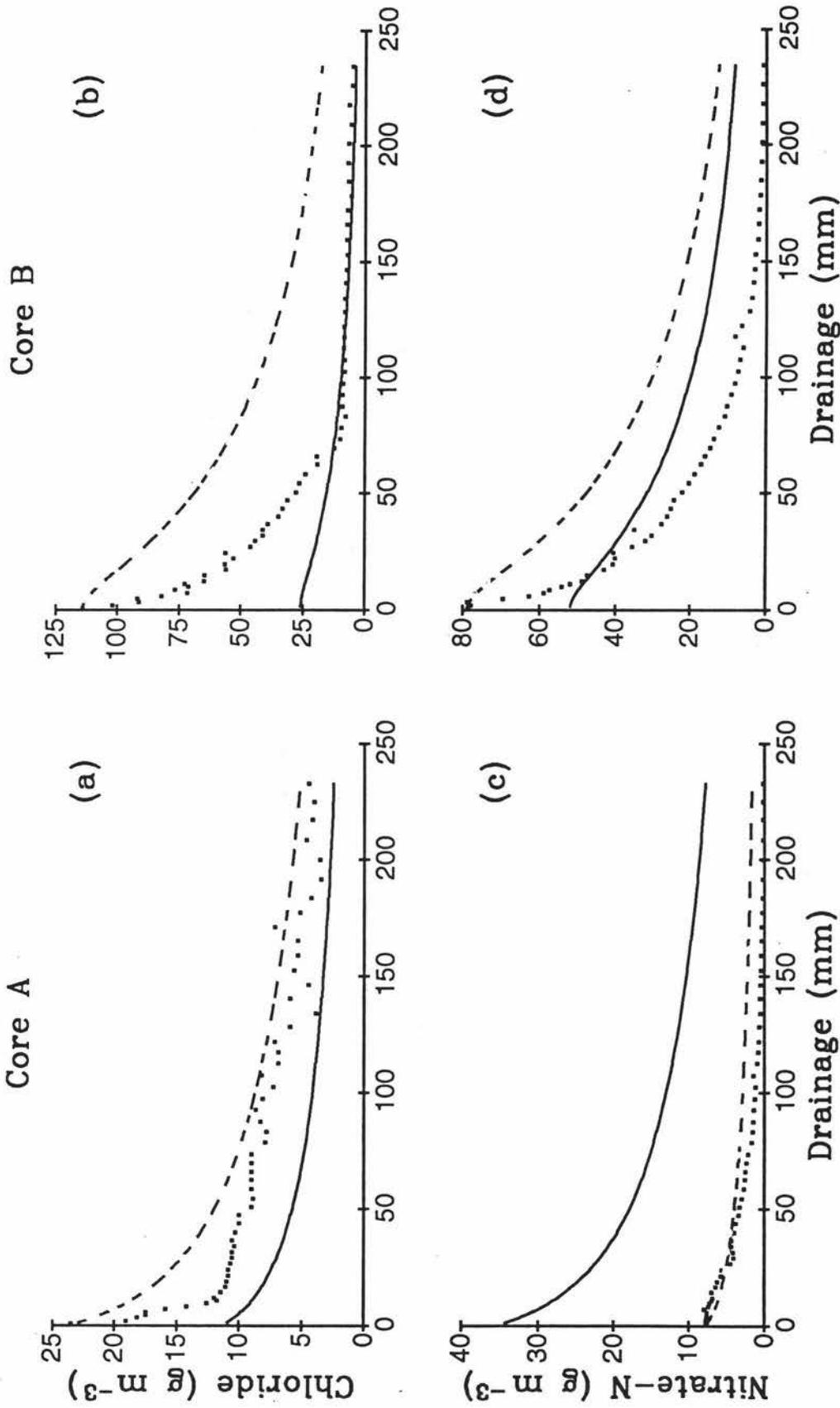


Fig. 4.2. Measured and predicted concentrations of resident chloride (a and b) and nitrate (c and d); measured (■), predicted using the estimated soil solution concentration (—), and predicted assuming  $C_1$  as the concentration in first effluent sample (---) for cores A and B

For both cores A and B it appeared that chloride did not leach out as fast as would be predicted using the chloride concentration in the first effluent, but it leached out faster than would be predicted from the mean chloride concentration in the soil solution for the whole core. This suggested non-uniform chloride distribution has an effect on predictability of leaching losses. Chloride concentration in the transport volume appeared to be higher than the estimated mean chloride concentration for the whole core for the whole of experiment for core A, but for the first 70 mm drainage only for core B.

From Figure 4.2 (c) and (d) the effects of bypass flow were more obvious for nitrate. For core A, loss of nitrate was greatly overestimated when the estimated mean nitrate concentration in the whole core was used while the initial concentration in the effluent was satisfactory for modelling the effluent curve. For core B, use of the concentration in the first effluent volume overestimated leaching loss (as for chloride); and using the estimated concentration of nitrate in the whole core also overestimated leaching loss, except for the first 20 mm or so of drainage. In this case the concentration of nitrate in the transport volume seemed to be lower than the estimated average concentration in the whole core.

The skewed distribution for the pdf of travel pathways obtained with this soil (see Figs 4.3 a and b) and with other structured soils in an undisturbed state (White *et al.*, 1986; Dyson and White, 1987; White, 1989) suggested the possibility of substantial bypass flow. In this situation, if the concentration of the resident solute of interest is not uniform within the transport and non-transport volumes, predictions based on an average solute concentration for the whole soil volume may not accurately follow the measured concentrations in the effluent (White, 1989; White and Magesan, 1991).

The chief problem seems to be in obtaining an accurate estimate of the initial nitrate concentration in the transport volume of the soil. As discussed in section 3.5.1 a great variability in soil nitrate concentration on a macroscale was observed. Also evidence for differences in nitrate concentration on a microscale i.e. between the interior and exterior of aggregates within each large core were possible and have been observed in other studies (White, 1985).

As explained in Chapter 3, the estimated mean concentration of chloride and nitrate for core B might be wrong because the site used for taking the undisturbed soil core was thought to be an urine spot (note the very high soil nitrate and chloride concentrations). However, that does not solve the problem for core A where there is no evidence of concentration by urine. So as explained earlier, non-uniform distribution of solutes could be the most probable reason for the discrepancy between measured and predicted effluent concentrations. This suggests that a better prediction could be obtained for a soil having a uniform initial distribution of resident solute.

The main conclusions from this experiment are (1) it is difficult to predict the leaching of resident solutes if the initial soil solution concentrations are not exactly known, (2) there is conflicting evidence as to whether the concentration of solute in the first effluent enables a reasonable prediction of the leaching losses of a resident solute to be made and (3) the estimation of resident solute concentrations in soil solutions under grazed pastures using point sampling techniques may not be reliable.

#### 4.4.2. Experiment 2

##### 4.4.2.1. *Using bromide breakthrough curves to characterize solute pdfs*

The pulse input method is preferable to the step-change in input method for obtaining the solute pdf (Jury and Roth, 1990). The bromide pulse efflux data were fitted to equation (4.6) as described in section 4.3. Figures 4.3 (a) and (b) show the fitted and measured effluent concentrations for cores C and D as a function of cumulative drainage. The simulation was excellent for core D and gave parameter values of  $\mu = 3.943$  and  $\sigma = 0.696$  for the bromide pdf. However, the simulation for core C was not as satisfactory ( $\mu = 3.898$  and  $\sigma = 1.879$ ), particularly after 60 mm drainage. Both have almost the same median travel time but core C has a much larger variance, indicating a more skewed pdf. However, the breakthrough data for core C could be interpreted as showing two peaks - one at c. 25 mm drainage and the other a much broader peak at c. 60-100 mm drainage. The early sharp peak could be due to transport of bromide ions through a minor part of the transport volume which might have transported the ions quickly, whereas flow through the rest of the transport volume could have caused the second wider peak. For cores of similar length and initial water content at the same input rate, those two soils represented

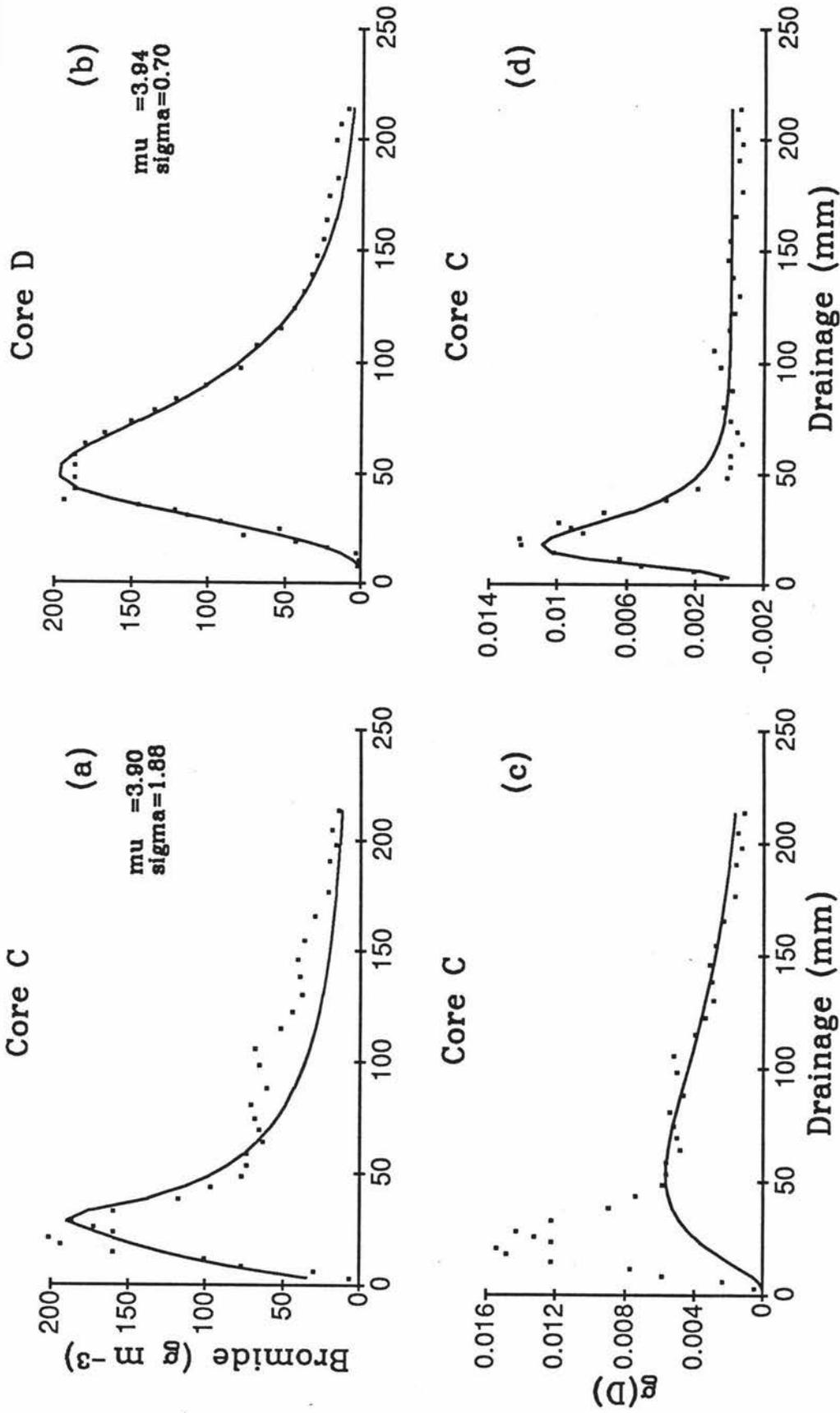


Fig. 4.3. Measured ( $\blacksquare$ ) and fitted (—) bromide concentrations (a and b) for cores C and D. Also shown are the measured ( $\blacksquare$ ) and resolution of the components of bromide pdf (—) for core C (c and d)

different breakthrough behaviour for bromide. The differences could be ascribed to differences in the geometry of the conducting channels, which determines the distribution of pore water velocities. Similar observations had been made by White *et al.* (1986) for bromide pulse inputs to mole drains in the field and with undisturbed cores in the laboratory (Beven and Young, 1988).

The pdf for core C could be thought of as a composite of two density functions representing two populations of travel pathlengths, with modal values of  $I$  around 25 and 75 mm, respectively. Thus one way of addressing this problem is to decompose the pdf into two functions. The first can be obtained by fitting a lognormal function to the tail of the breakthrough curve (Figure 4.3 c). The fitted values of this function are then subtracted from the measured values of  $f(I)$  at the appropriate values of  $I$  and the residuals fitted with a lognormal function (Figure 4.3 d). The solid lines in Fig. 4.4 (a) represents the integrals of the component lognormal functions for all values of  $I$ . The labels "early" and "late" indicate that the integrals were obtained by fitting lognormal functions for the early and the tail part of the breakthrough curves (Fig 4.3 c and d). Fig. 4.4 (b) shows the summing of these integrals to give a pdf (dashed line) and the best-fitting of the resultant curve (solid line) which produced the parameters  $\mu = 3.99$  and  $\sigma = 0.93$ . Note that compared with the first estimates of  $\mu$  and  $\sigma$  above, the centre of location of the pdf now occurs at a larger value of  $I$  but the variance, and hence the inferred dispersion of the solute, has markedly decreased.

#### 4.4.2.2. *Modelling the leaching of resident tritium*

As explained in Chapter 3, a pretreatment with tritiated water was carried out in the laboratory to create a uniform distribution of tritium in the soil solution. The parameters obtained from the bromide pulse data were used to model the subsequent leaching of this resident tritium. Figure 4.4 (c) and (d) show the predicted and measured relative concentration of tritium as a function of cumulative drainage for cores C and D. In both cases, the simulated concentrations were less than the measured values and the amount of resident  $^3\text{H}$  leached was underestimated. This is consistent with an anionic tracer such as Br being excluded, because of charge effects, from part of the water-filled pore volume that was accessible to  $^3\text{H}$  (Corey *et al.*, 1963; White *et al.*, 1984).

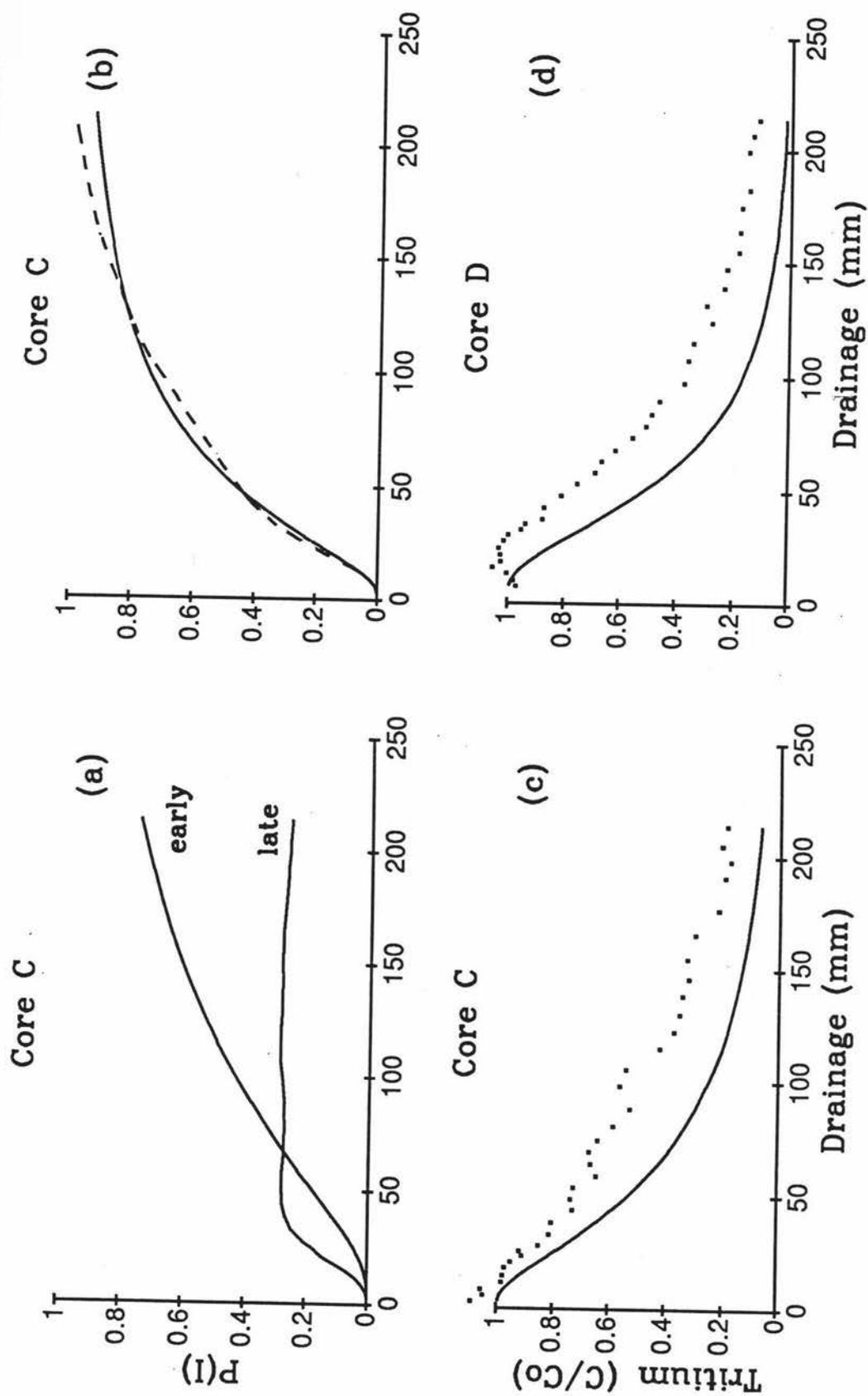


Fig. 4.4. Details for (a) and (b) are given in the text. (c) and (d) show the predicted using parameters derived from the bromide pdf (—) and measured (•) and measured (■) relative concentrations of resident tritium in the drainage from cores C and D

### 4.4.3. Experiment 3

#### 4.4.3.1. *Using tritium and chloride BTCs to characterize solute pdfs*

In this experiment considerable care had been taken to create a uniform distribution of chloride through the soil volume immediately before the soil cores were collected (see Chapter 3). Figures 4.5 (a) and (b) show the plots of the measured and fitted (using equation 4.5) relative concentration of tritium as a function of cumulative drainage for cores E and F in the first phase of the experiment. Figures 4.5 (c) and (d) are similar plots for chloride in the second phase of the experiment. The tritium pdf for core F was more highly skewed than for core E, with a shorter median pathlength and a greater variance. This difference is also evident in the second half of the experiment with chloride, although the variances are smaller. The values of  $\mu$  and  $\sigma$  for the best fitted data are shown on Figure 4.5.

Breakthrough curves for chloride and tritium were markedly asymmetric and unlike those reported for columns of packed aggregates (Elrick and French, 1966). The volumetric water content of the cores while applying tritium was different from when chloride was applied. This was because tritiated water was applied in the first phase to the soils taken from the field, whereas chloride was applied soon after the conclusion of tritiated water application. The flow in all cases was largely unsaturated. The relative concentration of chloride approached 1.0 earlier than for tritium. The reasons could be due to anion exclusion of chloride and the different flow rates at which tritium (5 mm/hr) and chloride (3 mm/hr) were applied.

#### 4.4.3.2. *Modelling the leaching of resident chloride and nitrate*

Figure 4.6 (a and b) shows that in the first phase of the experiment the efflux of the resident chloride was well modelled by the parameters derived from the tritium breakthrough when the estimated mean chloride concentration in each core was used as the initial soil solution concentration. This can be attributed to the uniform distribution of chloride in the soil solution initially, the reasons for which were explained in Chapter 3. However, this result contrasts with what was found for nitrate, where use of the estimated mean concentration seriously overestimated the efflux of nitrate (Figs. 4.6 c and d). Measurements of nitrate concentration made by extracting the whole soil volume overestimated the concentration in the transport

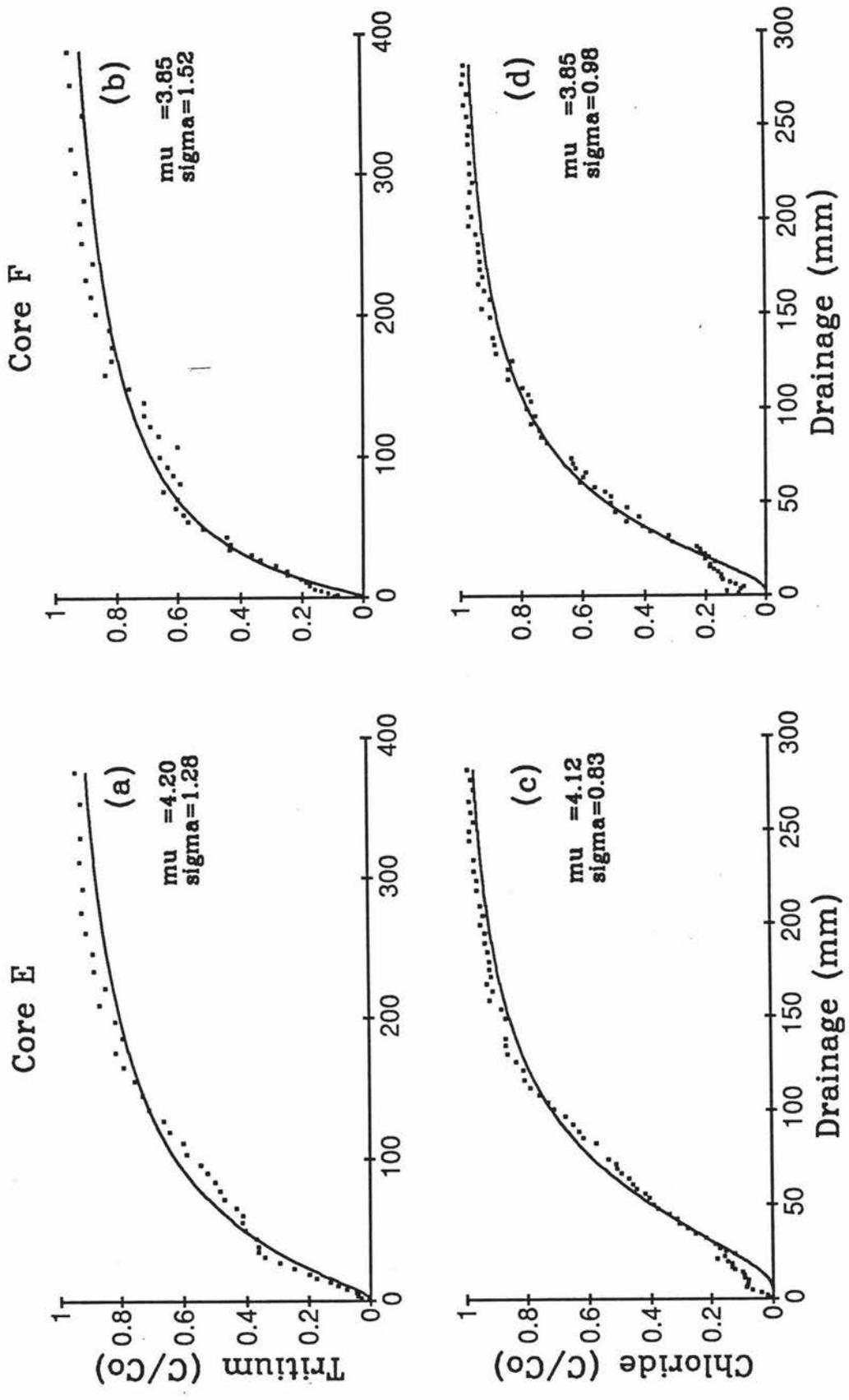


Fig. 4.5. Measured (■) and fitted (—) relative concentration of tritium (a) and (b) in the first part of the experiment; and chloride (c) and (d) in the second part of the experiment for cores E and F

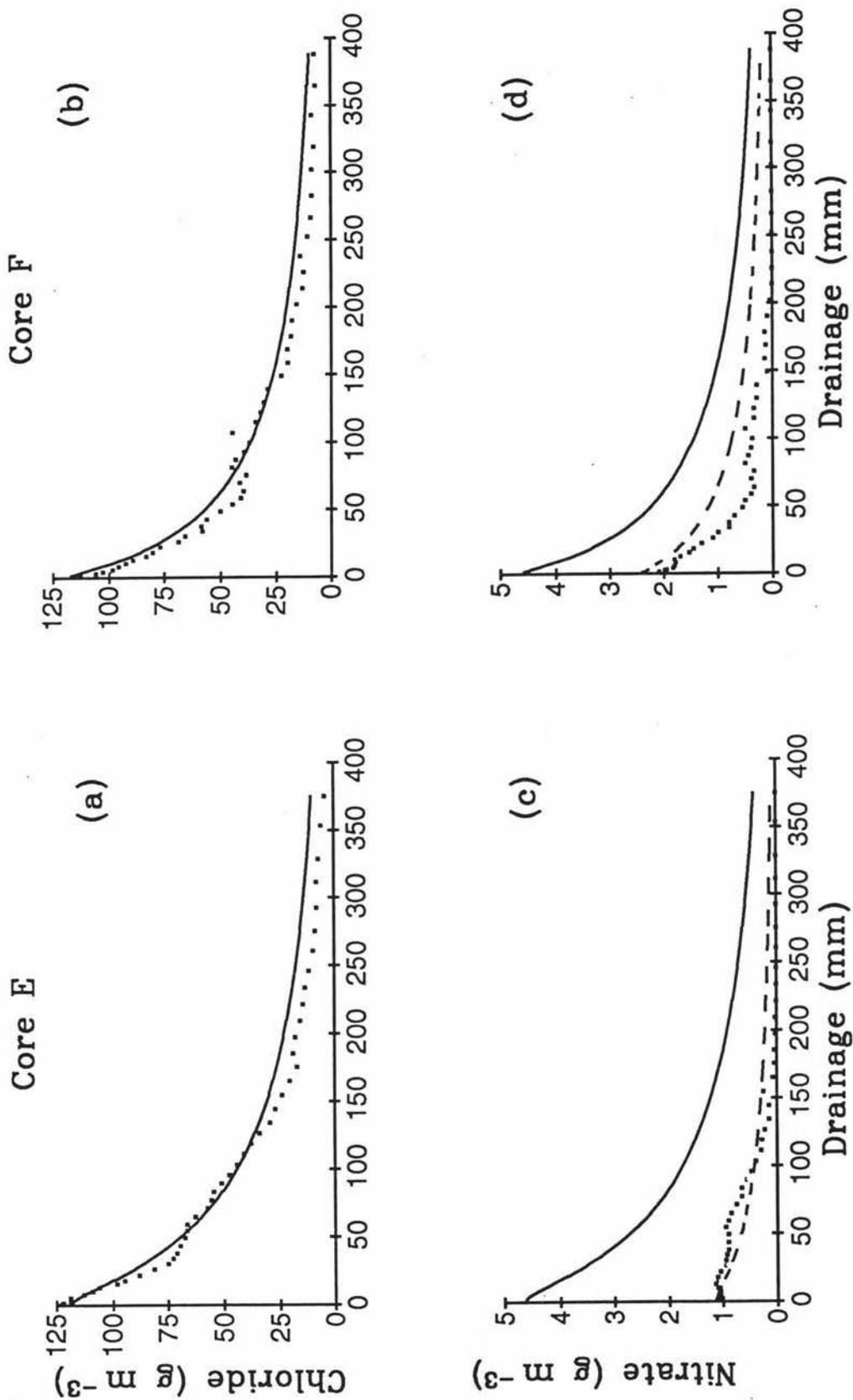


Fig. 4.6. Measured and predicted concentrations of chloride (a) and (b) and nitrate (c) and (d) for cores E and F; measured ( $\blacksquare$ ), predicted with the estimated soil solution concentration (—), predicted assuming  $C_i$  from the concentration in first effluent (---)

volume, which was only a small fraction of the total water volume in the soil. However, assuming the concentration of nitrate in the first effluent sample to represent the concentration in the transport volume initially resulted in a much better prediction of the effluent nitrate concentration. Similar results were obtained by White (1989). The slight overprediction of nitrate loss from core F may have been the result of some denitrification in this core during the experiment, which reduced the nitrate concentration in the transport volume more than expected (White and Magesan, 1991).

It appears that the nitrate concentration in the transport volume of cores E and F was lower than suggested by the estimated mean concentration in the whole core. Indigenous nitrate present in the transport volume would have been flushed out during preliminary leaching in the field with chloride solutions (Chapter 2). However nitrate which remained within the aggregates was removed from the transport pathways during the subsequent leaching in the laboratory.

#### 4.4.3.3. *Modelling the leaching of resident tritium*

Either the parameters derived from the step-change input of chloride, or the square-pulse input of nitrate in the second part of the experiment, could be used to model the tritium efflux. However, it might be expected that the chloride or nitrate could be excluded from some of the pore volume accessible to tritium, due to anion exclusion and slower diffusion. Tritium would then behave somewhat differently to nitrate and chloride. If the mass balance of each of these applied solutes is known, then the parameters from any applied solute can be used to model the movement of another. If there is uncertainty about the mass balance, as in the case of nitrate which undergoes biological transformations such as denitrification, it is advisable to use the parameters from a conservative solute such as chloride. In this case values derived from chloride transport are used.

Figures 4.7 (a) and (b) show the predicted and measured relative concentration of the tritium. The model slightly underestimated tritium in the effluent solution (and hence underestimated the rate of tritium loss). The difference could be due to different diffusion rates. Similarly Figures 4.7 (c) and (d) show the predicted and measured

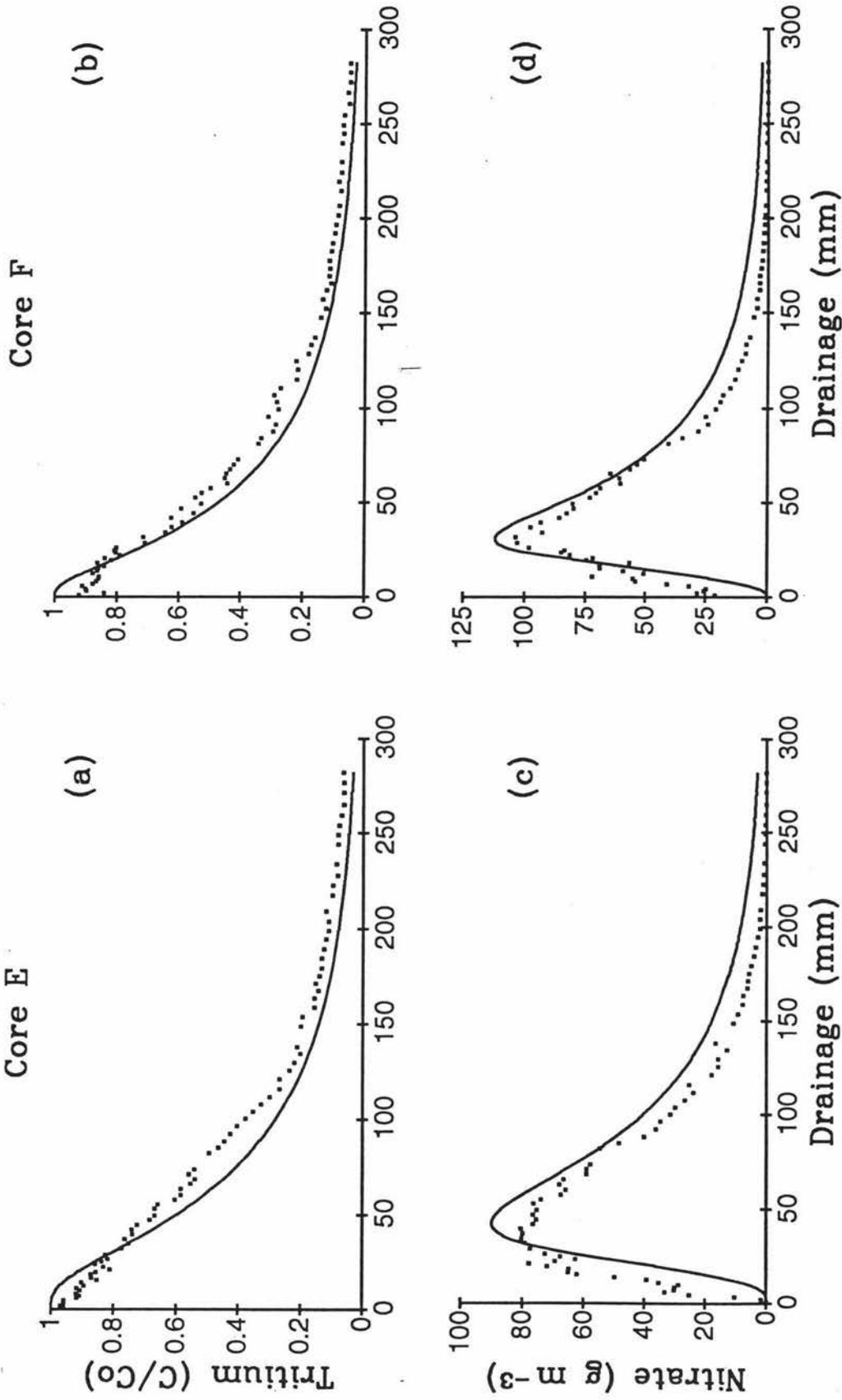


Fig. 4.7. Measured (■) and predicted (—) concentration of tritium (a) and (b) and nitrate (c) and (d) in the effluent during the second part of the experiment. The prediction was carried out with parameters derived from a step input of chloride during the second part of the experiment

concentration of nitrate in the effluent following the pulse applied in the second phase of the experiment. It can be observed that for both cores the prediction curve fits the data reasonably well. However the fit was not that good at the tailing end.

Some of the important conclusions from this experiment were

- (1) The breakthrough curves for chloride and tritium were different, perhaps due to anion exclusion (for chloride) and different flow rates;
- (2) It was possible to model the leaching of resident chloride well using parameters derived from a step input of tritium to the soil surface. This was attributed to the uniform distribution of chloride in the soil solution before leaching. However, the same parameters could not predict the leaching of resident nitrate well. The reason could be due to difficulty in estimating the appropriate concentration of nitrate in the "transport volume";
- (3) The parameters derived from a chloride step-change input were used successfully to estimate leaching of resident tritium and surface-applied nitrate.

#### 4.4.4. Estimation of model parameters

The model parameters  $\mu$  and  $\sigma$  for both step-change input and pulse input of externally applied solutes were estimated using the optimization program for equations 4.5 and 4.6, respectively. Tables 4.1 and 4.2 give the details on the cores used, external solute applied, rate of application and the estimated model parameters for step-change and pulse inputs, respectively.

From Table 4.1 it can be observed that the median travel pathlength for both tritium and chloride were similar. However, tritium had larger variances when compared to chloride. This might indicate that tritium had access to a greater range of pore sizes than the chloride ion which would be affected by anion exclusion. Similarly, the median travel pathlengths for bromide and nitrate applied as pulse inputs were almost the same. While the variances for nitrate in both cores were almost the same, they were quite different for bromide. This was mainly due to the different breakthrough curves obtained, and in particular, the suggestion of a bimodal pdf for bromide in core C.

*Step-change input*

Table 4.1. Model parameters for step-change input solutes

Cores	Solute applied	Flow rate (mm/hr)	$\mu$	$\sigma$
A	Tritium	5	3.963	1.936
B	Tritium	5	4.248	1.215
E	Tritium	5.3	4.198	1.278
F	Tritium	5.1	3.850	1.521
E	Chloride	3.4	4.123	0.830
F	Chloride	3.4	3.847	0.976

*Pulse input*

Table 4.2. Model parameters for pulse input solutes

Core	Solute applied	Flow rate (mm/hr)	$\mu$	$\sigma$
C	Bromide	4	3.989	0.926
D	Bromide	4	3.943	0.696
E	Nitrate	3.4	4.103	1.111
F	Nitrate	3.4	3.948	1.164

#### 4.4.5. Estimation of the solute transport volume

The solute transport volume for each core was estimated using the model parameters of Tables 4.1 and 4.2 for a step-change input and pulse input, respectively, of each solute. Tables 4.3 and 4.4 give the details of the cores, solute applied, estimated pathway length (both mean and median), and estimated fractional transport volume for step-change input and pulse input of solutes, respectively.

Some of the observations from Table 4.3 are (1) in general, mean pathway length and mean transport volume were greater than the median pathway length and median transport volume, (2) tritium had a longer mean pathway length and higher mean transport volume compared to chloride, although the median pathway lengths were reasonably comparable, and (3) the mean pathway length for tritium in core A was much greater than expected. Note the single pdf fitted to the tritium data for core A is not a very good fit. This was mainly because the variance for core A was very high. This suggests that the median travel pathway length is more appropriate to calculate the transport volume than the mean (Dyson and White, 1987).

Similar observations could also be made from Table 4.4 (pulse input data). Here, bromide in the two cores behaved differently for the mean pathway length and hence mean transport volume, whereas the median travel pathway lengths agreed very closely. Furthermore,  $\theta_{st}$  estimated from the median pathway length for nitrate was very similar to that for bromide, but  $\theta_{st}$  estimated from the mean pathway lengths were different. The bromide mean pathway length for core C was higher than expected. This was probably because of the bimodal distribution of travel pathways and higher variance in this core.

#### 4.5. CONCLUSIONS

A number of important conclusions were derived from the results presented in this chapter. They were :

- (a) Prediction of leaching losses of resident solutes can be difficult if the initial soil solution concentration is not exactly known.

*Step-change input*

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

Core	Solute applied	Pathway length (mm)		Transport volume $\theta_{st}$	
		Mean	Median	Mean	Median
A	Tritium	343	53	1.37	0.21
B	Tritium	146	70	0.59	0.28
E	Tritium	151	67	0.60	0.27
F	Tritium	149	47	0.60	0.19
E	Chloride	87	62	0.35	0.25
F	Chloride	75	47	0.30	0.19

*Pulse input*

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

Core	Solute applied	Pathway length (mm)		Transport volume $\theta_{st}$	
		Mean	Median	Mean	Median
C	Bromide	83	54	0.33	0.22
D	Bromide	66	52	0.26	0.21
E	Nitrate	112	61	0.45	0.24
F	Nitrate	102	52	0.41	0.21

- (b) The concentration of solute in the first effluent might be used to give a reasonable estimation of the initial concentration of resident solutes in the soil, especially for nitrate. A similar observation was made by White (1989).
- (c) Estimation of resident solute concentrations in the soil solution under grazed pastures by soil sampling may not be reliable and may be subject to large errors because of the variable input of dung and urine.
- (d) Breakthrough curves for chloride and tritium were different, possibly due to anion exclusion (for chloride) and different flow rates.
- (e) Leaching of resident chloride for a soil pretreated with chloride solution was well modelled using tritium parameters. However, the same parameters did not predict nitrate leaching well and that could be due to difficulty in estimating the appropriate concentration of nitrate in the soil.
- (f) Chloride parameters from a step-change input were used successfully to estimate leaching of resident tritium and surface-applied nitrate.
- (g) The median, not mean, travel pathway length was more appropriate to calculate the solute transport volume (Dyson and White, 1987).

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

**5.1. INTRODUCTION**

In this chapter rainfall, evapotranspiration and soil moisture data from the field experiment are given. Also solute concentration measurements in soil, suction-cup and herbage samples are presented and discussed.

As outlined in Chapter 1 the objective of the experiments was to measure the leaching of indigenous soil nitrate and chloride under field conditions. Bromide was used as a tracer for the movement of water and indigenous soil solutes. As described in Chapter 2, NaBr at a rate of 200 kg Br/ha and urea at a rate of 120 kg N/ha were applied on 29 May 1990 to paddocks A and B, respectively. Urea was also applied on 13 September 1989 at a rate of 50 kg N/ha to both paddocks. The effect of fertilizer N on soil mineral N concentrations ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) was assessed by regular core sampling to mole drain depth; also samples of soil solution were obtained from suction cup samplers. Soil samples were analysed for bromide and chloride as well as inorganic N.

**5.2. RAINFALL AND POTENTIAL EVAPOTRANSPIRATION DATA**

The quantity of drainage that occurs during a drainage period can be estimated from the amount of rainfall and evapotranspiration that occurred and some assumptions about soil water storage. Thus rainfall and evaporation data are relevant to this study.

The amounts of rainfall received during the months of September and October 1989 were 25 and 123 mm, respectively. Only these two months in 1989 were relevant to the study of nitrate leaching. Monthly rainfall for 1990 and 1991, together with the long term averages (obtained from the New Zealand Meteorological Service) for 1990 and 1991 is shown in Fig. 5.1. Rainfall was unevenly distributed although the

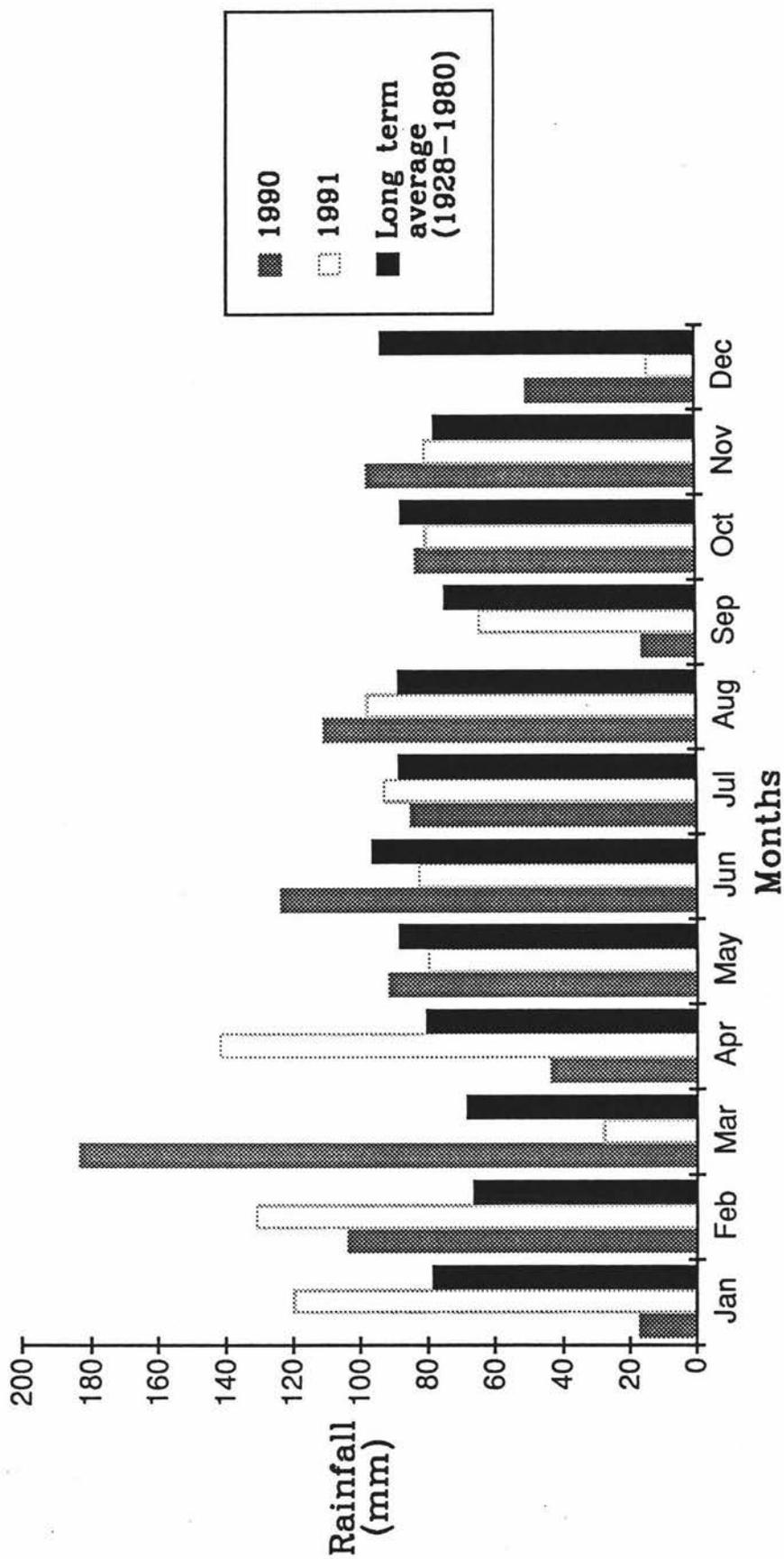


Fig. 5.1. Monthly rainfall, together with the long term average, for 1990 and 1991

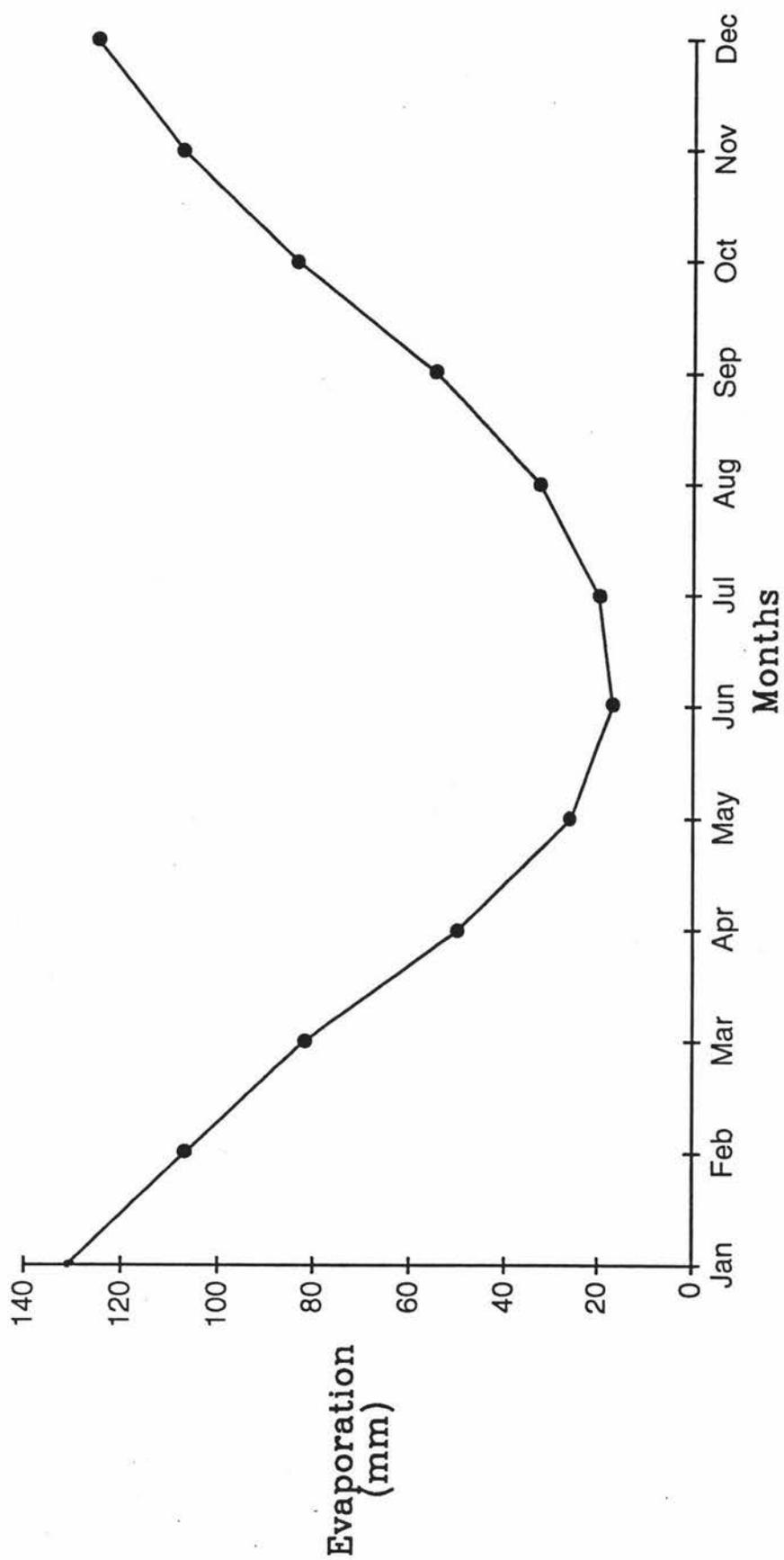


Fig. 5.2. Penman longterm evapotranspiration data (NZ Meteorological Service)

total rainfall received during 1990 and 1991 was similar, being 1014 and 1007 mm, respectively. The long term average annual rainfall in Palmerston North is 995 mm.

Long term average monthly Penman "potential" evaporation is shown in Figure 5.2. Comparing Figures 5.1 and 5.2, the winter excess of rainfall over evaporation is evident.

### **5.3. SOIL MOISTURE DATA**

The mean volumetric water contents measured at the various soil samplings during 1990 and 1991 are given in Figures 5.3, 5.4 and 5.5. They were calculated from the measured gravimetric water contents and the bulk density profile. The bulk density values at different depths of Tokomaru silt loam soil were taken from earlier published data of Scotter *et al.* (1979) and Bramley (1989). The soil moisture contents at each sampling were comparable for paddocks A and B throughout the experimental period, except for the values in the top two layers (0 - 50 mm and 50 - 150 mm depths) of paddock B always being greater than paddock A. The soil dries out over summer when potential evapotranspiration is higher than the rainfall. April-May is usually the recharge period. The soil is usually near 'field capacity' from June to September.

### **5.4. SOLUTE CONCENTRATIONS IN SOIL**

#### **5.4.1. Bromide**

The distribution of bromide in the soil at different times during the 1990 drainage period is shown in Figures 5.6 and 5.7. The samples from the first and second soil samplings (5 April and 28 May 1990) were not analysed for bromide on the assumption that there was no bromide in the soil before sodium bromide application. By 29 June 1990, a month after bromide application on 29 May 1990, most of the bromide had moved below 200 mm (Figure 5.6). At the next soil sampling the concentration of bromide at all depths except 0-50 mm had decreased compared to the previous sampling. This could be because bromide immediately under the grass leaves or stems has less opportunity to get leached (Scotter and Kanchanasut, 1981).

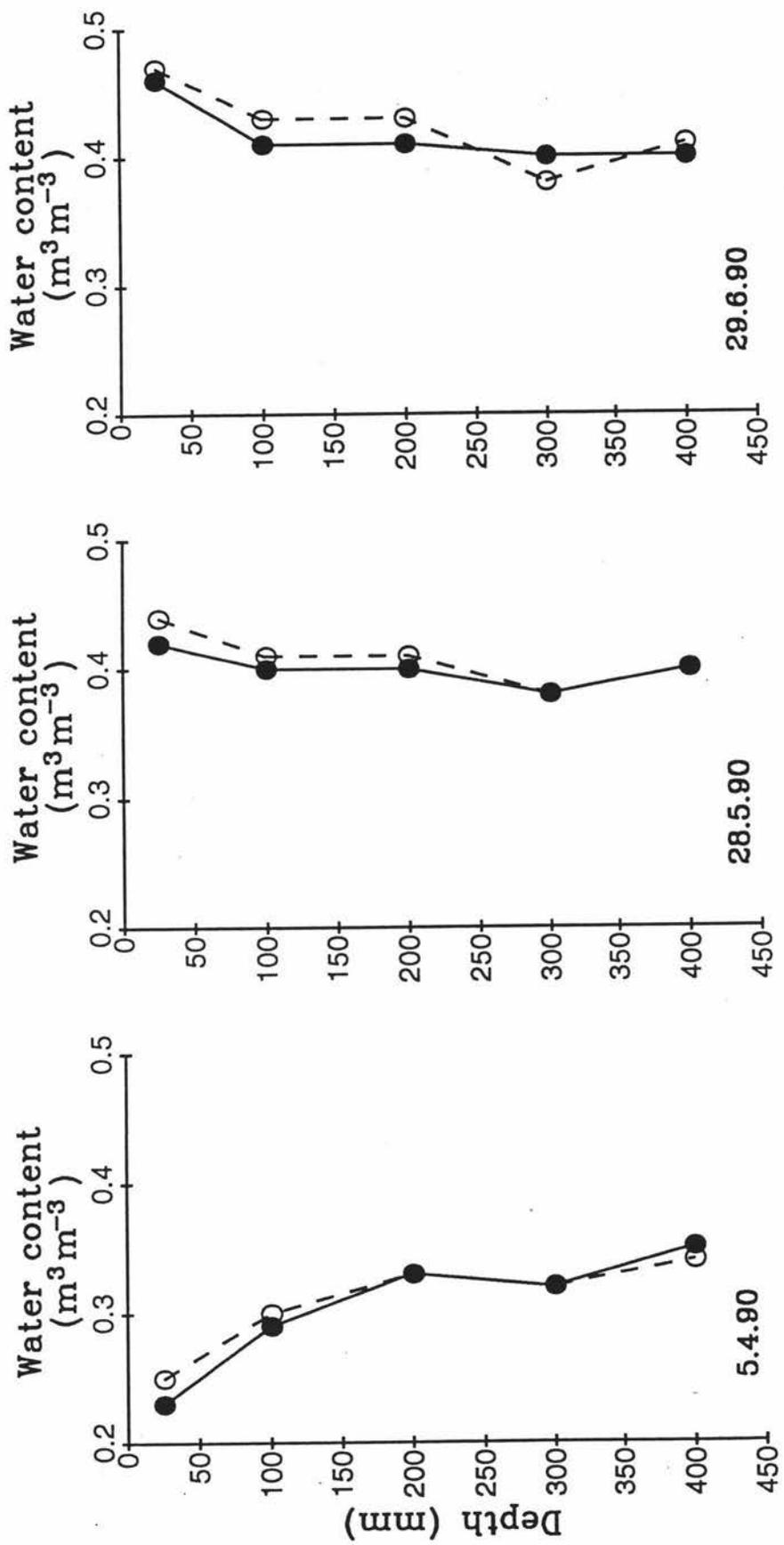


Fig. 5.3. The mean volumetric water content profiles for the first three soil samplings in 1990 for paddocks A (●) and B (○)

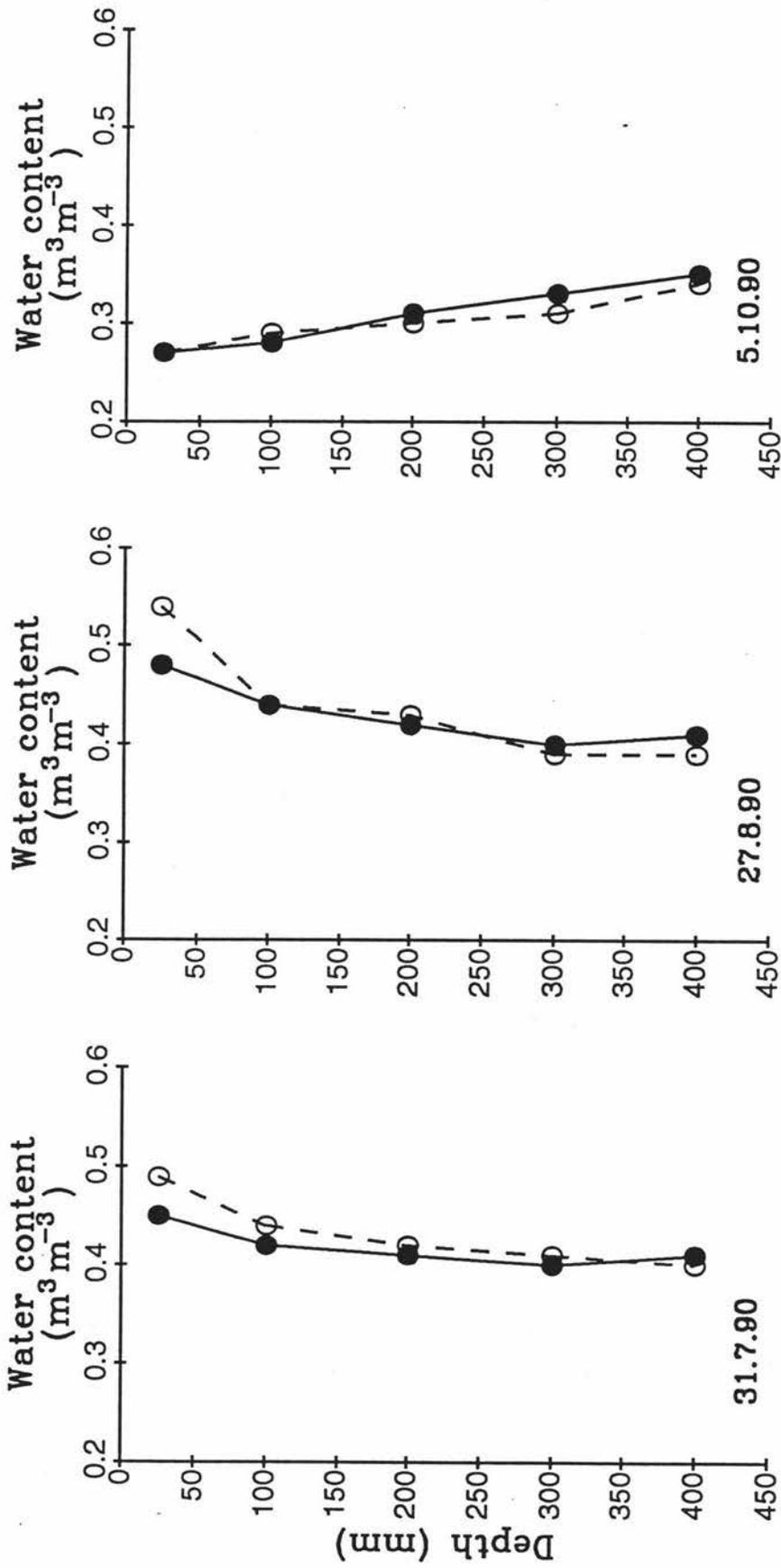


Fig. 5.4. The mean volumetric water content profiles for the last three soil samplings in 1990 for paddocks A (●) and B (○)

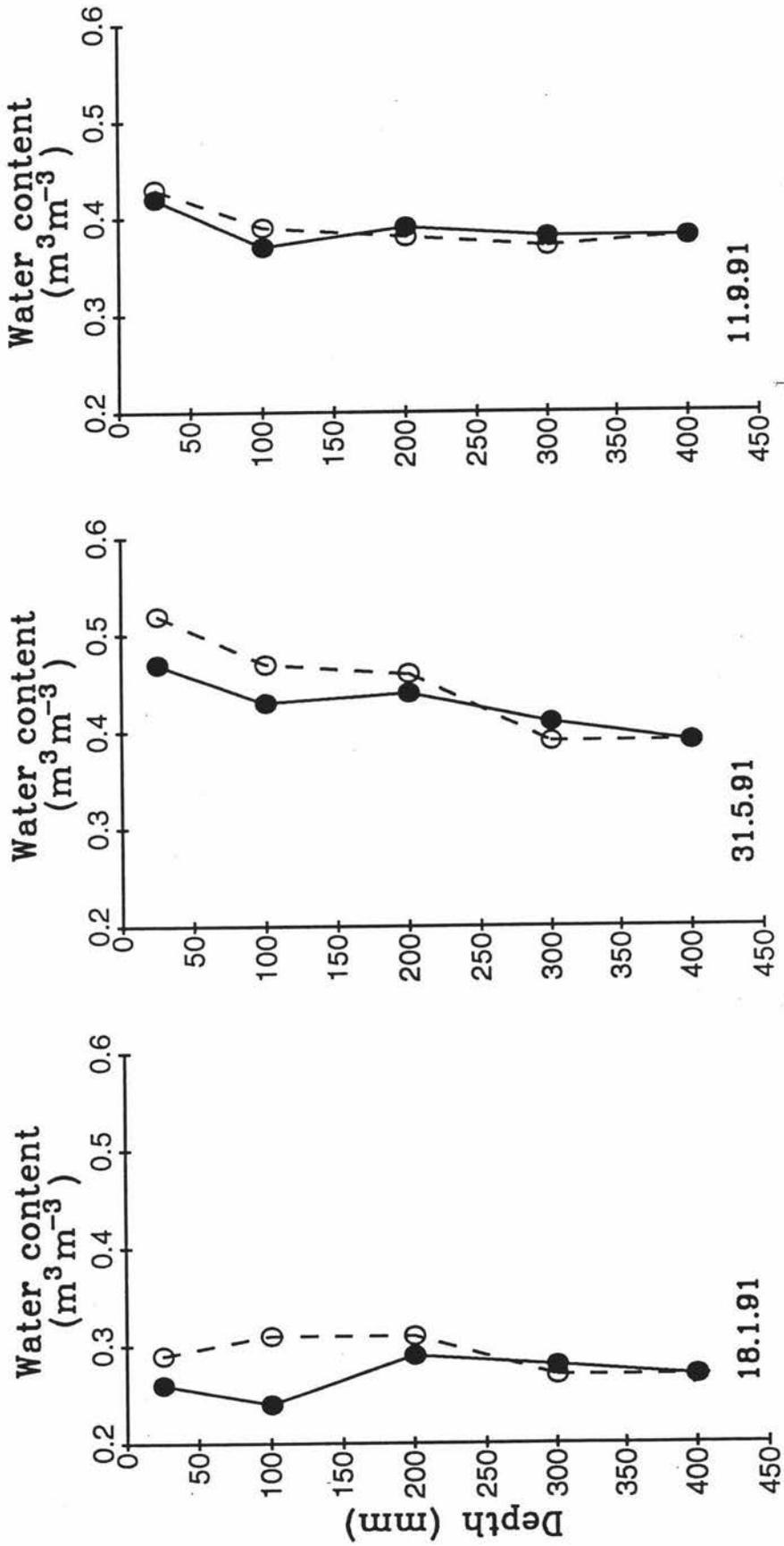


Fig. 5.5. The mean volumetric water content profiles for three soil samplings in 1991 for paddocks A (●) and B (○)

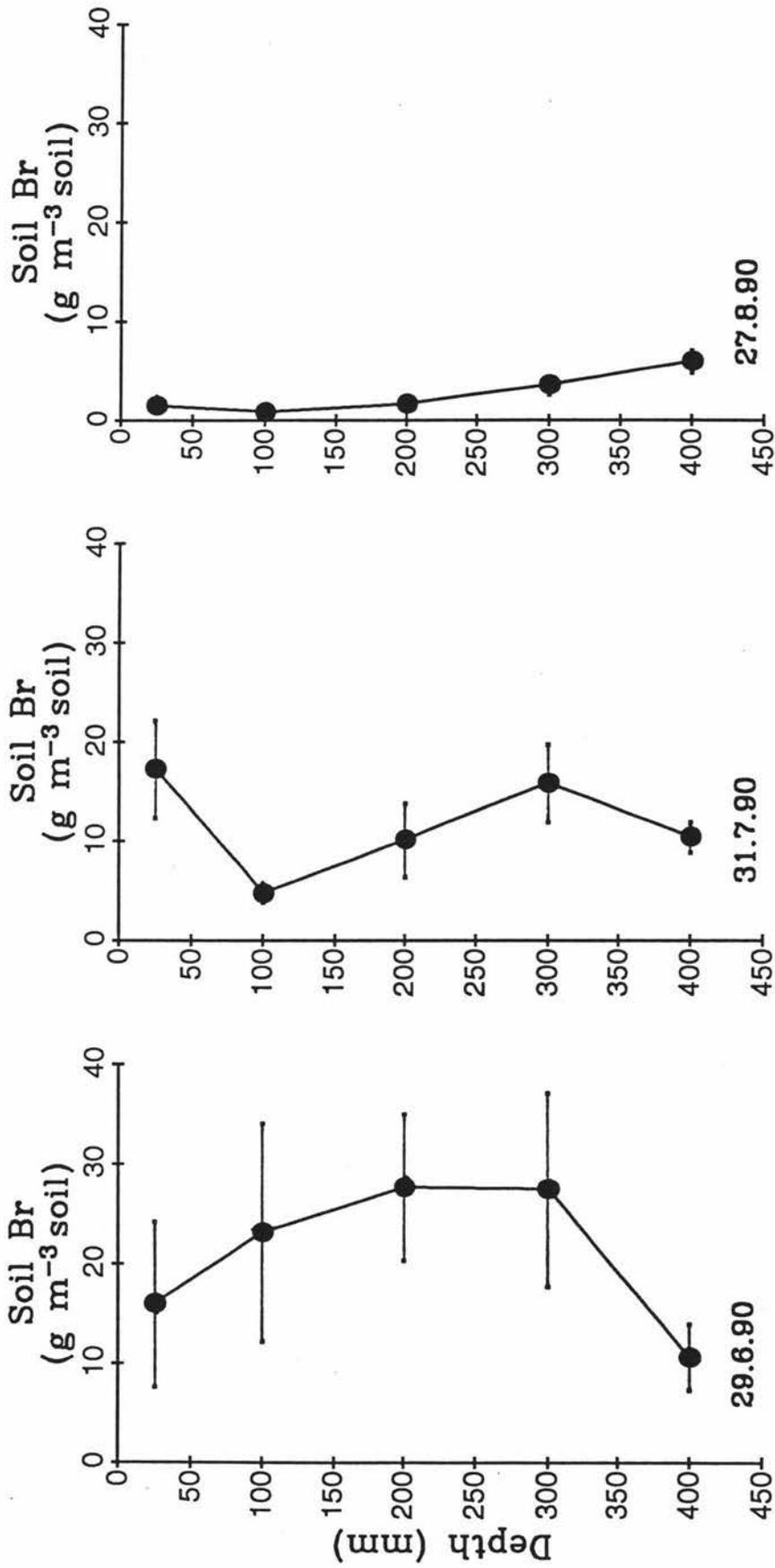
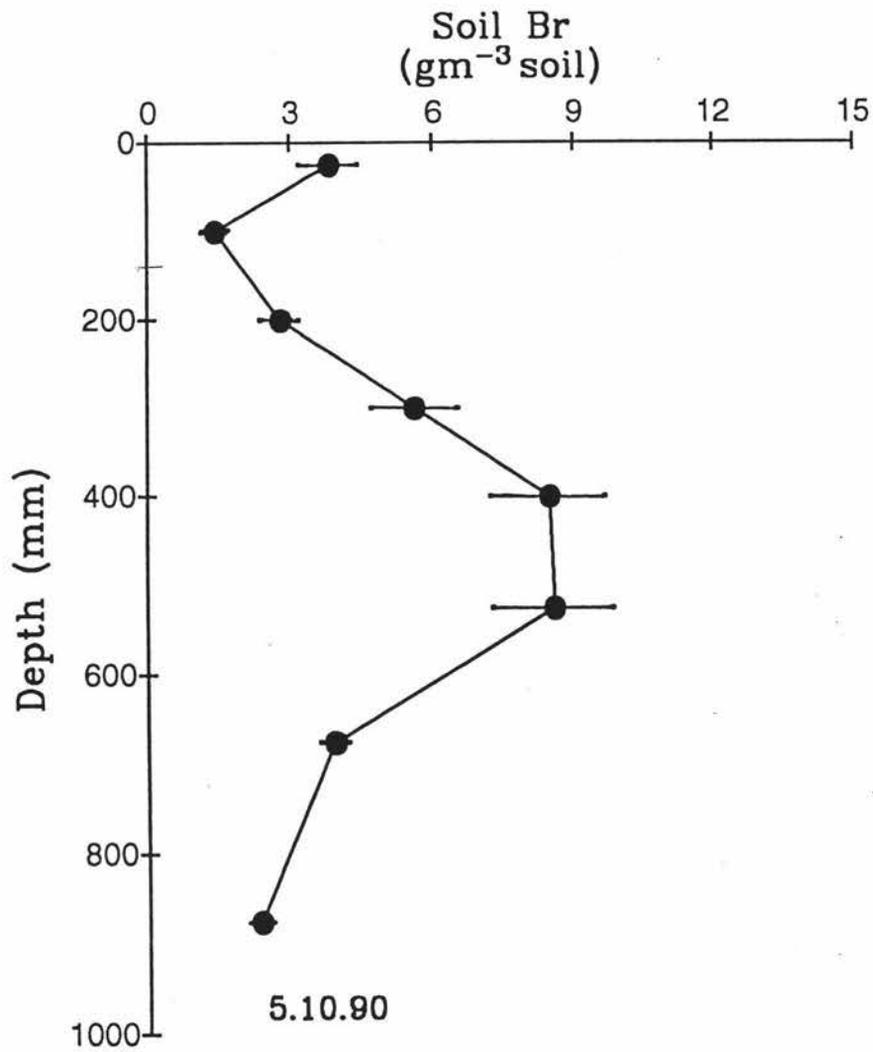


Fig. 5.6. The distribution of bromide in the soil profile of paddock A in 1990 for the first three soil samplings after Br application (means and standard errors are shown)



**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)

By the next soil sampling on 27 August 1990 the concentration of bromide in the soil had decreased even further.

The soil samples were taken down to a depth of 1 m (Figure 5.7) in the final soil sampling on 5 October 1990. The purpose of such deep sampling was to estimate deep percolation of bromide below mole drain depth. A total of 45 kg Br/ha was recovered in the top metre of soil, and 25 kg Br/ha (12.4 % of the applied bromide) was recovered from below mole depth. Some bromide probably went below 1 m. Pollok (1975) observed extensive root growth between the structural soil units in the impermeable B horizon (approximately 300 mm - 700 mm depth) and the fragipan (about 700 mm), and suggested that the cavities left by these roots would allow some water and hence solutes to move through the fragipan in Tokomaru silt loam. The concentration of bromide in the soil was highest around mole depth (350 - 650 mm).

#### 5.4.2. Chloride

The paddocks exhibited similar initial soil chloride concentrations with concentration decreasing with depth. The concentration of chloride in the soil decreased, in general, as the 1990 drainage season progressed (Figures 5.8 and 5.9). The concentration of chloride in rainfall was around 4 g m<sup>-3</sup>. Similar observations were made by Scotter *et al.* (1991) at the same site during 1989. Whether the concentration of chloride in soil increases or decreases is determined by the balance between rainfall input and leaching. There was 136 mm of rain between 5 April and 28 May. It was the period of soil rewetting. The chloride distributions with depth was more uniform at the 28 May sampling; apparently some chloride had moved from the surface layers to lower in the profile. At the next soil sampling (29 June 1990) chloride concentration increased with depth indicating the downward movement of chloride due to rainfall. On 31 July, the chloride concentration in the surface layer increased in both paddocks, probably due to an input of chloride in the urine of the grazing sheep. However, at the next soil sampling, which was carried out soon after "unplanned" grazing (section 5.5), no increase in concentration in the surface layer was apparent. Similar low soil chloride concentrations were also observed on 5 October 1990.

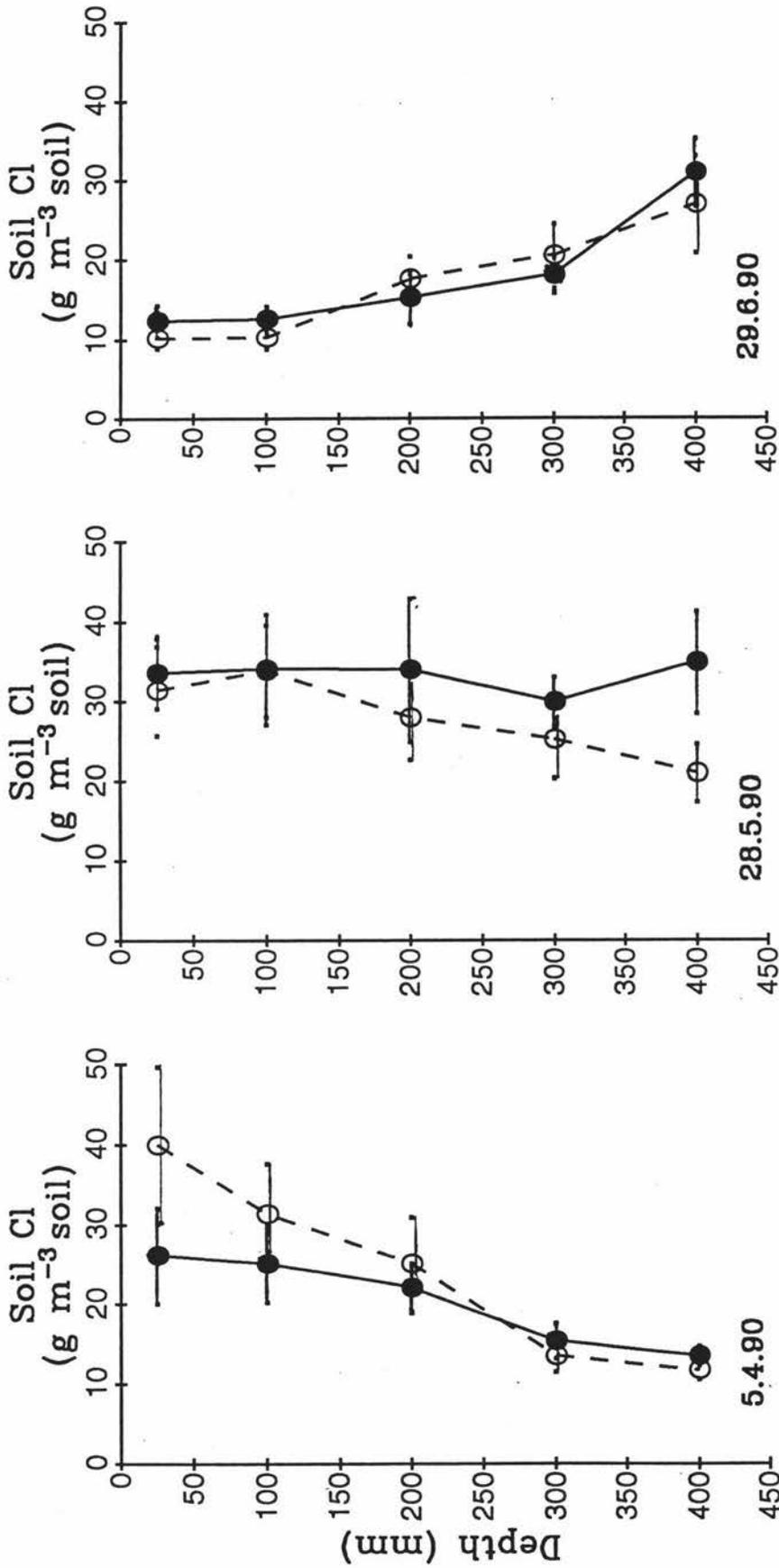


Fig. 5.8. The distribution of chloride in the soil profiles of paddocks A (●) and B (○) in 1990 for the first three soil samplings (means and standard errors are shown)

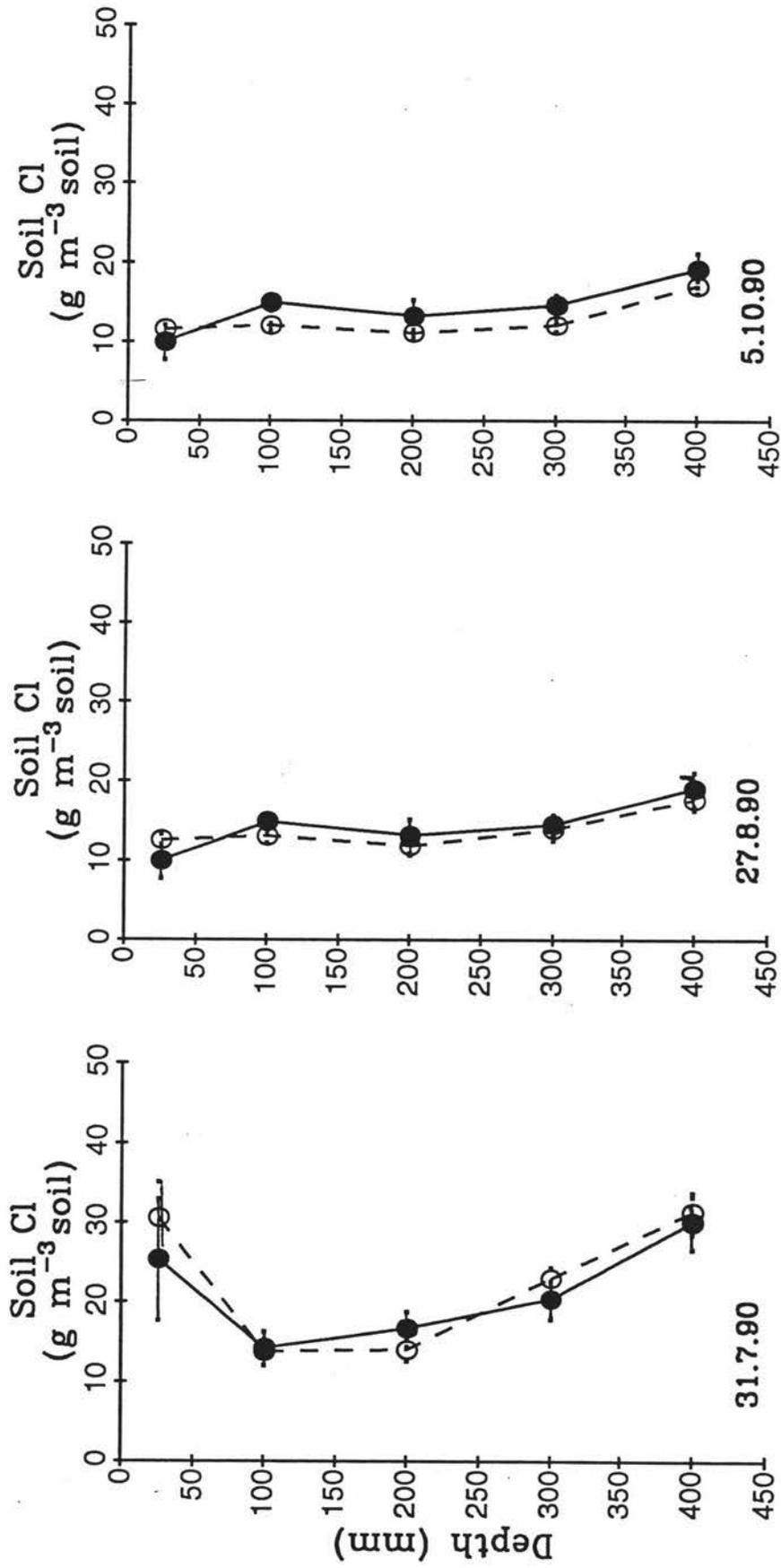


Fig. 5.9. The distribution of chloride in the soil profiles of paddocks A (●) and B (○) in 1990 for the last three soil samplings (means and standard errors are shown)

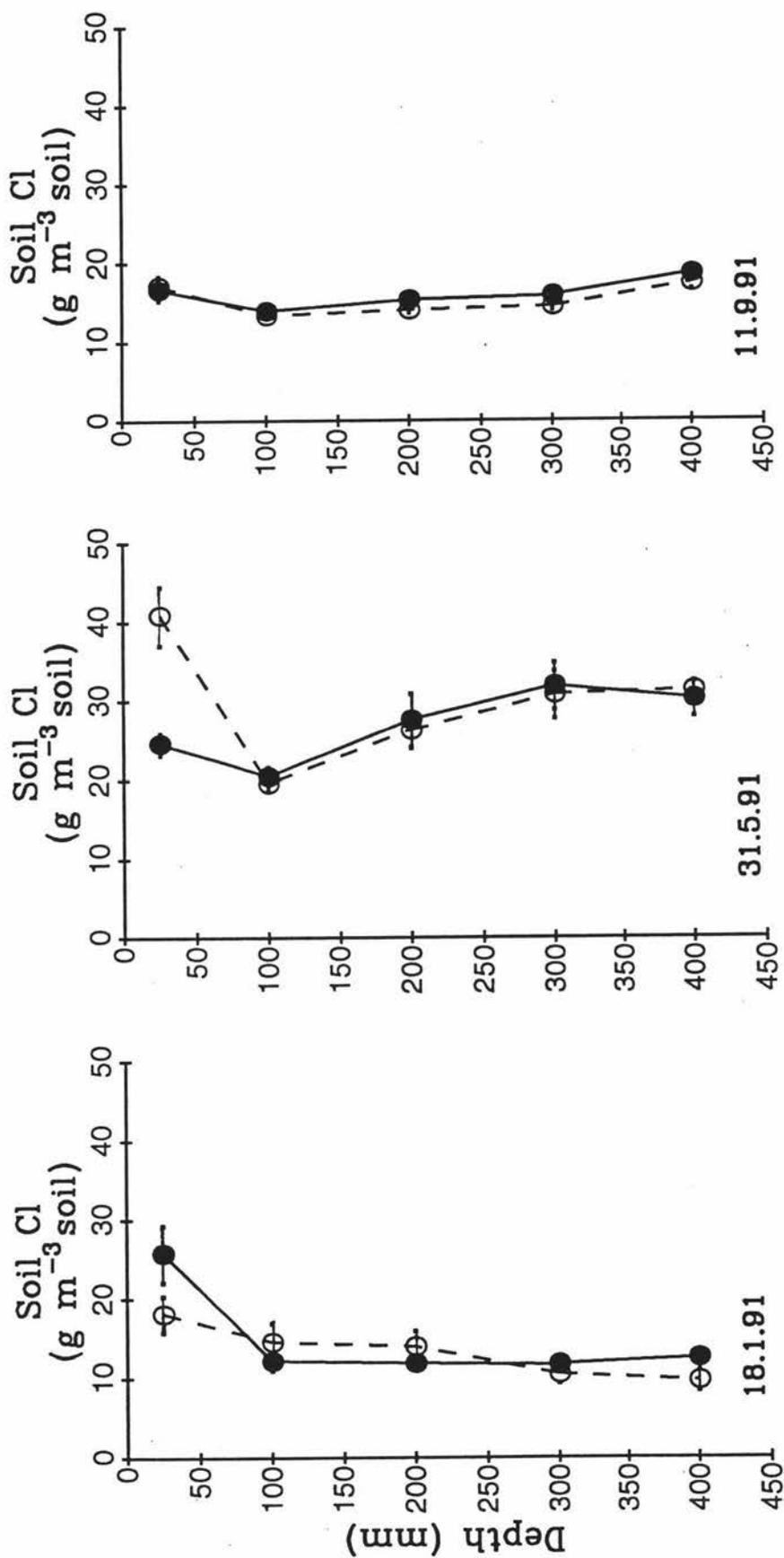


Fig. 5.10. The distribution of chloride in the soil profiles of paddocks A (●) and B (○) in 1991 for all soil samplings (means and standard errors are shown)

The soil chloride concentrations in the two paddocks were comparable to each other during 1991 (Figure 5.10) except in the 0-50 mm layer. The concentration in the soil profile during summer (18 January 1991) was slightly higher than that at the end of the 1990 drainage season. The chloride concentration increased further over summer-autumn as shown by the 31 May 1991 data. By the end of drainage season (11 September) the concentration had decreased again.

#### 5.4.3. Nitrate-N

The distribution of nitrate-N in the soil samples collected at various times from paddocks A and B as a function of depth for the 1990 drainage period is shown in Figures 5.11 and 5.12. In April and particularly in May a high concentration of nitrate was found near the soil surface in both paddocks. This high concentration was most probably due to mineralization. White *et al.* (1983) attributed the high autumn concentration to be due to a flush of mineralization of soil organic N, especially in the top 200 mm, as the soil rewetted. Grazing (2 - 5 May 1990) could have also been a factor in increasing the concentration of readily mineralizable N in the surface layer of soil. The effect of a spatially variable input of excretal N may be the reason for the standard errors of nitrate concentrations, particularly in the surface soil.

The concentrations in the soil samples taken on 29 June 1990 (one month after urea application) were lower than the previously measured soil nitrate concentrations. There was 117 mm of rain between 28 May and 29 June. This rain would have caused leaching, because the rain in the previous month had rewetted the soil to 'field capacity'.

Between 29 June and 31 July the concentration of nitrate in the topsoil increased in both paddocks (Figure 5.12). This increase was probably due to grazing between 10 and 14 July 1990. Nitrate concentrations were considerably lower at the next sampling on 27 August 1990. Note the different scales on the x-axis for the different dates. The decrease in concentration was probably due mainly to plant uptake and leaching. The low soil nitrate concentrations were reflected in low drainage nitrate concentration towards the end of the drainage season. The concentration in the soil profile was almost the same on 5 October as on 27 August 1990.

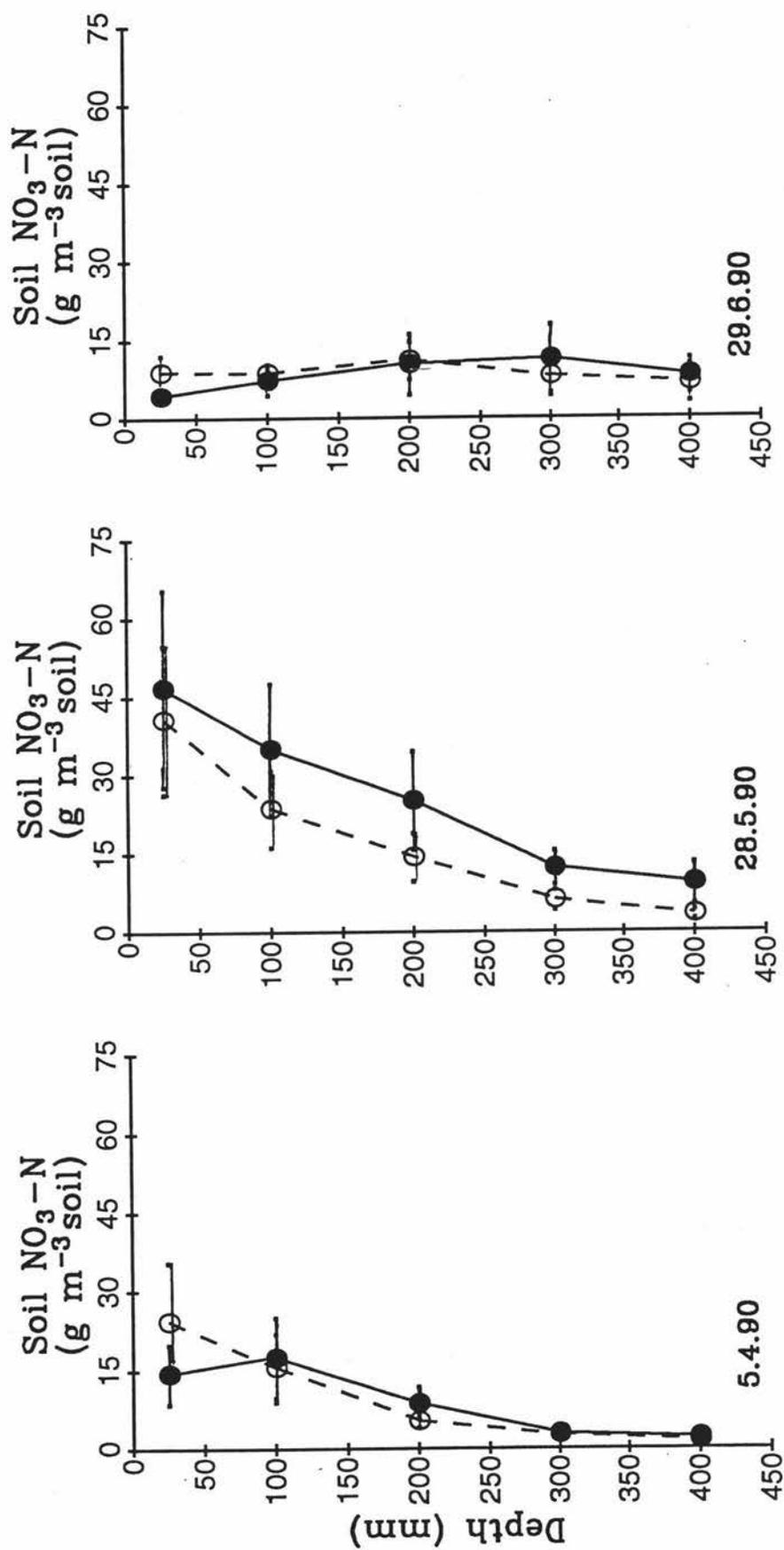


Fig. 5.11. The distribution of nitrate in the soil profiles of paddocks A (●) and B (○) in 1990 for the first three soil samplings (means and standard errors are shown)

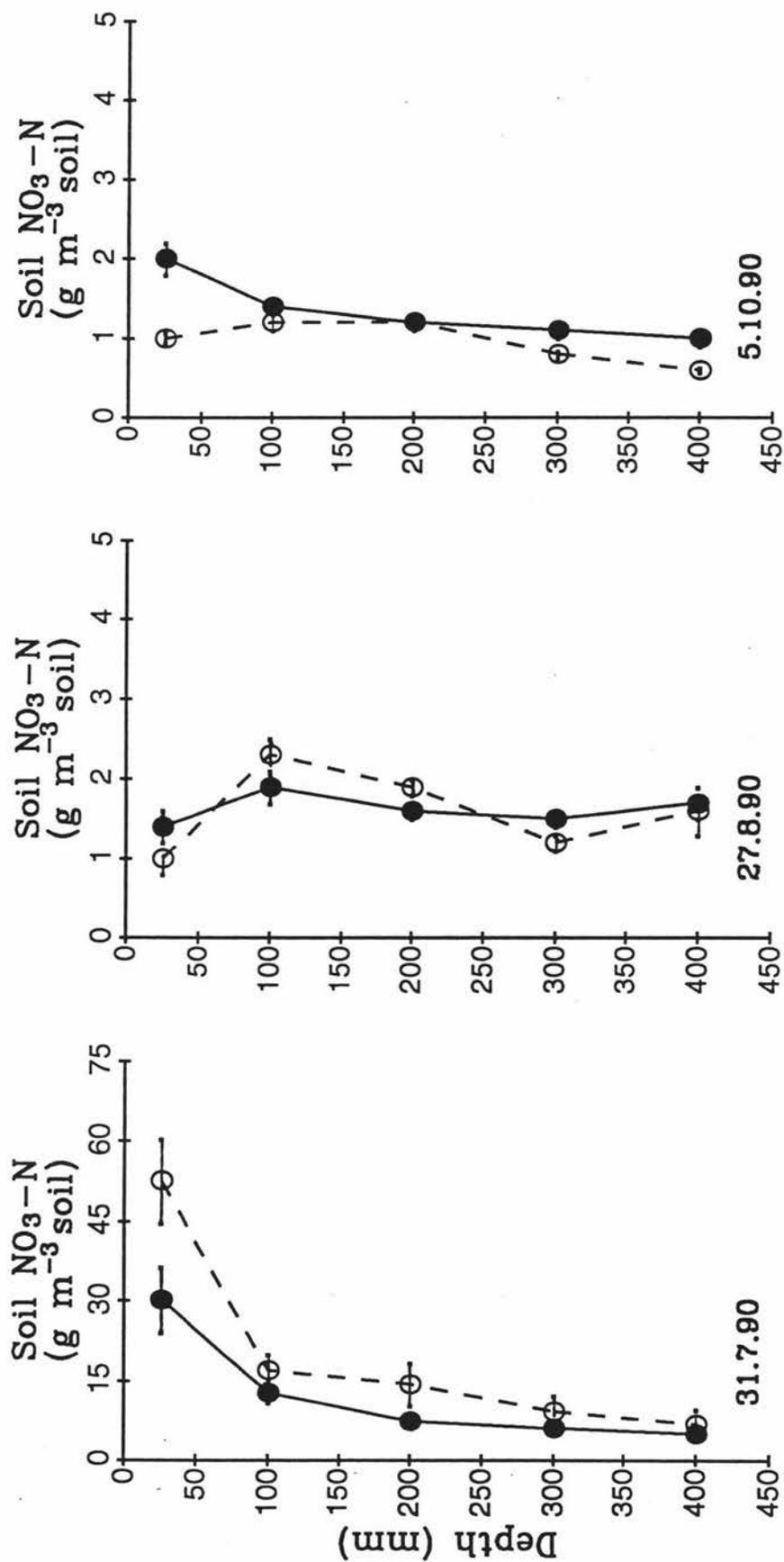


Fig. 5.12. The distribution of nitrate in the soil profiles of paddocks A (●) and B (○) in 1990 for the last three soil samplings (means and standard errors are shown)

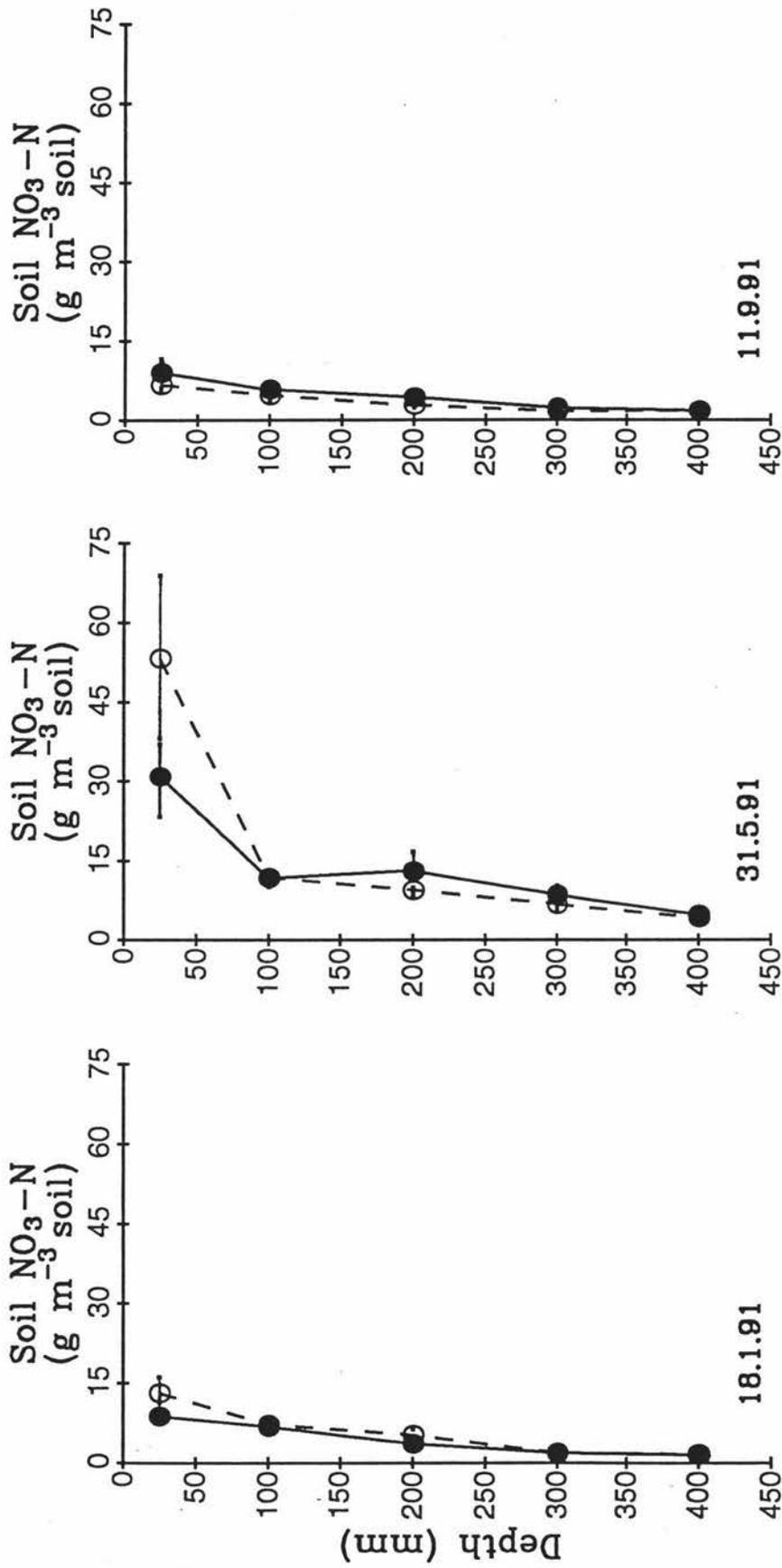


Fig. 5.13. The distribution of nitrate in the soil profiles of paddocks A (●) and B (○) in 1991 for all soil samplings (means and standard errors are shown)

Soil nitrate concentrations during 1991 are shown in Figure 5.13. The nitrate profiles on 18 January and 31 May 1991 showed generally higher soil solution nitrate levels than the last sampling in 1990, although no nitrogen fertilizer was applied over the summer. The increase in concentration during autumn would be due to mineralization of organic N (White *et al.* 1983) and also due to grazing returns. At all three soil samplings in 1991 the concentration was higher in the surface soil than the subsoil. The distribution was similar in paddocks A and B.

#### **5.4.4. Ammonium-N**

The distribution of ammonium-N as a function of depth for paddocks A and B during 1990 is shown in Figures 5.14 and 5.15. The distribution of ammonium in the top layer of paddock B was greater than that in paddock A except on 31 July 1990. It is interesting that 31 July was the only occasion when nitrate concentrations in B were consistently higher than in A. In general, B remained wetter than A, particularly in the surface layers, and this may have led to more denitrification at certain times of the year. In all other layers the ammonium concentration in the soil in the two paddocks was comparable, except on the 28 May when the ammonium concentration in the 50-150 mm depth of paddock B was unusually high. In general, the variability was largest in the top layer and decreased with depth.

### **5.5. EFFECT OF SHEEP GRAZING**

Sheep grazing happened on four occasions during the 1990 drainage season (Chapter 2). On 25 August 1990 the gate of paddock B was accidentally opened and an unknown number of sheep grazed the pasture. The effect of this unplanned grazing is uncertain, but not likely to be large. To avoid possible complications, the soil and herbage was sampled as soon as possible thereafter.

#### **5.5.1. Time effects**

During the drainage season solute concentrations in the soil profile usually decreased due to leaching of solutes. However, the soil samples taken after grazing on 28 May and 31 July 1990 showed an increase in the concentrations of nitrate-N and ammonium-N in the top layer (0-50 mm) and to some extent in the 50-150 mm

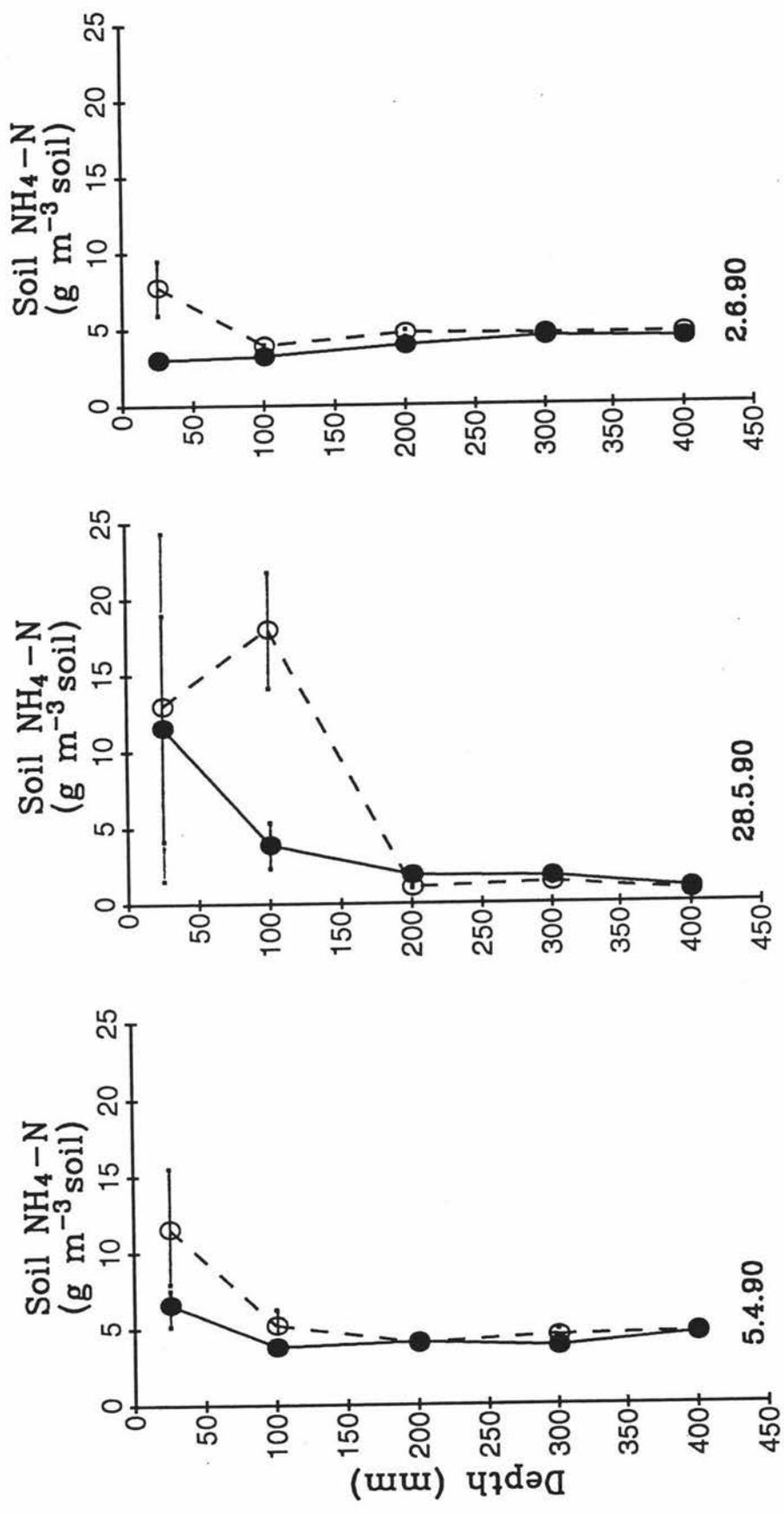


Fig. 5.14. The distribution of ammonium in the soil profiles of paddocks A (●) and B (○) in 1990 for the first three soil samplings (means and standard errors are shown)

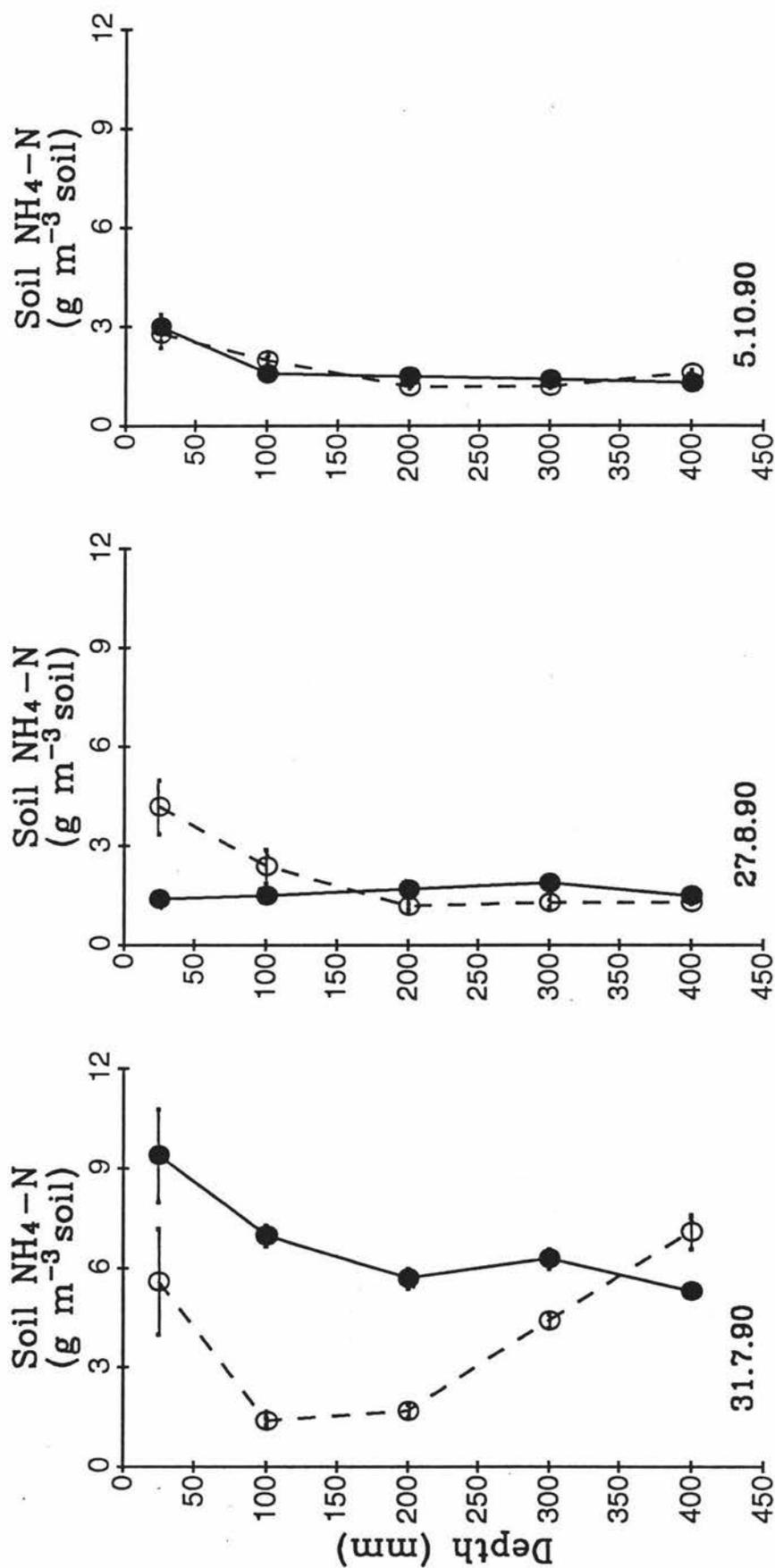


Fig. 5.15. The distribution of ammonium in the soil profiles of paddocks A (●) and B (○) in 1990 for the last three soil samplings (means and standard errors are shown)

layer. After the first grazing, chloride concentration in the top layer did not increase appreciably, but did increase after the second grazing period.

### 5.5.2. Depth effects

High concentrations of mineral N and chloride were observed at all depths in some soil samples, especially soon after a grazing period. Table 5.1 gives the mean concentration of solutes (the standard errors are given in parenthesis) for different layers on 28 May 1990 and also for the individual site 9 where the concentration of solutes was greater at all depths compared to the mean concentration. The high concentrations at all depths could be due to urine patches.

Variability of solute concentrations in the top soil after grazing was greater than that in the lower layers. This was probably due in part to the uneven distribution of animal returns (urine and dung patches) all around the paddock. The movement of solutes to deeper into the soil profile due to "hot spots" (Ryden *et al.*, 1984; White, 1984) was observed. Ball and Ryden (1984) concluded that if mineral N was aggregated by sheep and cattle into excreta, urine patches in particular, pulses of nitrate could move to below the zone of root uptake. Under wet conditions a large proportion of this N may be lost as nitrate in drainage water (Field and Ball, 1982). This would be particularly true in dairy pasture where the larger amount of urine from the cattle compared to sheep falls on a small area creating temporary surface saturation, which might result in preferential flow. This effect is expected to be less in sheep-grazed pasture, although possible as observed in this study.

## 5.6. SUCTION CUP SAMPLING

Suction cup samples were collected just before the fertilizer application on 29 May 1990 to measure the background concentration of solutes. From then on, samples were collected approximately every fortnight. Suction was applied soon after a rainfall event and the samples were collected the next day. The samples were collected from suction cups at two different depths (200 mm and 450 mm). Although the same suction of 80 kPa was applied to all the suction cups, the amount of sample collected differed from cup to cup. The amount ranged from 8 to 75 ml.

**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

Depth (mm)	Mean conc. (g m <sup>-3</sup> soil)			Site 9 conc. (g m <sup>-3</sup> soil)		
	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>
0 - 50	40.7 (14.2)	13.0 (11.3)	31.4 (5.6)	159.0	39.9	54.1
50-150	23.7 (7.3)	8.0 (3.8)	33.9 (5.8)	51.9	24.0	65.9
150-250	14.4 (4.6)	1.1 (0.03)	28.0 (5.3)	36.6	1.8	55.4
250-350	6.2 (1.9)	1.4 (0.14)	25.2 (4.8)	9.9	1.8	50.3
350-450	3.4 (0.9)	0.8 (0.03)	21.0 (3.6)	7.7	1.8	34.3

The samples from paddock A were analyzed for bromide and nitrate, and those from paddock B were analysed for chloride and nitrate. Analysis for ammonium-N in the first set of samples showed that only 2 out of 40 samples had a concentration of about  $0.3 \text{ g m}^{-3}$ , and the rest had a lower concentration. So the rest of the samples were not analysed for ammonium-N.

### 5.6.1. Bromide

As expected, the concentration of bromide at both depths in paddock A increased from a very low value on 29 May 1992 to a peak and then decreased. As was also expected, the deeper suction cups responded more slowly than the shallower ones (Figure 5.16a). Although the number of cups sampled at the lower depth was only four, the concentration was less variable compared to the upper depth. The variability decreased at both depths with time.

### 5.6.2. Chloride

Figure 5.16b shows the chloride concentration for paddock B. The concentration decreased with time at the upper depth, whereas it maintained almost the same concentration at the lower depth for most of the season. This indicates more effective leaching of indigenous solutes from the surface layers than the deeper layers.

### 5.6.3. Nitrate-N

The concentration of nitrate in suction cup samples for paddocks A and B is given in Figure 5.17. In paddock A, the concentration of indigenous nitrate in both upper and lower layers decreased from the second sampling onwards. But, in paddock B, the concentration in the upper layer increased further after the second sampling and then decreased. In the lower layer the concentration increased from a low value to a peak and then decreased, similarly to that for bromide in paddock A. The differences between the paddocks probably indicate the effect of urea application to paddock B. The standard error for mean nitrate concentrations was greater than that of bromide.

Steenvoorden *et al.* (1986) showed that for experiments on cut grassland with an even distribution of fertilizers and animal manures, four suction cups per field were

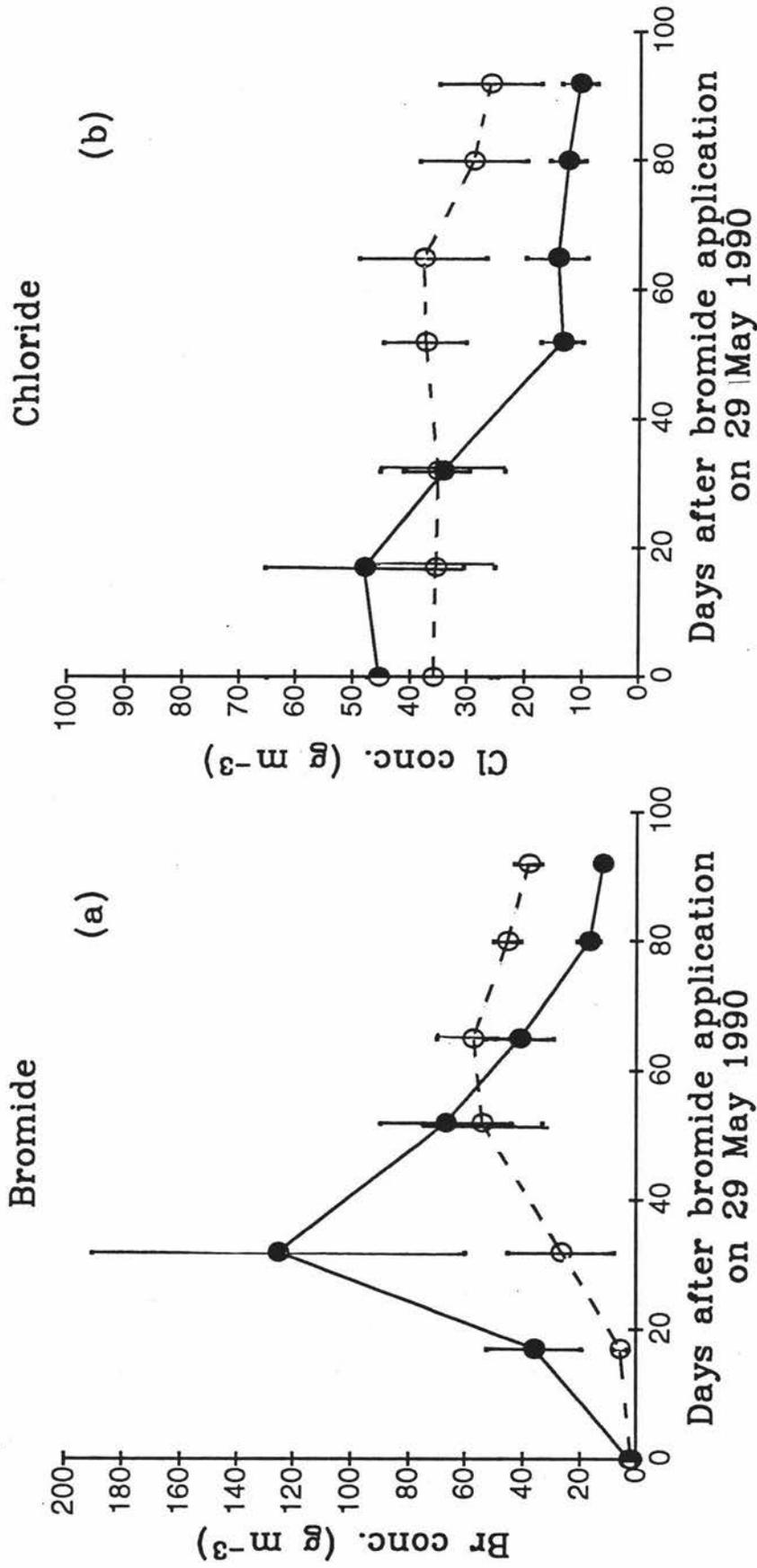


Fig. 5.16. Bromide and chloride concentrations in suction cup samples at 200 mm depth (●) and 450 mm depth (○) of paddock A and paddock B, respectively (means and standard errors are shown)

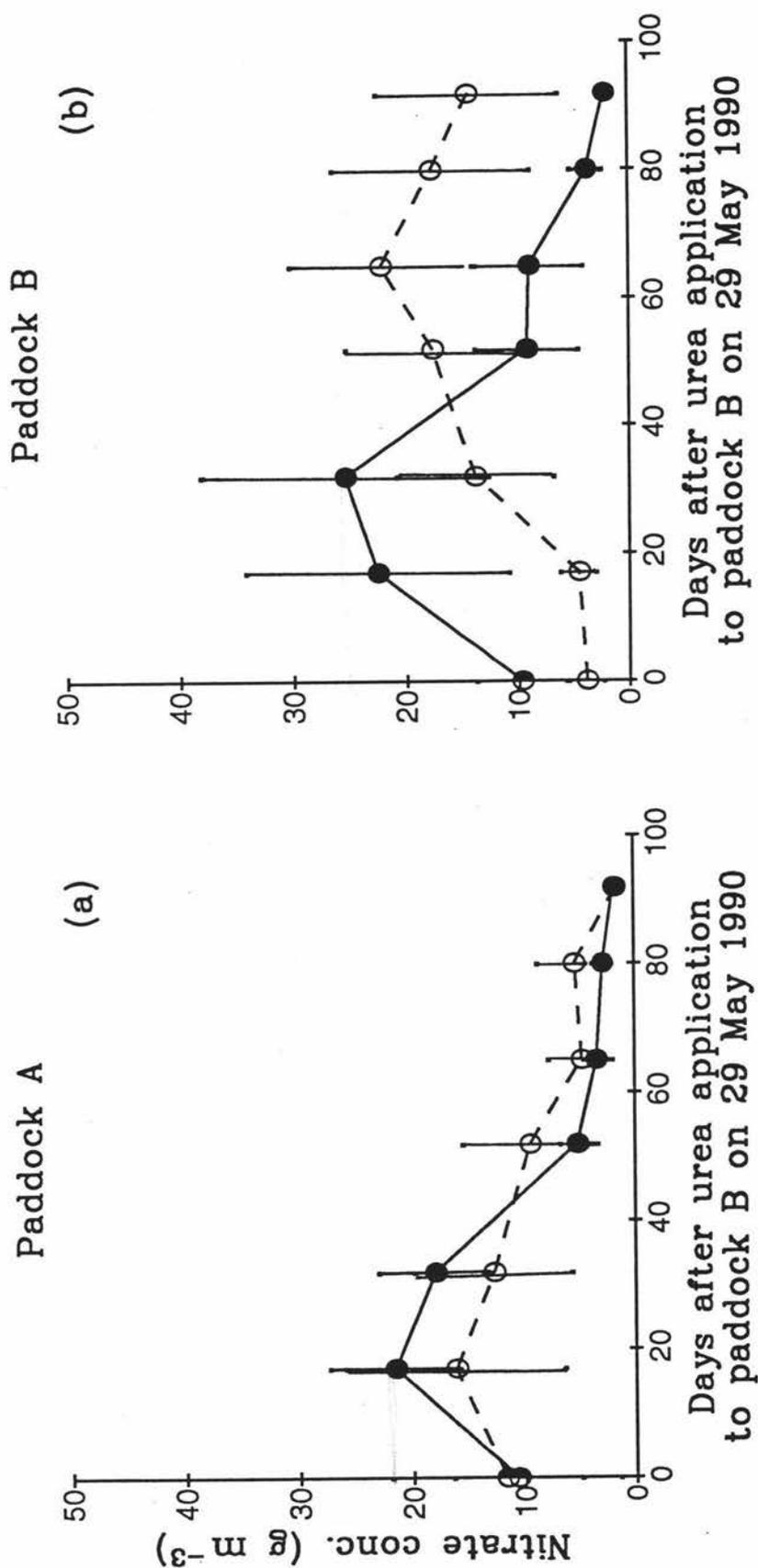


Fig. 5.17. Nitrate concentrations in suction cup samples at 200 mm depth (●) and 450 mm depth (○) of paddocks A and B (means and standard deviations are shown)

sufficient to produce reliable average values, which was true in the case of bromide. But this is certainly not true for nitrate and chloride in the grazed pastures because the concentration of nitrate and chloride in individual suction cups varied markedly due to the deposition of excreta at random. So under grazed field conditions bromide is a better tracer than chloride.

#### 5.7. COMPARISON OF SOLUTE CONCENTRATIONS IN SOIL SOLUTION

Solute concentrations in the soil solution, as measured on soil extraction or suction cup samples, are compared in Figures 5.18 and 5.19. Concentrations in the soil extracts, previously expressed in  $\text{g m}^{-3}$  soil, were converted to a soil solution basis by dividing by the appropriate volumetric water content. The units are  $\text{g m}^{-3}$  soil solution. Soil extraction concentration is given for the 150 - 250 mm and 350 - 450 mm depths. Suction cup samples are for the samples collected at about 200 mm (upper) and 450 mm (lower) depths.

Bromide concentrations in the soil samples were generally lower than the suction cup samples at both the upper and lower depths, throughout the drainage season. For example, in the upper depth of soil two months after bromide application the soil extract contained  $26 \text{ g Br m}^{-3}$ , while the suction cup concentration was  $41 \text{ g Br m}^{-3}$ . At the lower depth the soil extraction concentration was  $26 \text{ g m}^{-3}$  while the suction cup concentration was  $57 \text{ g m}^{-3}$ . So, for an externally applied solute, the suction cup solution concentration was greater than the soil extraction concentration during the drainage season.

For indigenous chloride the results were opposite to those for bromide; the soil extraction concentration was always greater than the suction cup concentration at both depths. For example, on 28 May 1990, the soil extraction concentrations at the two depths were  $69$  and  $53 \text{ g m}^{-3}$ , while suction cup concentrations at both depths were  $45$  and  $36 \text{ g m}^{-3}$ . So, for an indigenous solute, soil extraction concentration was greater than the suction cup concentration during the drainage season.

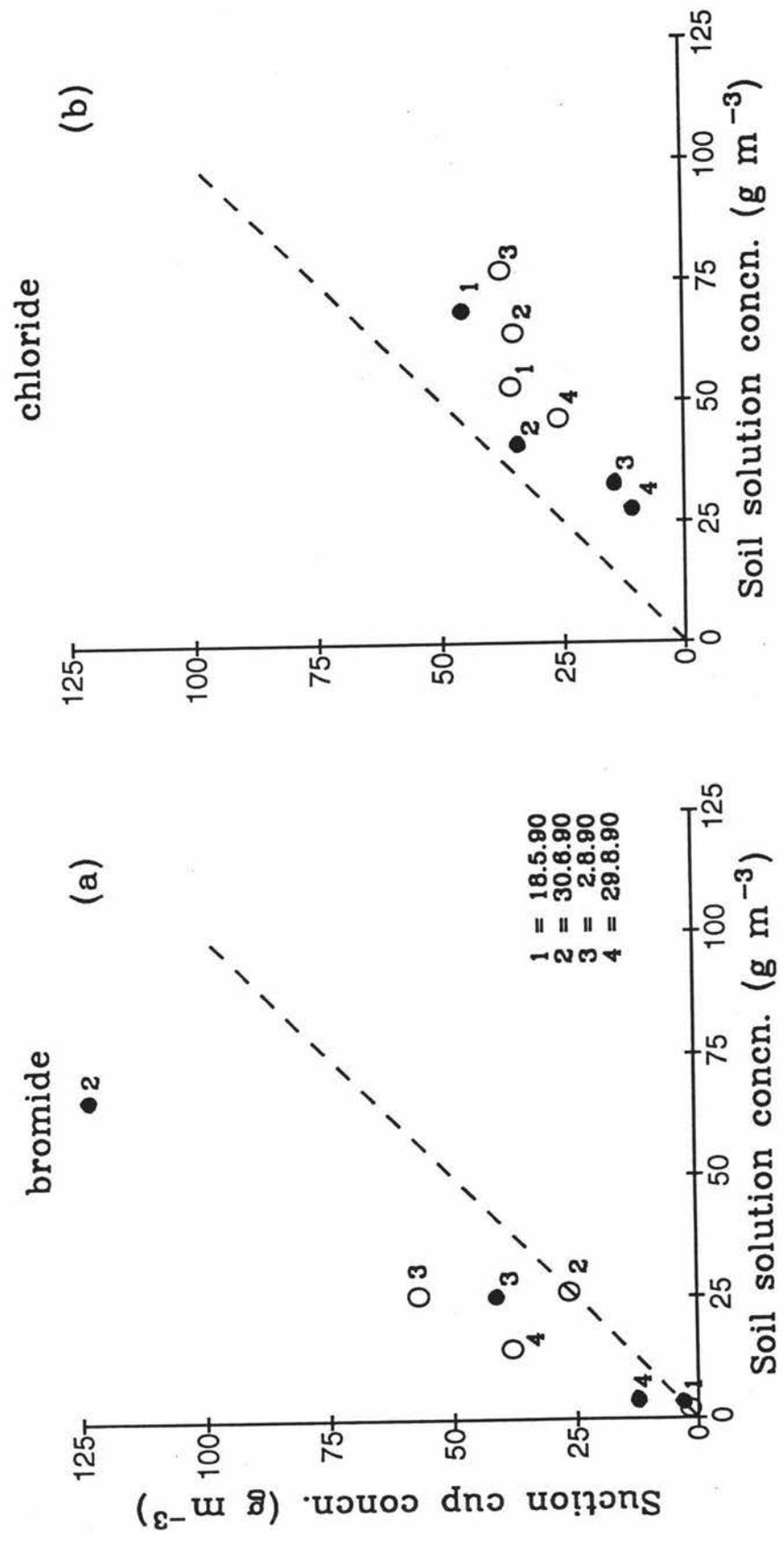


Fig. 5.18. Relationship between suction cup solution concentration and soil solution concentration for applied bromide (paddock A) and indigenous chloride (paddock B) at 240 mm depth (●) and 450 mm depth (○)

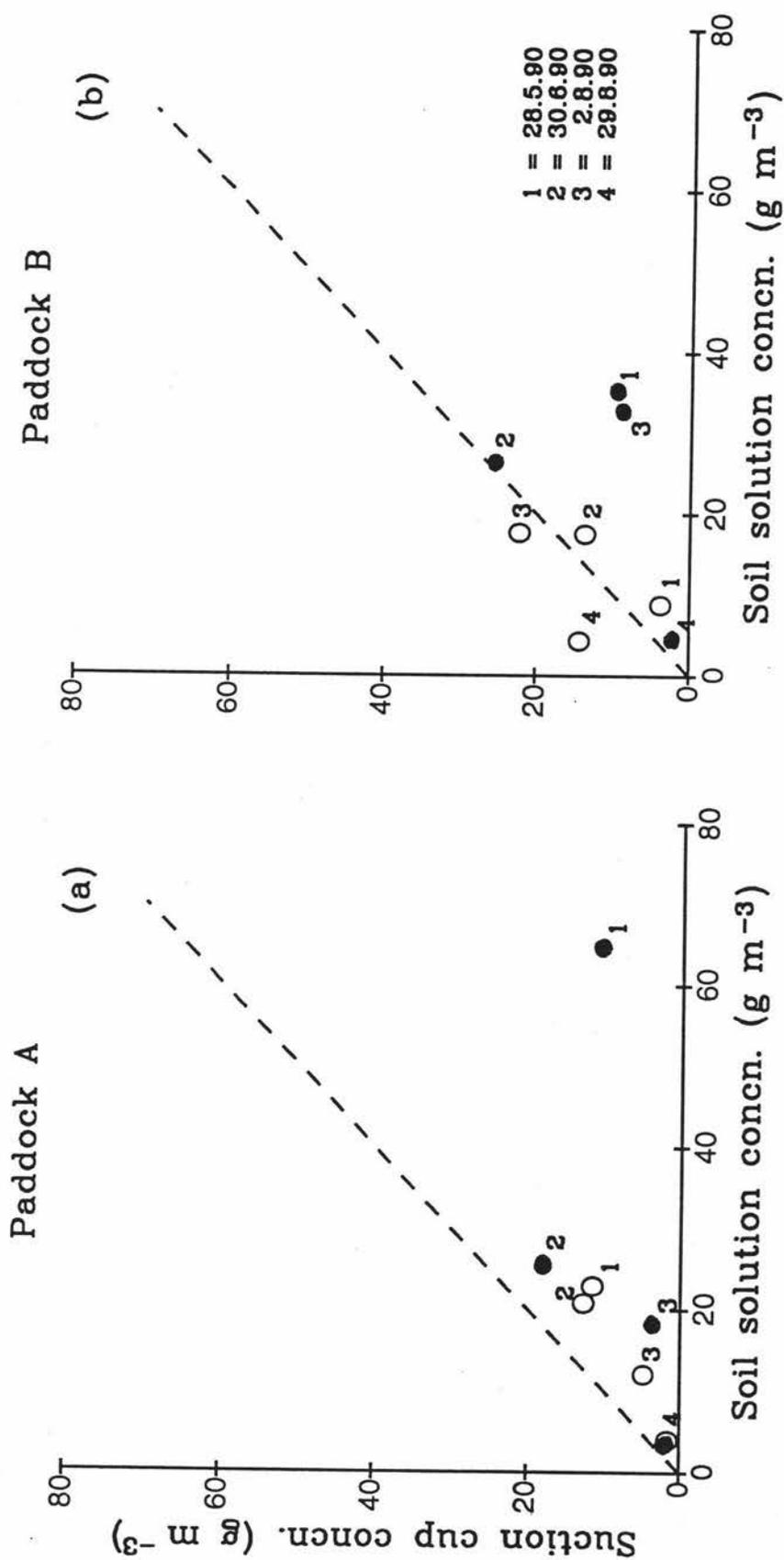


Fig. 5.19. Relationship between suction cup solution concentration and soil solution concentration for nitrate in paddocks A and B at 200 mm depth (●) and 450 mm depth (○)

As shown in Figure 5.19 the nitrate concentration in the soil solution from paddock A was greater than the suction cup concentrations, which is similar to the results for chloride discussed above. For paddock B, the concentration in soil extracts was greater than the suction cup concentrations at all samplings only in the top depth, perhaps showing the effect of mineralization. The soil extract concentration is expected to be greater than the suction cup concentration at the first sampling (before urea application). The only strange value is the 150-250 mm, third sampling. The other values have all shifted to the left when compared with the values in Figure 5.19a (indigenous nitrate in paddock A) or the indigenous chloride values for paddock B (Figure 5.18b). However, during the third and fourth sampling, suction cup concentration was greater than the soil extract concentrations at the lower depths, presumably showing the influence of urea application.

## 5.8. HERBAGE PRODUCTION

Cumulative dry matter production for both paddocks is given in Table 5.2. The dry matter production for paddocks A and B was 5931 and 7720 kg ha<sup>-1</sup>, respectively, for the seven months from the end of April to the end of November 1990.

**Table 5.2.** Cumulative herbage production during the 1990 drainage season (kg dry matter ha<sup>-1</sup>)

Date	Paddock A	Paddock B
27.4.90 - 2.7.90	711	1233
27.4.90 - 28.8.90	1762	2575
27.4.90 - 4.10.90	3590	4891
27.4.90 - 20.11.90	5931	7720

From the first sampling onwards the dry matter production in paddock B was consistently greater than that in paddock A. This was probably due to a nitrogen response to the urea application on 29 May in paddock B and to a temporary plant

growth suppression due to bromide application in paddock A. In paddock A the herbage production was 711 kg/ha from 27 April to 2 July (> 2 months) and 1051 kg/ha from 2 July to 28 August (< 2 months). This shows that the growth rate was faster in the second period than the first. In both paddocks, the fastest growth period was during late spring and early summer, when generally favourable conditions for plant growth occurred, with warm weather and moisture not limiting.

## 5.9. PLANT UPTAKE

The amount of solute uptake was calculated from the dry matter production and herbage concentration of that solute.

### 5.9.1. Bromide

Figure 5.20a shows the cumulative amount of bromide uptake by the pasture in paddock A as a function of cumulative evapotranspiration. The amount of bromide taken up by the plants during the 1990 drainage season was 26.5 kg Br/ha which is equal to 13.3 % of the Br input. This result is very similar to that of Kanchanasut and Scotter (1982) who showed in a field study on Tokomaru silt loam soil, that about 13.5 % of the applied bromide was taken up by the grass plants during the 100 days after bromide application. These values are much higher than in a laboratory column study in which Gish and Jury (1982) showed that only 2 % of the applied Br was taken up by wheat. However, the value is less than that obtained by Owens *et al.* (1985) who found in a field study that 30 % of applied Br was taken up by the grass and returned to the soil surface after the grass had decayed.

### 5.9.2. Chloride

The cumulative chloride uptake as a function of cumulative evapotranspiration is given in Figure 5.20b. A total of 54 and 50 kg Cl ha<sup>-1</sup> was taken up by the pasture in paddocks A and B, respectively during the drainage season of 1990. The chloride concentration in the plants was similar for both paddocks at approximately 2 %. This value is slightly high when compared to values of 1.5 % reported by Goh *et al.* (1979) and Heng (1991).

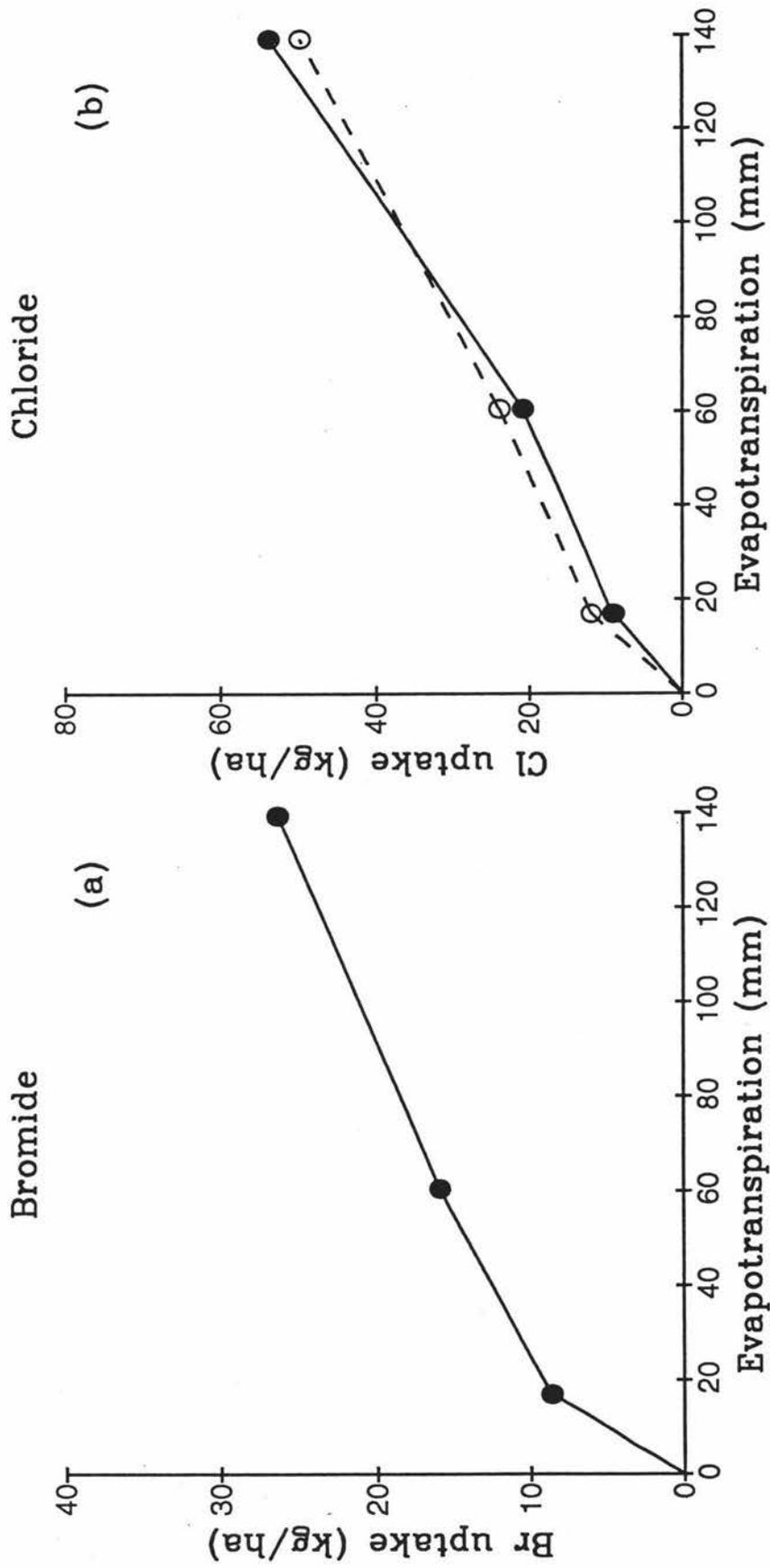


Fig. 5.20. Bromide and chloride uptake by plants as a function of estimated evapotranspiration for the 1990 drainage season for paddocks A (●) and B (○)

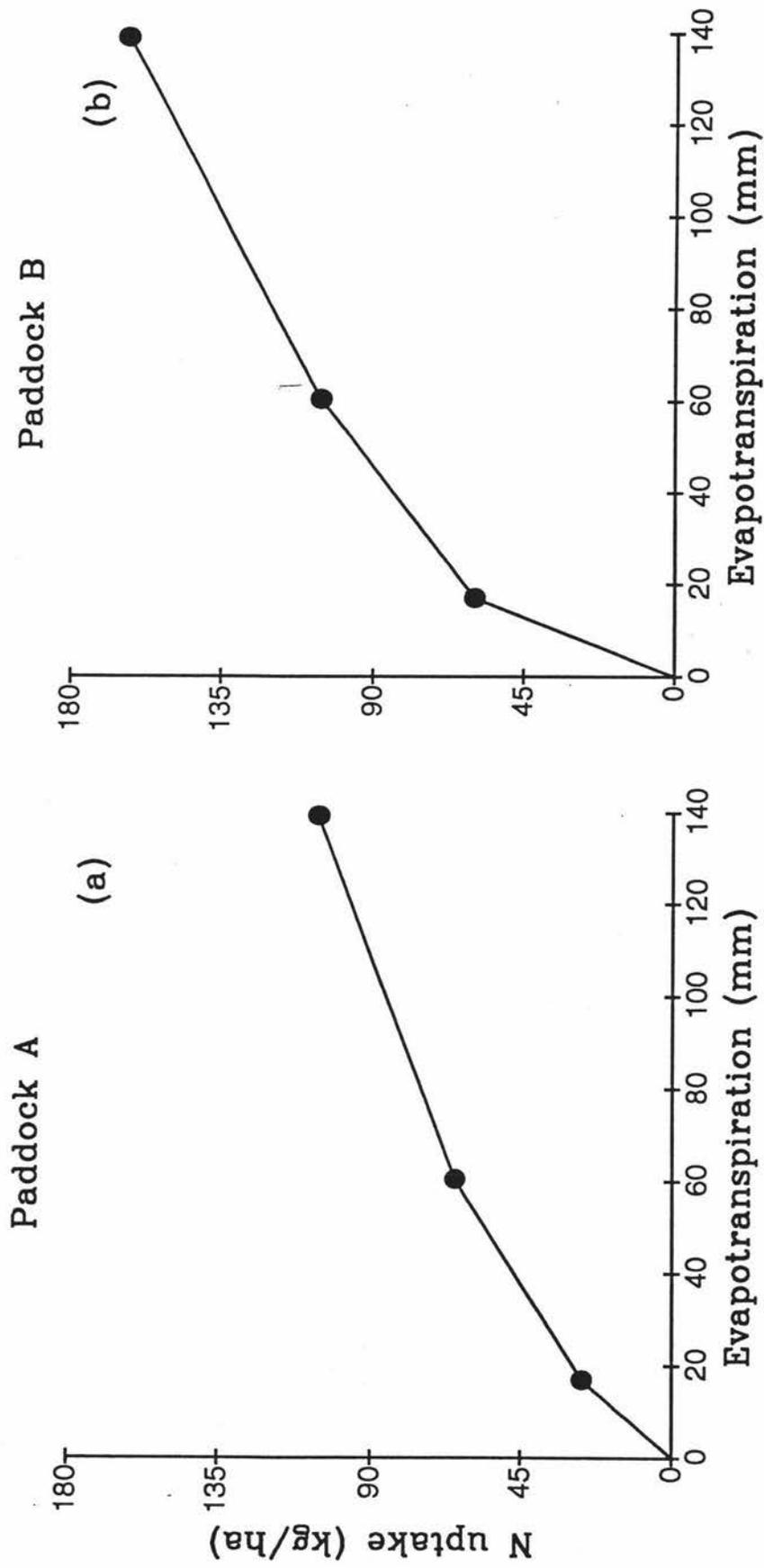


Fig. 5.21. Nitrogen uptake by plants for the 1990 drainage season

### 5.9.3. Nitrogen

Figure 5.21 shows the cumulative N uptake for both paddocks for the period 27 April to 4 October 1990. After the application of urea on 29 May 1990 there was a response in both herbage production and N concentration in paddock B. N concentrations in herbage of both paddocks were similar at the start with 3.5 %. After the urea application the concentration of N in herbage was 3.8 % for paddock A and 4.9 % for paddock B.

### 5.10. CONCLUSIONS

Several important conclusions can be drawn from this work. For example :

- (a) Nitrate and chloride concentrations in soil increased over the summer-autumn period. Nitrate concentration increased probably due to the net mineralization of soil organic N. Chloride in soil increased due to atmospheric input and a lack of leaching. Both solutes were also recycled through grazing. The effect of grazing was observed particularly in the surface soil. As expected, the concentration of these solutes decreased towards the end of the drainage season, due to leaching losses. Although denitrification in the winter was possible, because the soil was drained the effect is expected to be low.
- (b) High concentrations of both mineral N and chloride were observed at all depths in some soil cores, especially after grazing. Such localized movement of solutes (nitrate and chloride) to deep in the soil profile was probably due to urine "hot spots" - high concentrations in relatively small areas.
- (c) For suction cup samples, the concentration of bromide at both sampling depths increased with time to a peak and then decreased. There was a differential time delay in the rise in concentration between the upper and lower depths.
- (d) The soil solution concentration measured by soil extraction was compared with suction cup sample concentration. Solute concentrations measured by extracting a volume of soil represent volume-averaged concentrations (Jury and Roth, 1990), in contrast to flux-averaged concentrations (mass of solutes per volume of moving water) which can only be unambiguously measured by sampling the soil drainage water. In structured soils in which not all the soil

water is effective in solute transport, the volume-averaged concentration is not expected to be the same as the flux-averaged concentration measured at the same time. Suction cup samples of the soil solution may provide representative measurements of the flux-averaged concentration of solutes being leached through the soil.

It was found that for an externally applied solute which is not present in the soil initially, such as bromide, the suction cup concentration was consistently greater than the volume-averaged concentration of bromide. In contrast for a conservative indigenous solute, such as chloride, the volume-averaged concentration of resident solute was consistently greater than the suction cup concentration during the drainage season. The same result was obtained for soil-generated nitrate in the paddock to which no fertilizer N was applied. However, in the paddock to which 120 kg N/ha of urea was applied, suction cup and soil extract concentrations were roughly comparable. This reflected the dual influence of both the surface-applied and soil-generated sources of nitrate.

## CHAPTER 6

### LEACHING RESULTS AND MASS BALANCES FOR FIELD EXPERIMENTS

#### 6.1. INTRODUCTION

The field study was carried out on a mole-pipe drained site to estimate solute leaching from the root zone. In Chapter 5 the results of soil, suction cup samples were given. In this Chapter the leaching of solutes, changes in solute concentration with drainage flow rate, and the mass balance for different solutes are discussed.

It is known that solute concentrations in drainage vary with discharge. Intermittent sampling during drainflow is unsatisfactory (Kolenbrander, 1969; Cooke and Williams, 1970) because the concentration can vary unpredictably with flow rate (Wild and Cameron, 1980; White, 1985). To calculate solute loads accurately it is essential that the sampling frequency is sufficient to characterize concentration changes during rapidly changing discharge. In this study a sample was collected for every 600 litres (0.48 mm) of drainage passing through the V-notch weirs. The product of the measured solute concentration in the sample and the flow volume gave the amount of solute leached.

In the present study, the paddocks were periodically mob-grazed by sheep, the stocking rate and the duration of grazing depending upon the dry matter production during the period before grazing. The effect of such grazing on nitrate leaching was also studied because only a few studies of this have been carried out in New Zealand (e.g. Sharpley and Syers, 1979; Field *et al.*, 1985).

#### 6.2. DRAINAGE AND LEACHING RESULTS

The drainage period is defined here as the period from the day when the first drainage occurred in the calendar year until the day when the drainage finally ceased. Due to a total of 123 mm rain during October 1989 five significant drainage events occurred and drainage samples were collected during each event. The total drainage collected during this month was 36 mm for paddock A and 29 for paddock B.

The total amounts of drainage collected from paddocks A and B for the 1990 drainage period were 266 mm and 236 mm respectively, with a difference of 30 mm (i.e. 11 %). Similarly the amount of drainage collected for 1991 was 339 mm for paddock A and 300 mm for paddock B, with a difference of 39 mm (i.e. paddock B again 11 % less than paddock A). This difference might be partly due to some overland flow from surrounding paddocks to paddock A (Heng, 1991) and partly due to overland flow from paddock B to the outside (due to a slight slope towards the pond) during intense stormflow events, assuming that deep percolation in both the paddocks was equal. Although the paddocks were mole-pipe drained, a few ponded areas (more on paddock B than A) were observed on both paddocks after high intensity storm events. The generally higher soil water content for B than A (see Chapter 5) suggests the drainage system in B was not as efficient as in A. Although the amounts of rain received in 1990 and 1991 were almost equal, the drainage collected during these two years was quite different. This was due to the different seasonal distribution of the rain.

Nitrate losses from the paddocks can be regarded as good estimates of total N lost, since the concentration of ammonium in the drainage water was negligible compared to that of nitrate, and nearly all of the excess water was lost in the mole-pipe drainage rather than by deep percolation (Scotter *et al.*, 1990).

### 6.2.1. Bromide

The concentration of bromide in the drainage from paddock A was measured only during the 1990 drainage period and is shown in Figure 6.1. The concentration of bromide in the drainage before bromide application was considered to be negligible. The concentration started at a low value and rose to a maximum after about 80 mm of drainage. The concentration remained approximately constant for about a further 50 mm drainage and then started decreasing. The amount of bromide leached in this drainage season was 103 kg/ha (52 % of the applied bromide). In Figure 6.1 some "dips" in the solute concentration could be observed both early and later in the drainage season. The dips were associated with flow rate changes during individual rain storms. These changes are discussed in Section 6.3.

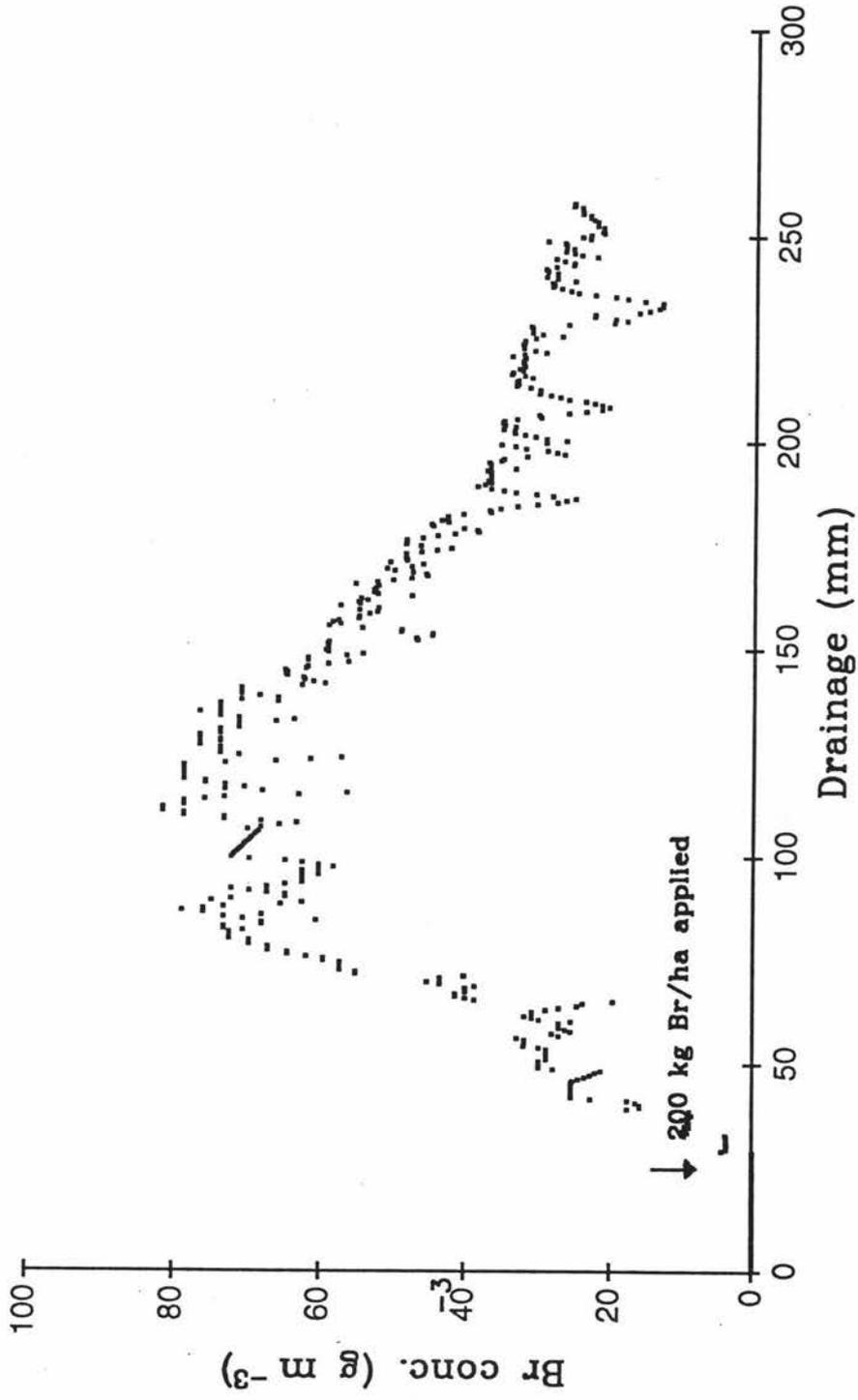


Fig. 6.1 Bromide concentration in the drainage water from paddock A collected during the 1990 drainage season

## 6.2.2. Chloride

### 6.2.2.1. 1989 Spring

After the urea application to paddocks A and B on 13 September 1989, there was a relatively dry period for one month and then drainage occurred on 14, 15, 17, 22 and 23 October. The concentration of chloride in the drainage from both paddocks is shown in Figure 6.2. The concentration in paddock A was slightly lower than that of paddock B before 13 September and the concentration in both cases fluctuated. The concentration of chloride in the drainage samples collected in October was much lower than that collected before the dry period. In paddock A, the concentration which ranged between 60 and 70 g m<sup>-3</sup> before dry period, decreased to 20 - 35 g m<sup>-3</sup> after that. Similarly, in paddock B, the concentration decreased from 70 - 85 g m<sup>-3</sup> to 25 - 35 g m<sup>-3</sup> afterwards. This indicates that during Spring when the grass is growing vigorously it takes up large amounts of chloride along with other nutrients.

### 6.2.2.2. 1990 Drainage season

Drainage occurred in early March in response to a heavy rainfall event (91 and 27 mm rain on 9 and 10 March 1990, respectively). Due to some practical problems, the drainage samples were not collected. The first drainage samples were collected on 4 May 1990. On 29 May 1990, NaBr was applied to paddock A and urea was applied to paddock B. The drainage samples collected before 29 May 1990 gave the background concentrations of nitrate, chloride and bromide.

The concentration of chloride in the drainage samples from paddocks A and B is shown in Figure 6.3. As expected, the concentration decreased from a higher concentration at the start of the drainage period to a lower concentration when drainage ceased. Similar observations were made by Haigh (1985) and Heng *et al.* (1991). The initial concentration in paddock A was about 60 g m<sup>-3</sup> whereas in paddock B the concentration was about 70 g m<sup>-3</sup>. These values are similar to those reported by Heng (1991). With drainage from successive rainfall events the amounts of chloride in the volume of soil interacting with the mobile soil solution would be depleted. Throughout a drainflow season diffusion from the immobile soil solution would occur to maintain levels in the mobile soil solution. With continual drainage of excess water from the system both mobile and immobile soil solution

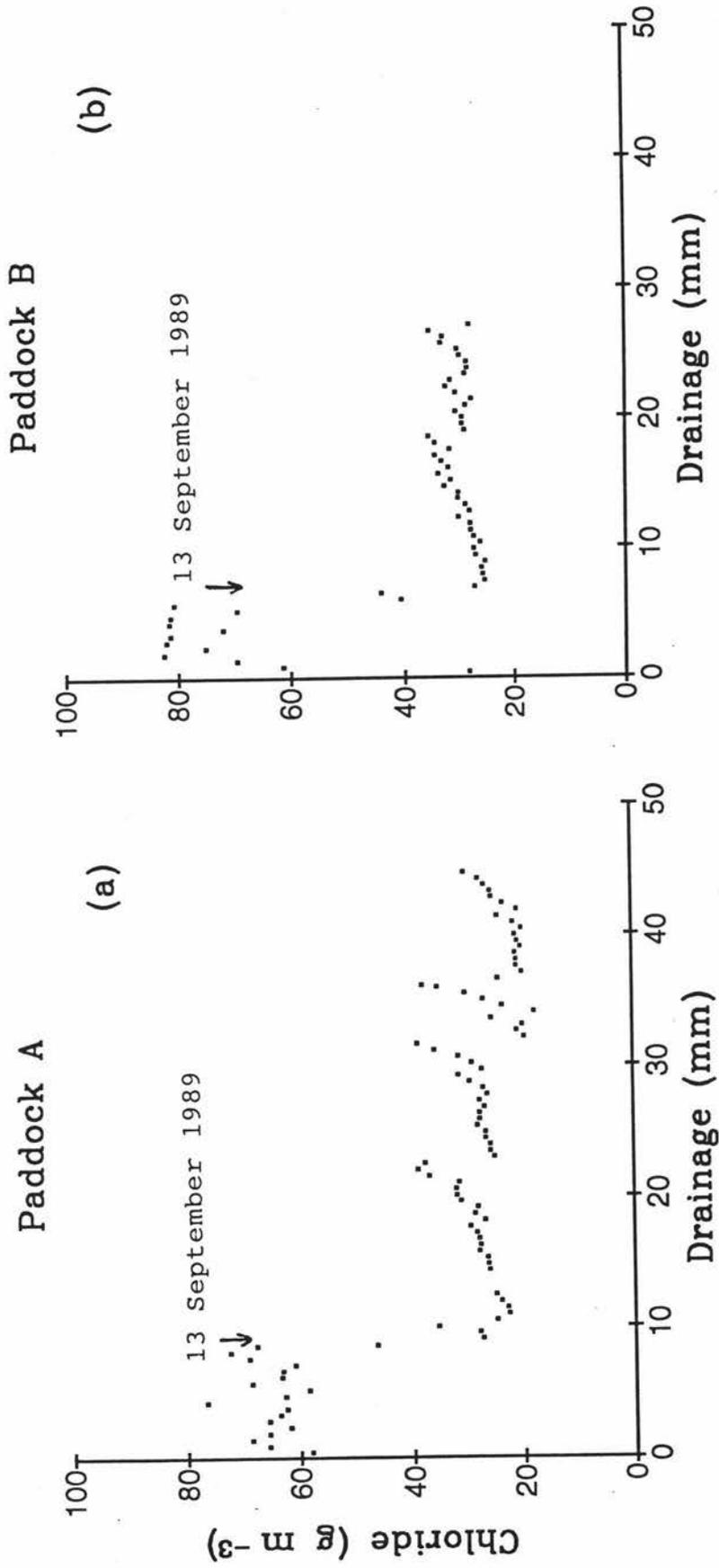


Fig. 6.2 Chloride concentration in the drainage water before and after urea application on 13 September 1989

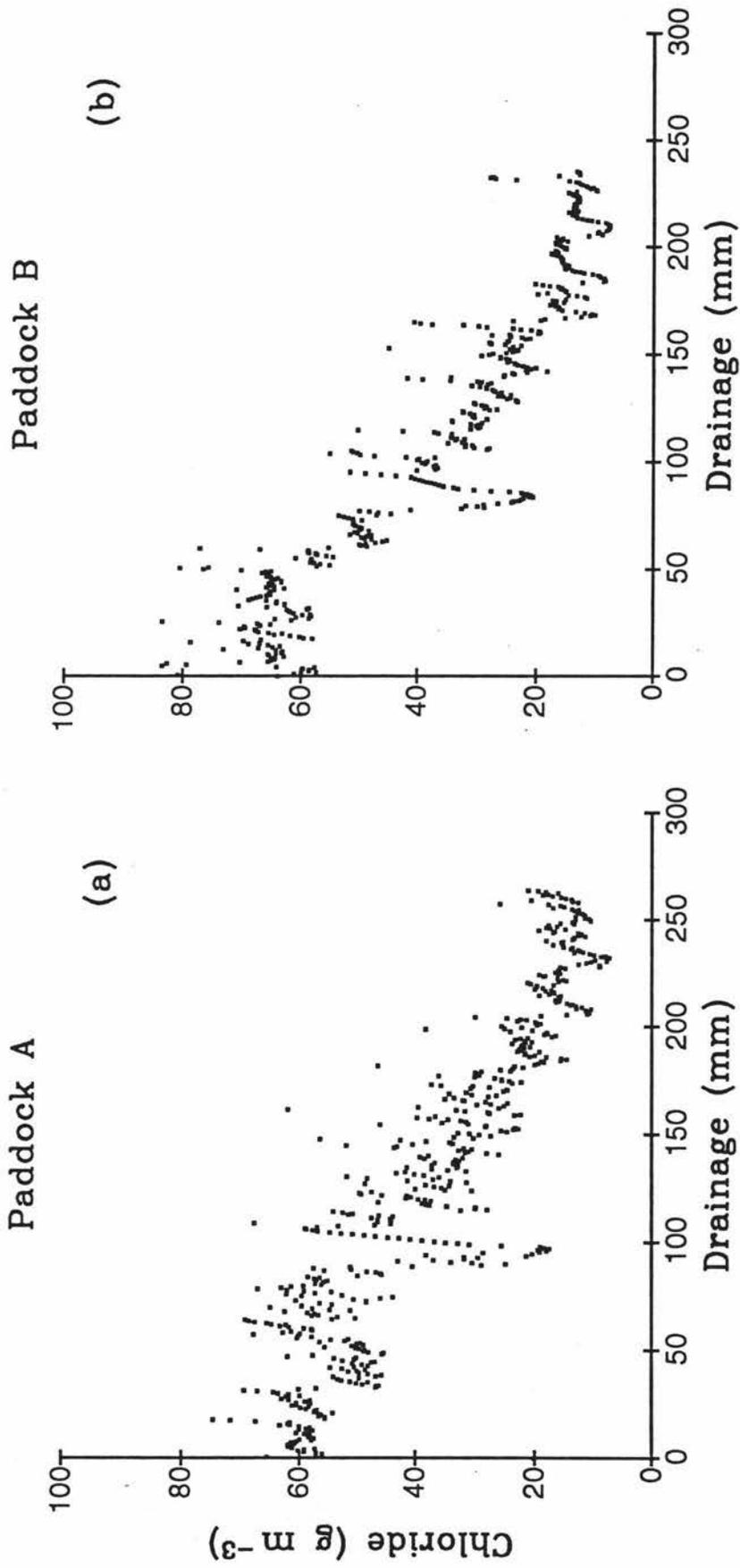


Fig. 6.3 Chloride concentration in the drainage water collected during the 1990 drainage season

concentrations would be depleted. Consequently solute concentrations in drainage water during a drainflow season gradually decreased. The amounts of chloride leached from paddocks A and B were 97 and 85 kg Cl/ha. This difference could be due to the different amounts of drainage collected.

### 6.2.2.3. 1991 Drainage season

Leaching usually occurs during autumn, winter and spring when the soil is relatively wet (Allison, 1968; McLean, 1977; Cameron *et al.*, 1978). However, leaching has also been observed at other times after a large rainstorm or irrigation, particularly immediately after fertilizer application (Balasubramanian *et al.*, 1973; Kissel *et al.*, 1974; Macduff and White, 1984; Haigh and White, 1986). Similar to 1990, there was a heavy rainfall event (75 mm rain) on 18 February 1991 and as a result about 29 mm of drainage was collected from paddock A and 10 mm from paddock B. The chloride leaching results for 1991 are shown in Figure 6.4. The concentration of chloride in drainage from paddock A started at  $48 \text{ g m}^{-3}$ , decreased to  $30 \text{ g m}^{-3}$  at high flow rate and then increased to  $43 \text{ g m}^{-3}$  as the drainage rate for the first major event declined. Similarly, the concentration from paddock B started at  $52 \text{ g Cl m}^{-3}$ , decreased to  $46 \text{ g m}^{-3}$  and then increased to  $53 \text{ g m}^{-3}$ . The amounts of chloride leached during that event from paddocks A and B were 10.2 and 3.2 kg/ha, respectively. The difference is mainly due the amounts of drainage collected.

Drainage began again on 11 April 1991. During this second drainage event in paddock A, the chloride concentration was  $26 \text{ g m}^{-3}$  at the start and decreased during the heavy flow and then increased. After about 70 mm of drainage (17 May 1991), the concentration reached a peak of  $45 \text{ g m}^{-3}$  and then decreased to  $6 \text{ g m}^{-3}$  after 336 mm drainage by 26 August 1991. For paddock B, during the second drainage event, the Cl concentration was  $28 \text{ g m}^{-3}$  at the start and decreased during the heavy flow and then increased. After about 36 mm of drainage (17 May 1991), the concentration reached a peak of  $59 \text{ g m}^{-3}$  and then decreased to  $3 \text{ g m}^{-3}$  after 296 mm drainage by 26 August 1991.

The amounts of chloride leached for this drainage season from paddocks A and B were 48 and 55 kg Cl/ha, respectively. This difference is mainly due to the different

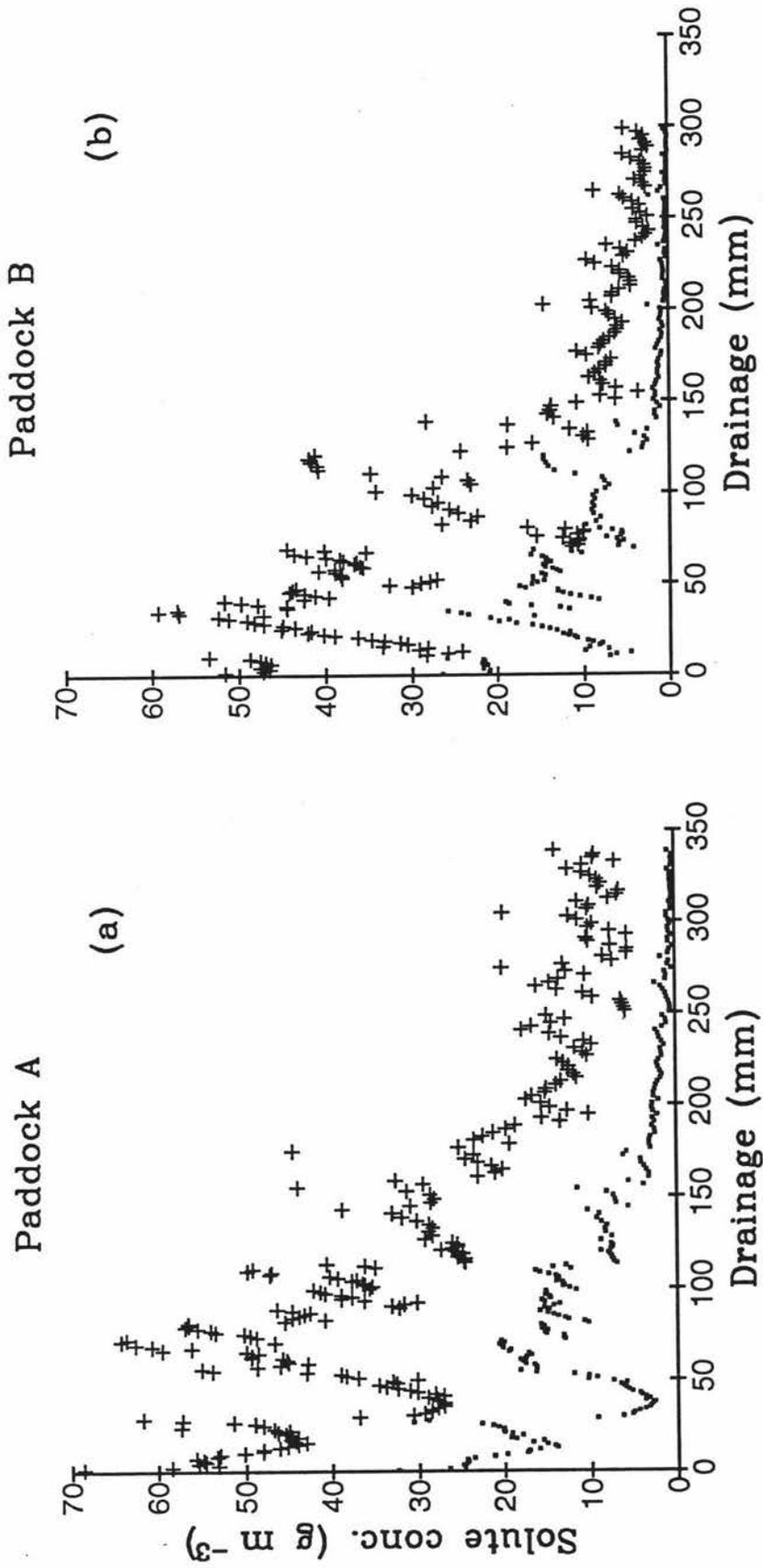


Fig. 6.4 Chloride (+) and nitrate (■) concentration in the drainage water during the 1991 drainage season

amounts of drainage collected, although different concentration levels in the drainage from the two paddocks also contributed to some extent.

### 6.2.3. Nitrate

#### 6.2.3.1. 1989 Spring

Figure 6.5 shows the concentration of nitrate-N in the drainage water before and after urea application. The arrow mark indicates the fertilizer application. The first drainage was collected one month after urea application. The nitrate concentrations were much lower than concentrations of chloride in drainage. The nitrate concentration in drainage from paddock A fluctuated from 1.0 to 3.5 g m<sup>-3</sup>, hardly a marked fluctuation. An even smaller fluctuation was observed in paddock B.

Comparing the concentration of nitrate-N in the drainage samples before and after the application of urea, it appeared that the application of urea did not cause any substantial increase in the rate of leaching of nitrate. The impact of the small quantity of urea (50 kg N/ha) added was negligible. The vigorously growing pasture was able to draw on the N from both the fertilizer and soil reserve. Nitrate-N concentrations were low when the urea was applied and they stayed low in the subsequent drainage. Low nitrate concentrations were also recorded in 1990 and 1991 for these paddocks by the end of winter. This contrasts with Wild and Cameron (1980) and Haigh and White (1986) who found that a secondary nitrate concentration peak occurred in spring after fertilizer application. A study group in United Kingdom (Anon., 1983) reported that after cold and wet winters nitrate leaching becomes negligible by early summer when plant growth accelerates and evapotranspiration exceeds rainfall. Plant uptake of N during this period of the year probably accounted for most of the applied N (Field and Ball, 1978). Any remaining N may have been immobilized by soil microorganisms.

#### 6.2.3.2. 1990 Drainage season

Nitrate concentration in the drainage collected from paddocks A and B is given in Figure 6.6. Drainage which occurred in early March was not collected. Drainage started again in April 1990. For paddock A, the nitrate concentration in the drainage started at about 17 g m<sup>-3</sup> and increased to about 33 g m<sup>-3</sup> after 35 mm drainage and

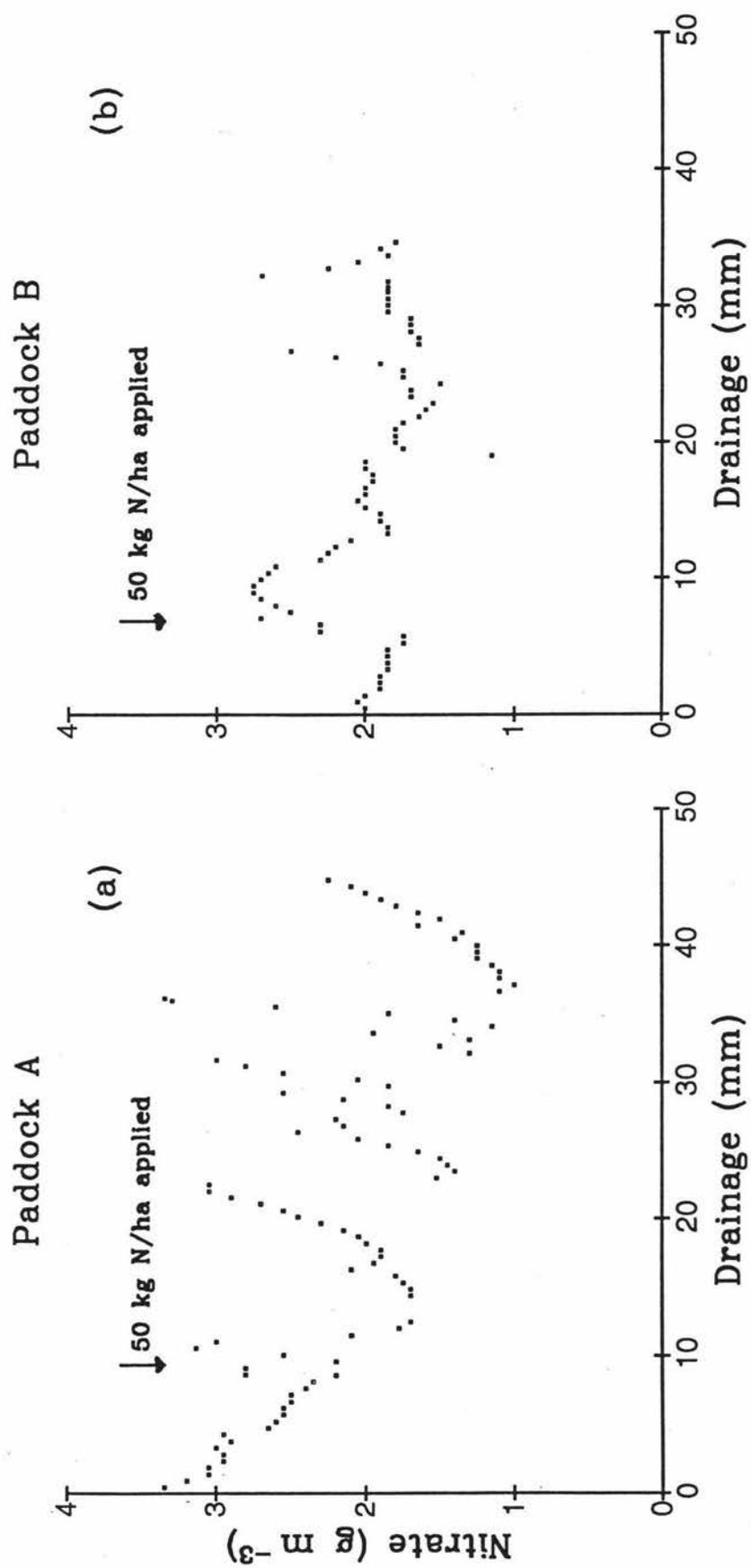


Fig. 6.5 Nitrate concentration in the drainage water before and after urea application on 13 September 1989

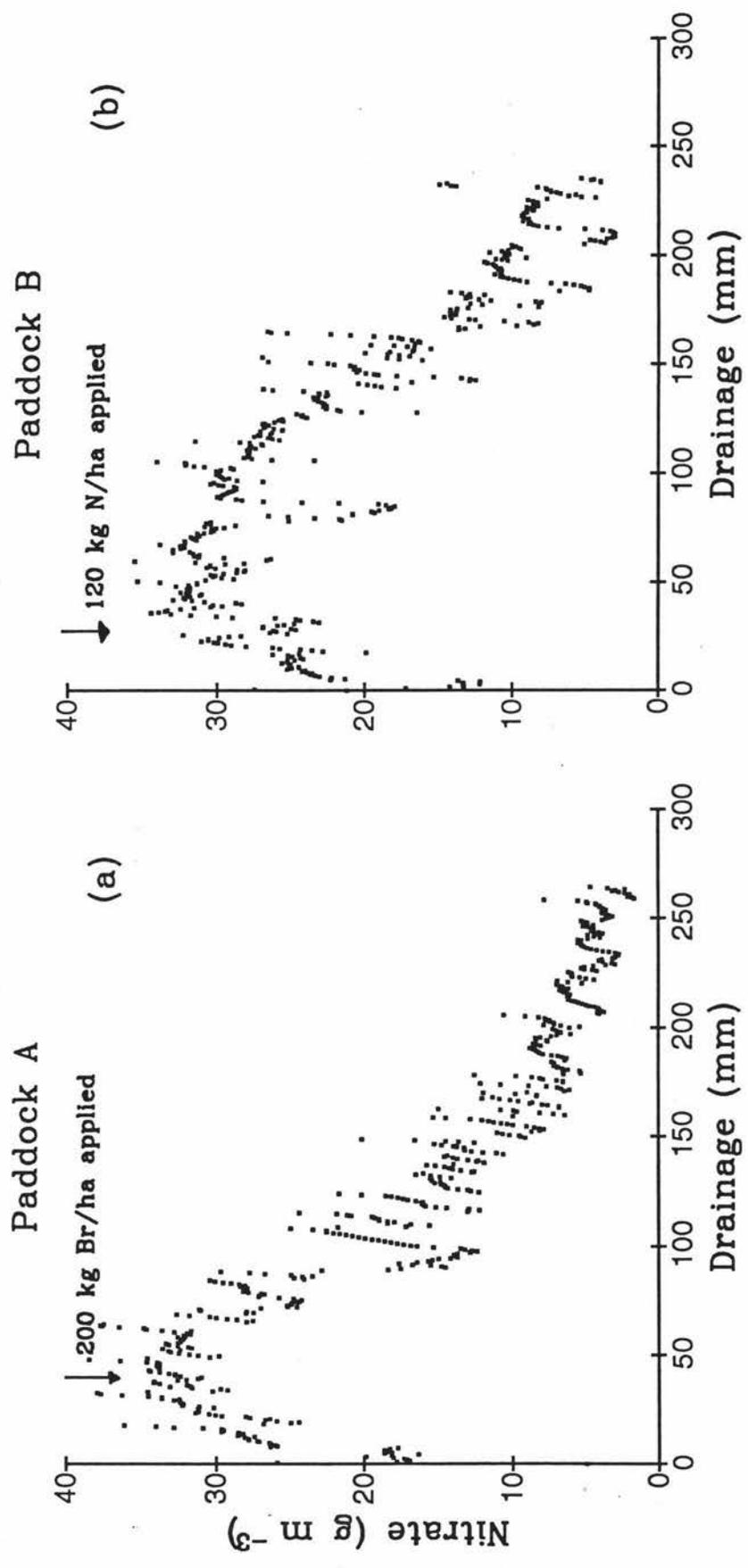


Fig. 6.6 Nitrate concentration in the drainage water collected during the 1990 drainage season

maintained approximately that value for the next 35 mm drainage. The concentration then decreased slowly to about  $3 \text{ g m}^{-3}$  after 260 mm drainage. The pattern of nitrate concentration in the drainage from paddock B was somewhat similar to the one from paddock A. However, after 100 mm of drainage the concentration from paddock B was slightly higher than from paddock A. Urea was applied to paddock B after 25 mm of drainage was collected (shown by an arrow mark on the figure), when the concentration had almost reached the peak value. Because of the urea application, it appeared that the peak in nitrate concentration in paddock B was maintained for a longer period than in paddock A before decreasing. The concentration eventually reached a final value similar to paddock A after 235 mm drainage.

✧ The concentration of nitrate is usually high at the start of the drainage season and decreases as time progresses (Sharpley and Syers, 1979; Turner *et al.*, 1979; Wild and Cameron, 1980; Haigh and White, 1986; Heng *et al.*, 1991). Here, the first drainage event of the season was missed. But after that the concentration in the drainage increased from a lower to a peak value. This could be due to the heavy rainfall during the summer as was observed in 1991 (Section 6.2.3.3). The amounts of nitrate-N leached during the drainage period (4 May to 28 August 1990) from paddocks A and B were 44 and 50 kg/ha, respectively.

The amount of drainage collected before fertilizer application from paddock A was 33 mm containing 9 kg N/ha, and from paddock B was 25 mm containing 6 kg N/ha. If the same amount of drainage had been collected from both paddocks, then the difference between the amounts collected would be negligible. The amount of drainage collected for the period between the day of urea application (29 May 1990) and the last day of drainage from paddock B was 210 mm, which contained 43 kg N/ha. If the same calculation is done for paddock A for the same period, the amount of nitrate-N leached was 34 kg N/ha. The difference between these two paddocks would then be 9.6 kg/ha which apparently came from the fertilizer applied. Thus, only 8 % ( $9.6 \text{ kg} / 120 \text{ kg} \times 100$ ) of the applied fertilizer appears to have been leached. Ball and Ryden (1984) reviewed N relationships in intensively managed temperate grasslands and concluded that generally no more than 5-15 % of fertilizer input is lost through leaching and denitrification.

Two grazing events occurred at approximately after 10 mm and 150 mm of drainage during the 1990 drainage period but no appreciable increase in nitrate or chloride concentrations was observed.

### 6.2.3.3. *1991 Drainage season*

The concentration of nitrate in the drainage in 1991 is given in Figure 6.4. The nitrate concentrations were lower than in 1990. The concentration in drainage from paddock A started at  $32 \text{ g m}^{-3}$ , decreased to  $14 \text{ g m}^{-3}$  at high flow rate and then increased to  $30 \text{ g m}^{-3}$  when the drainage rate for that event declined. Similarly, the concentration of nitrate in the drainage from paddock B started at  $27 \text{ g m}^{-3}$ , decreased to  $20 \text{ g m}^{-3}$  and then increased to  $26 \text{ g m}^{-3}$  at the end of the event. The amounts of nitrate leached during this particular event from paddocks A and B were 6.4 and 2.4 kg N/ha, respectively. The difference was due to the different amounts of drainage collected.

Drainage from both paddocks started again on 11 April 1991. For paddock A, the concentration was  $9 \text{ g m}^{-3}$  at the start, decreased during the highest flow rate and increased. After about 70 mm of drainage (17 May 1991), the concentration reached a peak of  $20 \text{ g m}^{-3}$  and then decreased steadily to  $0.4 \text{ g m}^{-3}$  after 336 mm drainage by 26 August 1991. The amount of N leached for the drainage season was 23 kg N/ha.

For paddock B, the concentration was  $7 \text{ g m}^{-3}$  at the start of the second drainage event, decreased during the highest flow and then increased. After about 36 mm of drainage (17 May 1991) the concentration reached a peak of  $26 \text{ g m}^{-3}$  and then decreased to  $0.3 \text{ g m}^{-3}$  after 296 mm drainage. Although the amount of drainage collected from paddocks A and B was different, the peak concentration was obtained on the same day. The amount of nitrate leached from paddock B for the drainage season was 17 kg N/ha.

Although cumulative drainflow was greater in 1991 than 1990, the amount of nitrate leached in 1991 was almost 50 % less than that in 1990. The change in solute concentration in the drainage during 1990 and 1991, especially nitrate, was probably associated with two factors: (1) the summer of 1989-90 was drier than that of 1990-

1991. Increased nitrate levels in drainage have been reported by Williams (1976), Garwood and Tyson (1977), Foster and Walling (1978) and Haigh (1985) following very dry summers; (2) the grazing periods were longer and the stocking density was greater during the summer of 1989-90 compared to that of 1990-91. These factors probably combined to give increased solute concentrations in the soil solution of the paddocks after the summer of 1990 compared to that of 1991. This increased solute concentration in the soil solution should be reflected in increased concentrations in drainage. The difference between years illustrates the dangers inherent in assuming one year's data are typical of all years.

In general, the concentration decreased as the leaching period progressed. The early part of 1991 consists of 2 major events, the first on 18 February, the second on 11 April 1991. Both of these (in both paddocks) show the "dilution effect", preferential flow of water through macropores bypassing much of the resident soil nitrate (Scotter and Kanchanasut, 1981). However, by 17 May the soil appears to have returned to "field capacity" and the expected pattern of leaching ensues - that is, an exponentially decreasing concentration of nitrate in the drainage with increasing cumulative drainage. If the drainage collected in February was not considered, then the pattern would be similar to the one observed in 1990 (an initial increase and then a decrease). The decrease in nitrate concentration between the end of the 18 February event and the start of the 11 April event could well be due to plant uptake of N exceeding any increase in soil mineral N through net mineralization.

The leaching pattern of chloride was similar to that of nitrate (Figure 6.4). This is similar to the results of Wetselaar (1962). The peak concentration of both nitrate and chloride in both paddocks was reached on the same day (17 May 1991) showing the similar behaviour of indigenous solutes. It appears that during the drainage season only leaching and plant uptake are major factors, because if biological transformations such as immobilization and mineralization were very important, they would have affected nitrate and not chloride. As a result the leaching patterns of nitrate and chloride would have been different.

### 6.3. DRAINFLOW RATES AND SOLUTE CONCENTRATIONS

In this section individual drainage events which occurred early and late in the 1990 drainage season are discussed. Hydrographs from mole drains have been found to be very "peaky" in nature (Childs, 1943; Leeds-Harrison *et al.*, 1982) and this peakiness is typically retained in the hydrographs of mole-tile systems (Trafford and Rycroff, 1973; Armstrong, 1983; Harris *et al.*, 1984). This could be due to a network of natural and artificial macropores connecting mole drains with the soil surface (Scotter and Kanchanasut, 1979; Leeds-Harrison *et al.*, 1982). Both paddocks had similar hydrographs in terms of their shape and response time. But in some of the drainage events the flow rate in paddock A was greater than in paddock B. In all hydrographs, a quick response to changes in rainfall intensity at peak flow rates was observed, with the flow rate declining almost instantly when rain stopped. This quick response is one of the characteristic features of a successful mole drainage system (Jarvis and Leeds-Harrison, 1987). In such drainage events the concentration is expected to vary with drainage flow rate. Thus, the change in concentration of externally applied solutes (bromide for paddock A and urea which hydrolysed and after subsequent nitrification produced nitrate for paddock B) and indigenous solutes (nitrate for paddock A and chloride for paddock B) in the drainage water in relation to drainage flow rate was studied.

#### 6.3.1. Effect of drainage flow rate on solute concentration in the drainage

##### 6.3.1.1. *Applied solutes*

Individual drainage events and their solute concentrations were analyzed and the results are presented in Figures 6.7 and 6.8. Drainage events occurred on 2, 6, 8, 14 and 20 June 1990 after fertilizer application on 29 May 1990. The concentration of applied solutes (bromide for paddock A and nitrate for paddock B) in the drainage water tended to increase during a flow event. An example of one major drainage event (20 June 1990) is shown in Figures 6.7. While high flow in response to rainfall commonly leads to dilution of resident solutes, in this case bromide and nitrate concentrations were maintained and even increased as the flow rate increased. This is an effect of the pulse inputs of Br and urea combined with preferential flow. Similar observations were made by Trudgill *et al.* (1981), Haigh (1985), and Milburn

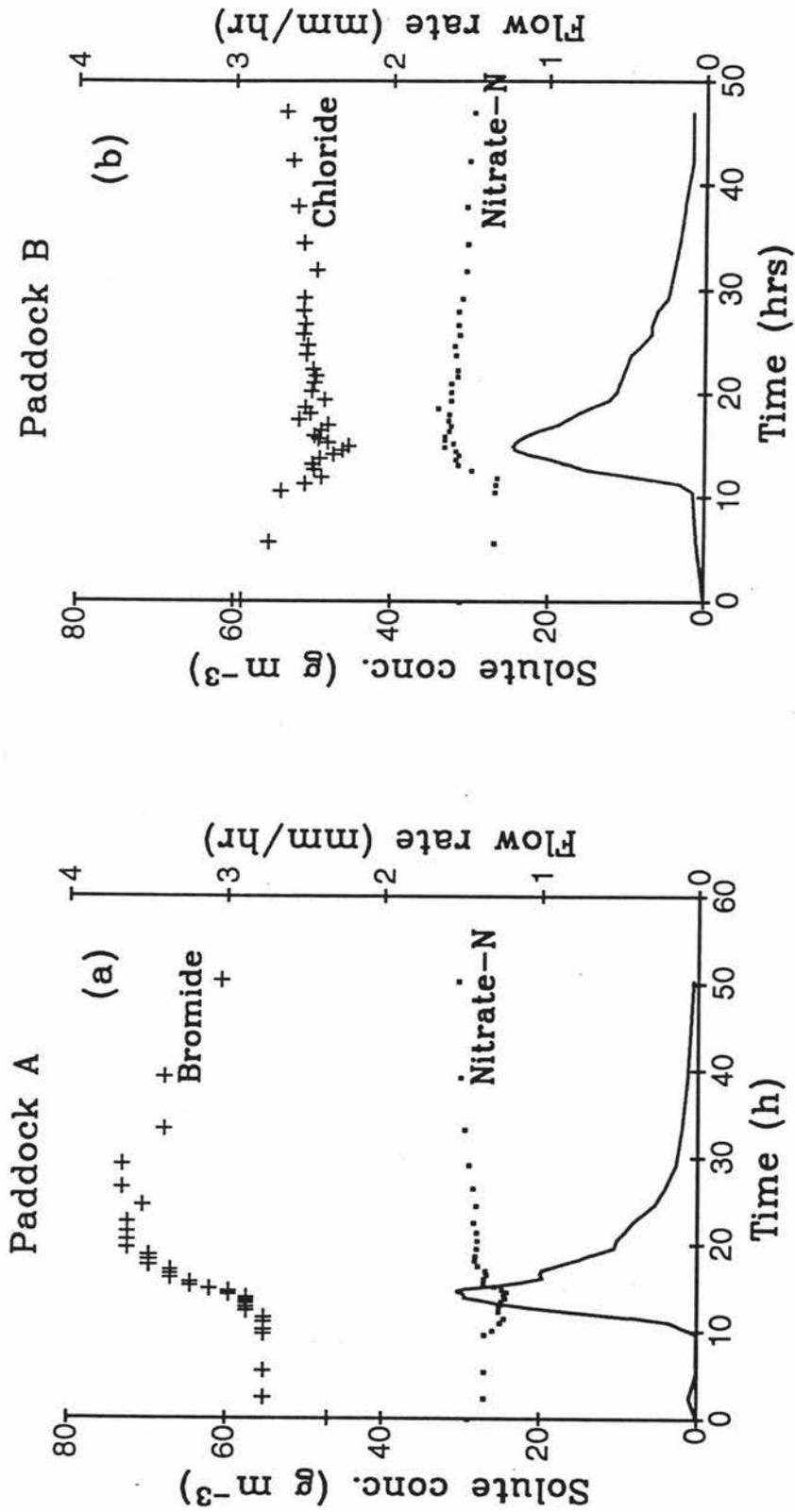


Fig. 6.7. Applied and indigenous solute chemographs for the 20 June 1990 drainage event

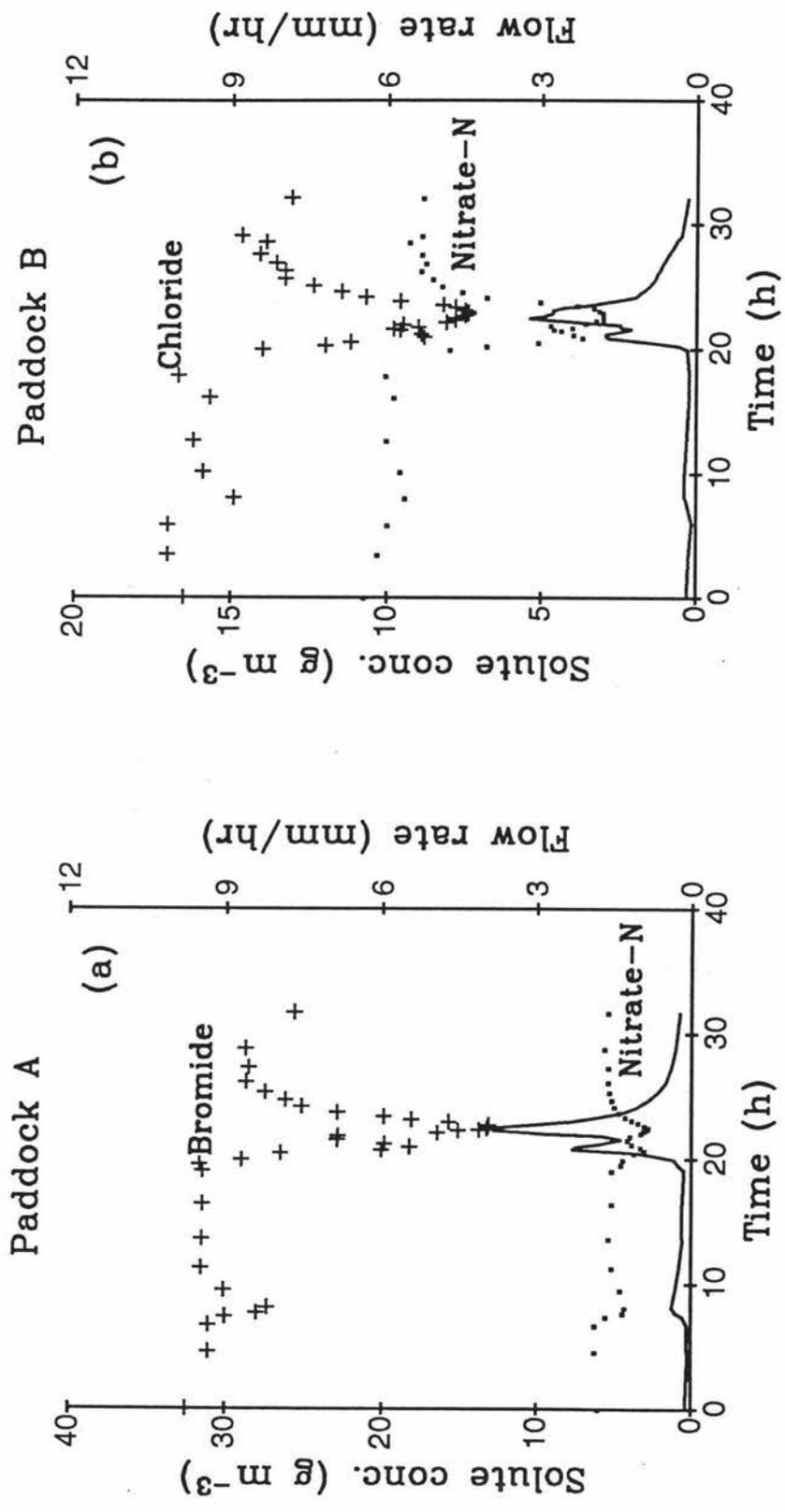


Fig. 6.8. Applied and indigenous solute chemographs for the 14 August 1990 drainage event

*et al.* (1990). Mohammed *et al.* (1984) observed that the greatest losses of bromide and native soil N per mm of drainage were from the early drainage events and they were related to the occurrence of preferential flow. However, later in the drainage season the concentration of applied solutes changed inversely with the drainage flow rate (Figure 6.8). Milburn *et al.* (1990) also found that the concentration of nitrate increased with increased in the drainage flow rate soon after the fertilizer application, but the concentration of nitrate decreased with an increase in drainage flow rate at a later time.

#### **6.3.1.2. Resident solutes**

Chemographs of indigenous nitrate (paddock A) and chloride (paddock B) were also studied (Figures 6.7 and 6.8). The concentration in the drainage was inversely related to flow rate, as expected. This form of chemograph is probably caused by low concentration rain water mixing with higher concentration mobile soil solution. At high flow rates the input water moves through the soil more rapidly, resulting in less mixing with the mobile soil solution and consequently lower concentrations in the drainage water. This behaviour was observed both early and late in the drainage season.

In summary, early in the drainage season the concentration of an applied solute increased with increasing flow rate, and then decreased as the flow rate decreased; while the indigenous solute concentration decreased with the increasing flow rate and increased with decreasing flow rate. However, over time applied solutes became indigenous and the chemographs of all solutes show a similar form, with a dilution of the mobile soil solution by rain water occurring. Clearly, the longer the time interval between the application of a solute (Br or urea) and a drainage event, the less meaningful is the distinction between an applied (introduced) solute and a resident (indigenous) solute.

### **6.4. COMPARISON OF SOLUTE CONCENTRATIONS IN DRAINAGE AND SOIL SOLUTION**

A comparison of solute concentrations in the soil solution as measured by soil

extraction and suction cup samples was given in Figures 5.18 and 5.19. Soil extraction concentration is given for the 150-250 mm and 350-450 mm depth. Suction cup results are for the samples collected at about 200 and 450 mm depth. The drainage samples were collected at 450 mm depth from the mole drains. Here we compare the solute concentration in the drainage with the soil solution concentration. Average solute concentrations in the drainage was calculated by dividing the amount of solute leached in a particular event by the amount of drainage collected during that event.

The average bromide concentration in the drainage water from paddock A one month after bromide application was  $80 \text{ g m}^{-3}$ . This value was greater than soil solution extraction concentrations at both depths ( $66$  and  $26 \text{ g Br m}^{-3}$  at upper and lower depths, respectively). But it is less than suction cup concentration at the upper depth ( $125 \text{ g Br m}^{-3}$ ) and greater than at lower depth ( $27 \text{ g Br m}^{-3}$ ). This shows preferential flow has occurred. One month later, the concentration of bromide in the drainage was  $49 \text{ g m}^{-3}$  which is greater than the soil extraction concentrations in both depths ( $26 \text{ g Br m}^{-3}$ ), but lies between the suction cup concentrations at the two depths ( $41$  and  $57 \text{ g m}^{-3}$  at the upper and lower depths, respectively). At the final sampling in August the bromide concentration in the drainage was  $23 \text{ g m}^{-3}$ . Once again it is greater than the soil extraction concentration at both depths ( $4$  and  $15 \text{ g Br m}^{-3}$ ) and lies between the suction cup concentrations at the upper and lower depths ( $12$  and  $38 \text{ g m}^{-3}$ ). Thus for an externally applied solute the flux-averaged concentration (measured in the drainage) was greater than its volume-averaged concentration in the soil solution, and also intermediate between the concentration measured in suction cup samples at the upper and lower depths. Note that simple averages of the upper and lower suction cup concentrations are  $76$ ,  $49$  and  $25 \text{ g m}^{-3}$  which are remarkably close to the drainage concentrations at these dates in Table 6.1.

On 28 May 1990, concentration of chloride in drainage water from paddock B was  $63 \text{ g m}^{-3}$ , which lies between the soil extraction concentrations at the two depths ( $69$  and  $53 \text{ g m}^{-3}$ ). The value was greater than the suction cup concentrations at both depths ( $45$  and  $36 \text{ g m}^{-3}$ ). On 29 June 1990 the chloride concentration in drainage was  $48 \text{ g m}^{-3}$ , which once again lies between soil extraction concentrations at the two

depths (41 and 64 g m<sup>-3</sup>). It was greater than the suction cup concentrations of 34 and 35 g m<sup>-3</sup> at the upper and lower depths, respectively. On 31 July 1990, the drainage chloride concentration was 28 g m<sup>-3</sup> which is close to the soil extraction concentration at the upper depth (33 g m<sup>-3</sup>) but much less than that at the lower depth (77 g m<sup>-3</sup>). However, 28 g m<sup>-3</sup> is almost the average of the suction cup concentrations at the two depths (15 and 38 g m<sup>-3</sup>). At the last sampling, the drainage chloride concentration was 19 g m<sup>-3</sup> which was lower than the soil extraction concentration at both depths. But once again it is close to the average of the suction cup concentrations at both depths (11 and 26 g m<sup>-3</sup>). So, if the solute is indigenous, it appears that the drainage concentration is close to soil extraction concentration early in the drainage season, but closer to the suction cup concentration later in the drainage season.

Nitrate concentrations in drainage from paddock A, where no urea applied, were closely related to soil extraction concentration throughout drainage season. Drainage concentrations were greater than suction cup concentrations, although not markedly so except on 28 May 1990. For paddock B, for the first sampling on 28 May 1990, a day prior to urea application, the drainage concentration was close to the soil extraction concentration. But at the second and fourth sampling the drainage concentration was slightly greater than both suction cup and soil extraction concentrations.

The amount of solute leached depends on the concentration and amount of water passing through the soil. Two simple approaches to estimating the concentration of the moving water are by soil extraction and suction cup sampling. Predicted seasonal leaching losses were then calculated as the sum of the products of monthly predicted drainage and the estimated concentration of the moving water. Table 6.2 shows the resulting predicted and measured losses from mole-tile drainage. The prediction was made by using the estimated solute concentrations obtained separately for upper and lower depths, but the average over a monthly period. The prediction was generally disappointing. Table 6.3, once again, shows the predicted and measured losses. But here the estimated concentration was taken as an average of measured concentrations at the lower and upper depths, and also the average over a

**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)

Date	Flow (mm)	Paddock A		Paddock B	
		Bromide	Nitrate	Nitrate	Chloride
28.5.90	32	2 (0.2)	32 (0.8)	26 (0.6)	63 (1.6)
29.6.90	114	80 (3.6)	20 (0.6)	29 (0.8)	48 (2.8)
31.7.90	176	49 (1.2)	9 (0.8)	20 (1.1)	28 (2.2)
27.8.90	260	23 (1.6)	3 (0.3)	9 (1.8)	19 (2.3)

**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

Solute	Predicted losses (kg/ha)				Loss measured in drainage (kg/ha)
	From soil extraction data		From suction-cup solution data		
	Upper	Lower	Upper	Lower	
Bromide	71	47	129	82	103
Chloride	93	147	58	80	68
Nitrate	59	35	21	19	35

**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

Solute	Predicted losses (kg/ha)		Loss measured in drainage (kg/ha)
	From soil extraction data	From suction-cup solution data	
Bromide	60	106	103
Chloride	121	70	68
Nitrate	47	21	35

monthly interval. For non-reactive solutes such as bromide (an externally applied solute) and chloride (an indigenous solute) the suction cup data provided better estimates of the leaching losses than did the soil extraction data. This indicates that not all solute present in the soil participates in solute transport. However for nitrate neither of these approaches provided accurate estimates of leaching losses. This was probably due to the dynamic nature and spatial variability of the biological transformations to which nitrate is subject in soil.

## **6.5. MASS BALANCE OF SOLUTES**

### **6.5.1. Bromide**

The monthly mass balance of bromide is shown in Table 6.4. Bromide measurements in drainage, herbage and soil are considered. For soil samples, only the top 450 mm depth is considered. It was assumed that sources such as rainfall and grazing animals supplied negligible amounts of bromide.

With the amount of bromide recovered (24.6 kg/ha between 450 and 1000 mm depth) below mole depth on 5 October 1990, the total recovery of bromide was 87.2 % of the applied bromide on that date. This relatively high recovery allows the data to be treated with some confidence.

### **6.5.2. Chloride and nitrogen**

The mass balance for chloride is given in Table 6.5. Initial soil samples were taken on 5 April 1990 and the final sampling was on 10 August 1990. The pasture utilization coefficient was assumed to be 80 % under mob-grazed conditions so that herbage chloride and nitrogen consumed during grazing was considered as 80 % of that present in the herbage. The amount of chloride and nitrogen deposited through animal excreta (dung and urine) was not measured in this experiment, but assumed to be 85 % of the intake amount. Since the measured concentration of nitrate in rainfall was negligible, atmospheric N input was taken as zero.

For the soil, the solute mass balance implies that the change in storage equals output minus input. Inputs are fertilizer, rainfall and animal return. Outputs are by leaching

**Table 6.4.** Bromide recovery (kg Br/ha) for various periods of the 1990 drainage season for paddock A

Paddock A	29.5.1990 to 29.6.1990	29.5.1990 to 31.7.1990	29.5.1990 to 27.8.1990	29.5.1990 to 5.10.1990
Drainage	34	78	103	103
Herbage	9	12	16	27
Soil	97	50	13	20
Sum	140	139	132	150
Percentage of applied	70 %	70 %	66 %	75 %

**Table 6.5.** Chloride and nitrogen mass balance for 1990 (between 29 May and 10 October 1990). The units are kg/ha.

Components	Chloride		Nitrogen	
	Paddock A	Paddock B	Paddock A	Paddock B
Fertilizer	0.0	0.0	0.0	+120.0
Rainfall	+ 19.0	+ 19.0	0.0	0.0
Animal return	+ 32.0	+ 30.0	+ 58.0	+ 68.0
Δ Herbage	- 28.0	- 28.0	- 81.0	-103.0
Leaching	- 97.0	- 85.0	- 43.0	- 49.0
Algebraic sum	- 74.0	- 64.0	- 66.0	+ 36.0
Δ Soil	- 35.0	- 45.0	- 45.0	- 50.0
Discrepancy	+ 39.0	+ 19.0	+ 21.0	- 86.0

and in the herbage grown between the start and end of the monitoring period.

For paddock A, 21 kg N/ha was apparently gained by the system whereas for paddock B, a loss of 86 kg N/ha was not accounted for. It was assumed that most of the unaccounted for nitrogen was immobilized when the urea was applied during late autumn. Also, there could have been some loss through volatilization or denitrification.

The factors which could account for the discrepancies in the bromide, chloride and nitrate balances are:

- (1) Solute accumulation by plant roots. As mentioned in Chapters 2 and 5, the measured data constitutes only the aerial section of the plants. It is assumed that the root biomass (and hence solute content) remains approximately constant over the measurement period. Since the plots were not heavily grazed and moisture was not limiting, this is a reasonable assumption.
- (2) Non-uniformity of urea and NaBr application.
- (3) For ease of sampling the soil samples tended not to include plant crowns, and the soil directly under them. Thus, due to interception and stem flow (Scotter and Kanchanasut, 1981), an unconscious bias probably occurred in the soil sampling, and this was probably one of the main reasons for the unaccounted for bromide.
- (4) In the case of nitrogen, biological transformations were not taken into account. It was possible that some of the N was immobilized in a form such that it does not reappear during the measurement period (hence is not detected in the soil, herbage or drainage components).
- (5) Movement below mole depth. It has been shown that some Br moved below mole drain depth.

## 6.6. CONCLUSIONS

The important conclusions that can be derived from this chapter are

- (a) Application of urea in Spring (1989) did not cause any substantial increase in the rate of leaching of nitrate. Vigorously growing pasture could have drawn

N from the fertilizer applied.

- (b) Although the cumulative drainflow was greater in 1991 than 1990, the amount of nitrate leached in 1991 was almost 50 % less than that in 1990. This was apparently due to the lower amount of nitrate present in the soil at the start of drainage season in 1991, due to less net mineralization during a wetter summer/autumn period.
- (c) The solute concentrations in the drainage water varied with the flow rate. Early in the drainage season the concentration of applied solute tended to increase with the increasing flow rate, whereas indigenous solutes decreased with increasing flow rate. However, later in the drainage season both applied and indigenous solutes behaved similarly, their concentrations being inversely related to flow rate.
- (d) Sheep grazing had little obvious effect on the concentration of solutes in the drainage collected after grazing.
- (e) In general, it was difficult to relate solute concentration in the drainage to that resident in the soil solution. For an applied solute such as bromide, the drainage concentration was closely related to the suction cup concentration throughout the drainage season. For indigenous chloride, the drainage concentration was related to the average value of suction cup concentrations at two depths. However for nitrate, neither suction cup concentration nor soil extraction concentration estimated adequately the drainage concentration.

## CHAPTER 7

### MODELLING MOVEMENT OF BROMIDE AND CHLORIDE UNDER FIELD CONDITIONS

#### 7.1. INTRODUCTION

As mentioned in Chapter 1, the overall aim of this study was to investigate the leaching of nitrate from soil under field conditions. However, before modelling nitrate leaching data, appropriate model parameters derived from field experiments using other tracers were obtained. Bromide and chloride, conservative and non-reactive solutes, were the tracers used.

Bromide and chloride leaching data obtained in the field (see Chapter 6) are modelled using transfer functions. Two approaches are followed. In the first approach, which is analytical, source-sink terms are treated as linear with drainage as explained later. If the plant uptake can be assumed to occur at the soil surface, is approximately linear with drainage and there is no grazing, and if the atmospheric input concentration in rainfall is constant, then the source-sink term can be treated simply. However, realistically, this simple situation would not normally arise. For example, there may be a dry period in winter, or grazing may occur. Under those situations the source-sink term needs to be treated as non-linear with drainage. In this second approach, which involves numerical solution of the transfer function equation, the source-sink terms are treated as non-linear functions of drainage, although plant uptake is still assumed to occur at the soil surface. This approach is discussed in the next chapter. In all cases, analytical forms of the probability density function for solute travel, either log-normal or exponential, are assumed.

A more specific objective of the work described in this chapter was to use the chloride and bromide data to get the probability density functions (pdf) for solute travel and to see if they are stationary from one drainage season to the next. Two experimental situations may be used to evaluate the pdf. The first is a Dirac delta pulse input in the flux. Surface applied fertilizer has been assumed to approximate as a Dirac delta pulse input (e.g. White, 1987; Heng, 1991). Second, a constant flux-

averaged concentration different to the soil solution concentration may be applied continuously at some time. This corresponds to a step change in input concentration (Heng, 1991). For these boundary conditions and certain analytical pdfs, the transfer function equation has analytical solutions from which the parameters in the pdf can be evaluated. The solutions for these two boundary conditions are given in the brief theory section below. Detailed theory relevant to a mole-pipe drained field is presented by Heng (1991). Some ways of accounting for the source-sink term are discussed.

## 7.2. THEORY

As discussed in Chapter 1, the "net applied water" form of the transfer function equation for steady flow of a conservative, non-reactive solute through soil from an input to an output surface is

$$C_{ex} = \int_0^I C_{ent}(I') f(I - I') dI', \quad (7.1)$$

where  $C_{ex}$  and  $C_{ent}$  are the output and the input concentrations [ $M L^{-3}$ ] respectively,  $I$  is net rainfall or drainage [L], and  $f(I)$  is the probability density function (pdf) [ $L^{-1}$ ] for solute travel through the soil expressed as a function of  $I$ .

Scotter *et al.* (1990) have shown that during and between drainage events the amount of water in the soil to mole drain depth varies less than 10 % and can be considered fairly constant. Under situations where changes in soil water storage can be ignored, and  $f(I)$  is not strongly dependent on the drain flow rate, Eq. (7.1) can adequately describe the movement of a conservative solute to a mole drain, even though the flow is not steady.

Eq. (7.1) has solutions which can be applied to different practical situations of interest. The solution of Eq. (7.1) for a solute of magnitude  $M_o$  [ $M L^{-2}$ ] applied as an impulse in the water flux at a certain time (Dirac delta input) is (White *et al.*, 1992)

$$C_{\alpha}(I) = M_o f(I) . \quad (7.2)$$

Surface application of a soluble tracer or fertilizer may approximate this boundary condition. For a step change in  $C_{out}$  from  $C_a$  to  $C_b$  at  $I = 0$  the solution is (White *et al.*, 1992)

$$C_{\alpha}(I) = C_a + (C_b - C_a) P(I) \quad (7.3)$$

where  $P(I)$  is the cumulative distribution function, defined by

$$P(I) = \int_0^I f(I') dI' . \quad (7.4)$$

Equation (7.3) can be applied to a situation where there is an initially uniform soil solution concentration,  $C_a$ , and a solution with a concentration  $C_b$  is applied to the surface for  $I \geq 0$ .  $C_b$  can also be considered as a net source/sink term, on the assumption that the sources and sinks are concentrated at the soil surface, and are proportional to  $I$ . As Equations (7.2) and (7.3) are linear, they can be superimposed to give (Heng, 1991)

$$C_{\alpha}(I) = M_o f(I) + C_a + (C_b - C_a) P(I) . \quad (7.5)$$

Equation 7.5 is the form in which the TFM is used here, assuming a linear source/sink term. Two analytical forms of the pdf are considered, log-normal and exponential. A lognormal distribution is considered for the pdf because it has been found to describe solute travel times or velocities in the field (Jury *et al.*, 1982) and in large cores (White *et al.*, 1984; White and Magesan, 1991). As discussed earlier the equation of a log-normal pdf is (Jury *et al.*, 1986; Dyson and White, 1987)

$$f(I) = \frac{\exp[-(\ln I - \mu)^2 / 2\sigma^2]}{\sqrt{2\pi} \sigma I} \quad (7.6)$$

where  $\mu$  and  $\sigma$  are the mean and standard deviation, respectively, of the log-normal distribution. Substituting Equation (7.6) into Equation (7.4) and integrating gives

$$P(I) = \frac{1}{2} \{1 + \operatorname{erf} [\frac{\ln(I) - \mu}{\sqrt{2}\sigma}]\} \quad (7.7)$$

for a log-normal pdf. Assuming an effectively well-mixed system, Scotter *et al.* (1991) predicted the leaching of chloride to a mole drain reasonably well. Highly skewed log normal pdfs and exponential pdfs may look very similar. Such a model pdf is consistent with a well mixed system in which mixing between the input and resident solutions occurs within a transport volume  $V_{st}$ . The pdf of such a system is of exponential form, i.e.

$$f(I) = a^{-1} \exp(-I/a) \quad (7.8)$$

with

$$P(I) = 1 - \exp(-I/a), \quad (7.9)$$

where  $a$  [L] is a fitted parameter.

The above equations are for solutes not adsorbed by the soil, such as bromide, chloride and nitrate. As explained in Chapter 4 the mean and median pathway lengths, and their corresponding solute transport volumes can be calculated using Equation 4.8.

### 7.3. BOUNDARY AND INITIAL CONDITIONS

In order to use the above equations, the parameters in them need to be evaluated. The amount of bromide applied as NaBr was 200 kg Br ha<sup>-1</sup> on 29 May 1990. However only 84 % of the bromide applied was recovered. The amount recovered was assumed to be  $M_0$ . Soil chloride and water content measurements made just before fertilizer application were used to calculate the initial average values of the soil solution concentration of chloride ( $C_0$ ). The initial resident soil solution concentration of chloride was found to be quite uniform throughout the profile to mole drain depth (c. 72 g Cl m<sup>-3</sup> in May 1990).

### 7.3.1. Source-Sink Term, $C_b$

The source-sink strength was calculated from variables such as plant uptake and atmospheric input.

#### 7.3.1.1. *Rainfall input*

An average of  $4 \text{ g Cl m}^{-3}$  was measured in rainwater over the experimental period. Similar measurements were made by Scotter *et al.* (1991) for the same site. An average contribution to  $C_b$  for chloride in rainfall was obtained by dividing the total rain Cl input over the drainage season by the predicted drainage,  $I$  (Heng, 1991). The estimated contribution to  $C_b$  for chloride in rainfall was  $5 \text{ g Cl m}^{-3}$ . Since negligible concentration of bromide was measured in rainwater, the concentration was assumed to be zero.

#### 7.3.1.2. *Herbage Uptake*

Herbage uptake was assumed to be proportional to predicted drainage (Figure 7.1), and was calculated as described by Scotter *et al.* (1991). The average contributions to  $C_b$  of  $-5.8 \text{ g Br m}^{-3}$  and  $-6.5 \text{ g Cl m}^{-3}$  from herbage uptake were obtained by dividing the total herbage uptake of Br or Cl for the season by the total drainage. It is interesting to note that for chloride the rainfall input was similar to plant uptake.

#### 7.3.1.3. *$C_b$ for bromide and chloride*

$C_b$  values for bromide and chloride were obtained by summing the individual contributions from the source-sink terms discussed above. Thus  $C_b$  values were  $-5.8 \text{ g Br m}^{-3}$  and  $-1.5 \text{ g Cl m}^{-3}$ . Having a negative net  $C_b$  value means that if drainage were to continue long enough, the physical impossibility of a negative concentration would be predicted. However, provided the effect of  $C_b$  is small relative to  $M_0$  and  $C_{ent}$ , assuming a negative  $C_b$  seems a reasonable approximate way to take account of a small net sink term distributed throughout the drainage season (Heng, 1991).

## 7.4. RESULTS AND DISCUSSION

### 7.4.1. Evaluating $f(I)$

The model predictions were obtained using Equation 7.5. A least squares

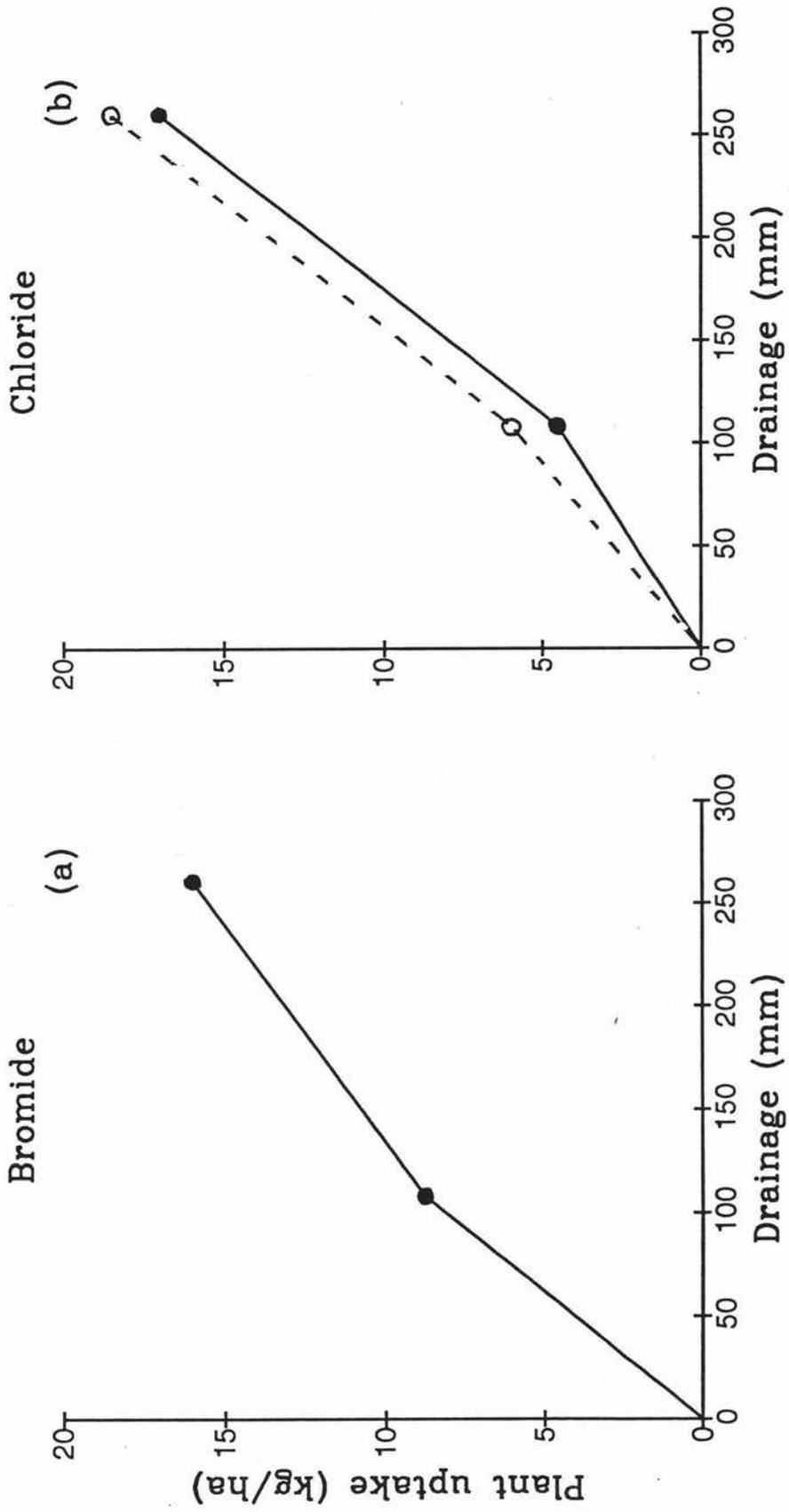


Fig. 7.1. Bromide (a) and chloride (b) uptake by pasture as a function of drainage for paddocks A(●) and B(○)

optimization program was used to find  $\mu$  and  $\sigma$  for a lognormal  $f(I)$  and  $a$  for an exponential form of  $f(I)$  (See Appendices 4 and 5). For bromide  $M_0$  was non-zero and  $C_s$  was zero. For chloride  $M_0$  was zero and  $C_s$  was not.

The measured and simulated drainage bromide concentrations for the 1990 drainage season are given in Figure 7.2. The estimated model parameters are  $\mu = 5.07$  and  $\sigma = 0.81$  for the lognormal  $f(I)$  and  $a = 285$  mm for the exponential form of  $f(I)$ . For bromide, the results show that the log-normal pdf was able to fit the data ( $R^2 = 0.87$ ) much better than the exponential pdf ( $R^2 = 0.02$ ).

The measured and simulated drainage chloride concentrations for paddock A for the 1990 drainage season are given in Figures 7.3. The initial soil solution chloride concentration was  $72 \pm 6$  g Cl  $m^{-3}$ . The best estimates are  $\mu = 4.65$  and  $\sigma = 1.32$  for a lognormal  $f(I)$  and  $a = 163$  mm for an exponential  $f(I)$ . Here the exponential pdf fitted the data ( $R^2 = 0.72$ ) slightly better than the lognormal pdf ( $R^2 = 0.69$ ), despite it having only one rather than two fitted parameters. However, it should be noted that the degrees of freedom for error (residual) in the regression will be slightly greater for the exponential than the lognormal model. The measured and simulated drainage chloride concentrations for paddock B for the 1990 drainage season are given in Figure 7.4. The best estimates are  $\mu = 4.55$  and  $\sigma = 1.14$  for a lognormal  $f(I)$  and  $a = 144$  mm for an exponential  $f(I)$ . In this case both lognormal and exponential pdfs fitted the data equally well ( $R^2 = 0.87$ ). The chloride model parameters derived from both paddocks A and B were similar. So data from the both paddocks were bulked together and the model parameters were estimated from the bulked data (Figure 7.5). The estimated parameters are  $\mu = 4.61$  and  $\sigma = 1.22$  for a lognormal  $f(I)$  and  $a = 151$  mm for an exponential  $f(I)$ . The estimated values are almost equal to the arithmetic mean of the values obtained from the individual paddocks.

The best-fit values of  $\mu$  and  $\sigma$ , or  $a$ , were substituted in equations (7.6) and (7.8), respectively, to obtain the graphs in Figure 7.6. Figure 7.6 shows the pdfs derived from the bromide and chloride data for log-normal and exponential  $f(I)$ . Although both bromide and chloride are conservative and non-reactive solutes, it is interesting

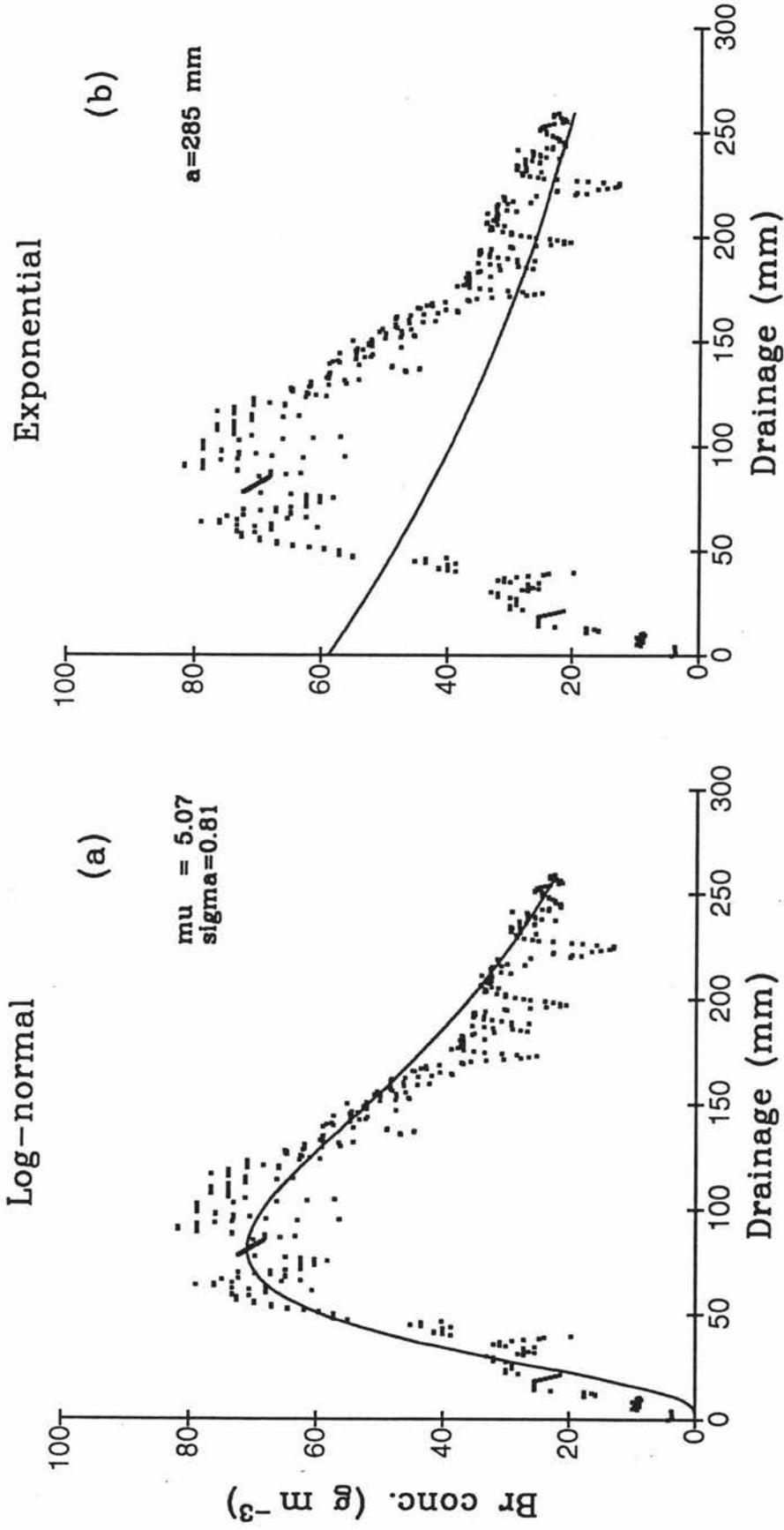


Fig. 7.2. Measured (■) and fitted (—) bromide concentrations in the drainage for the 1990 drainage season with (a) lognormal and (b) exponential pdfs

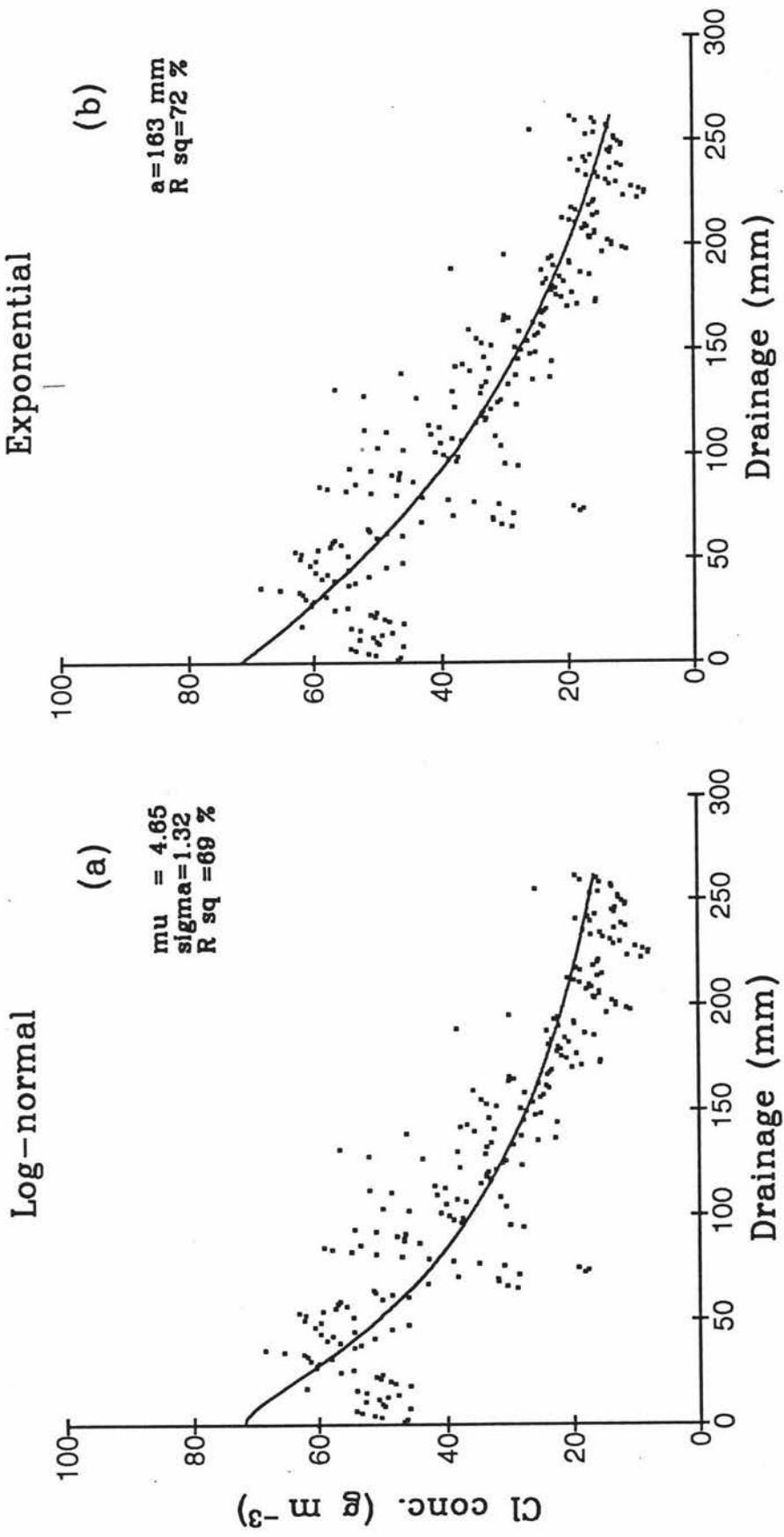


Fig. 7.3. Measured (■) and fitted (—) chloride concentrations in the drainage of paddock A for the 1990 drainage season with (a) lognormal and (b) exponential pdfs

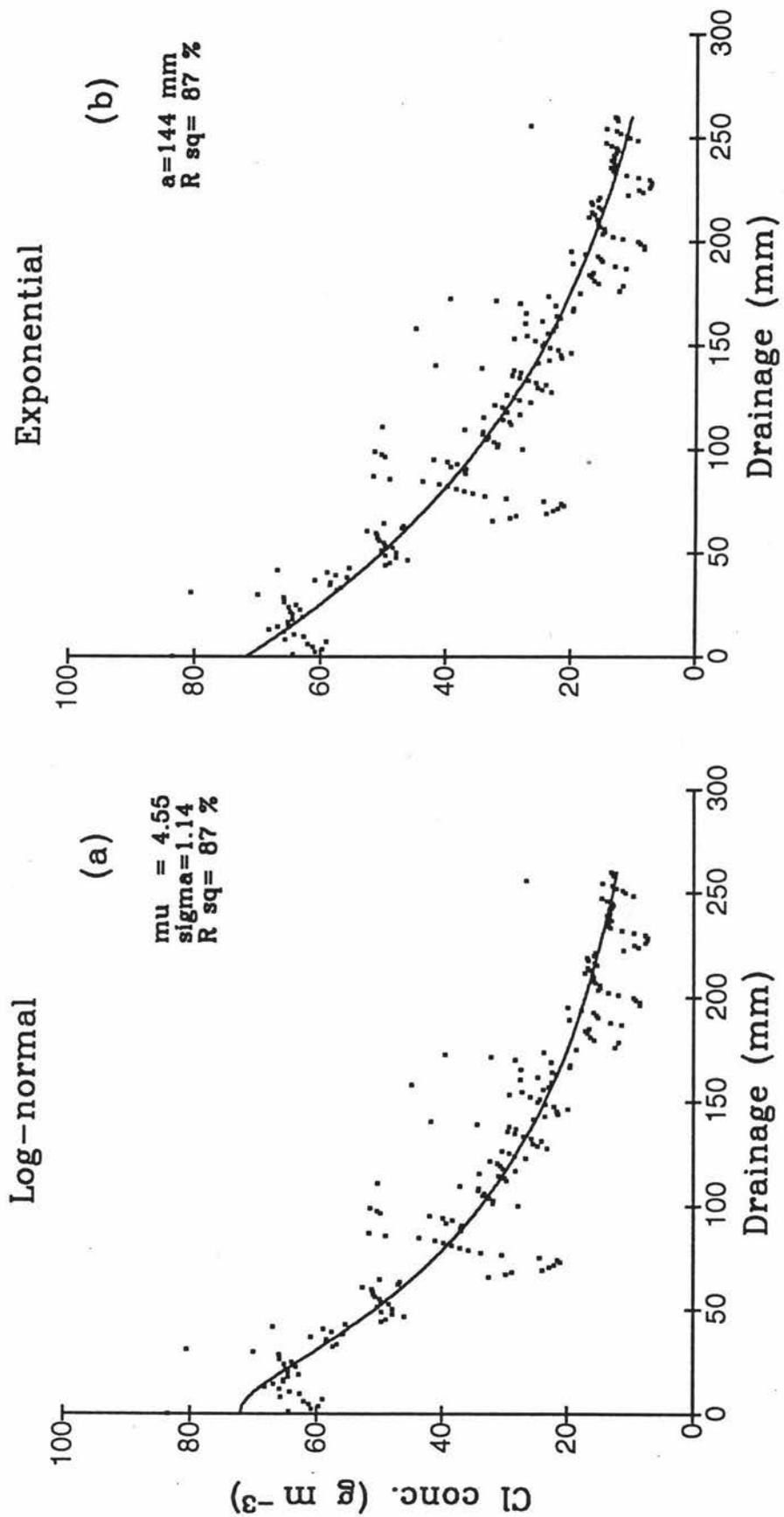


Fig. 7.4. Measured (■) and fitted (—) chloride concentrations in the drainage of paddock B for the 1990 drainage season with (a) lognormal and (b) exponential pdfs

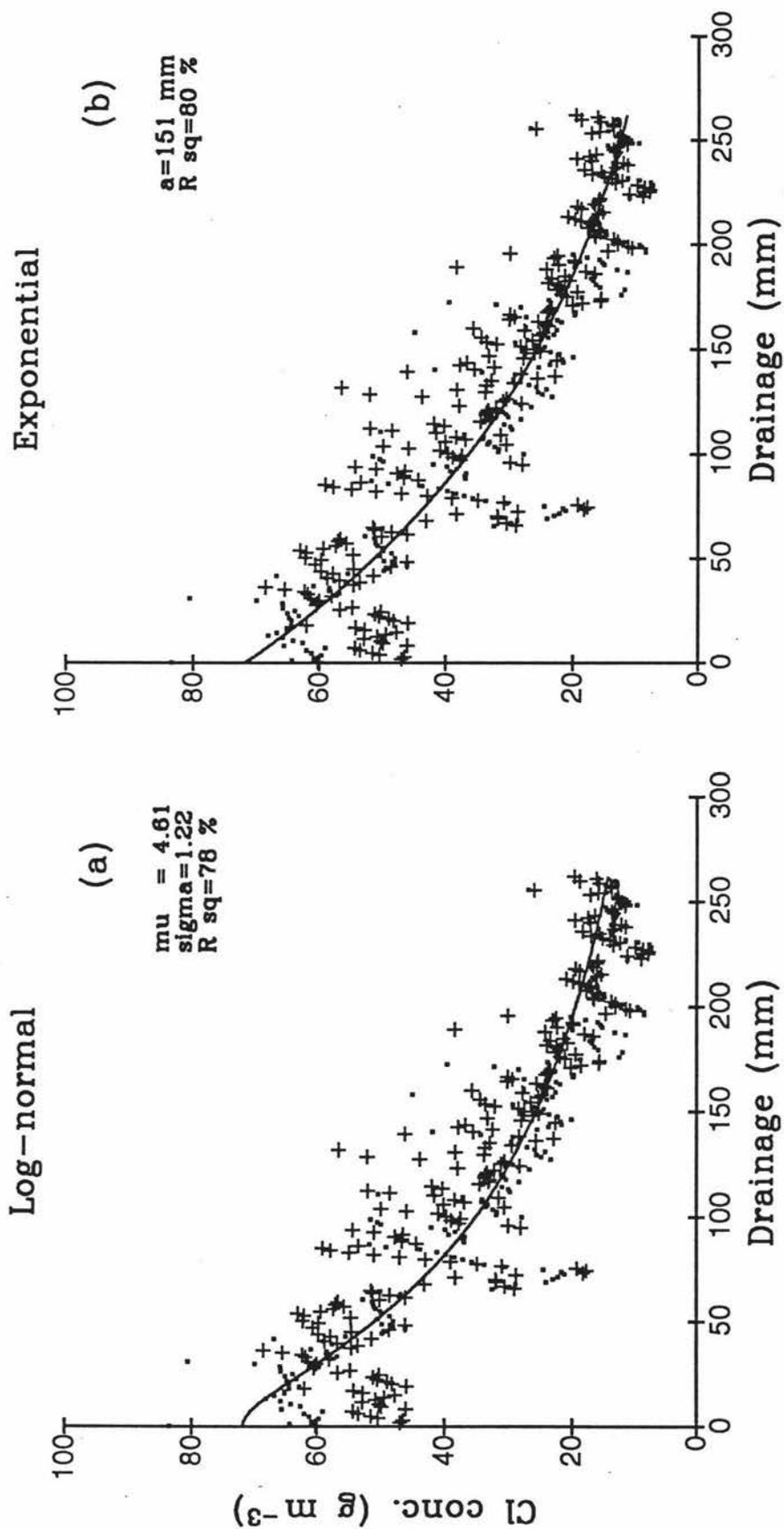


Fig. 7.5. Measured (+ and ■) and fitted (—) chloride concentrations in the drainage of paddocks A and B (data pooled together) for the 1990 drainage season with (a) lognormal and (b) exponential pdfs

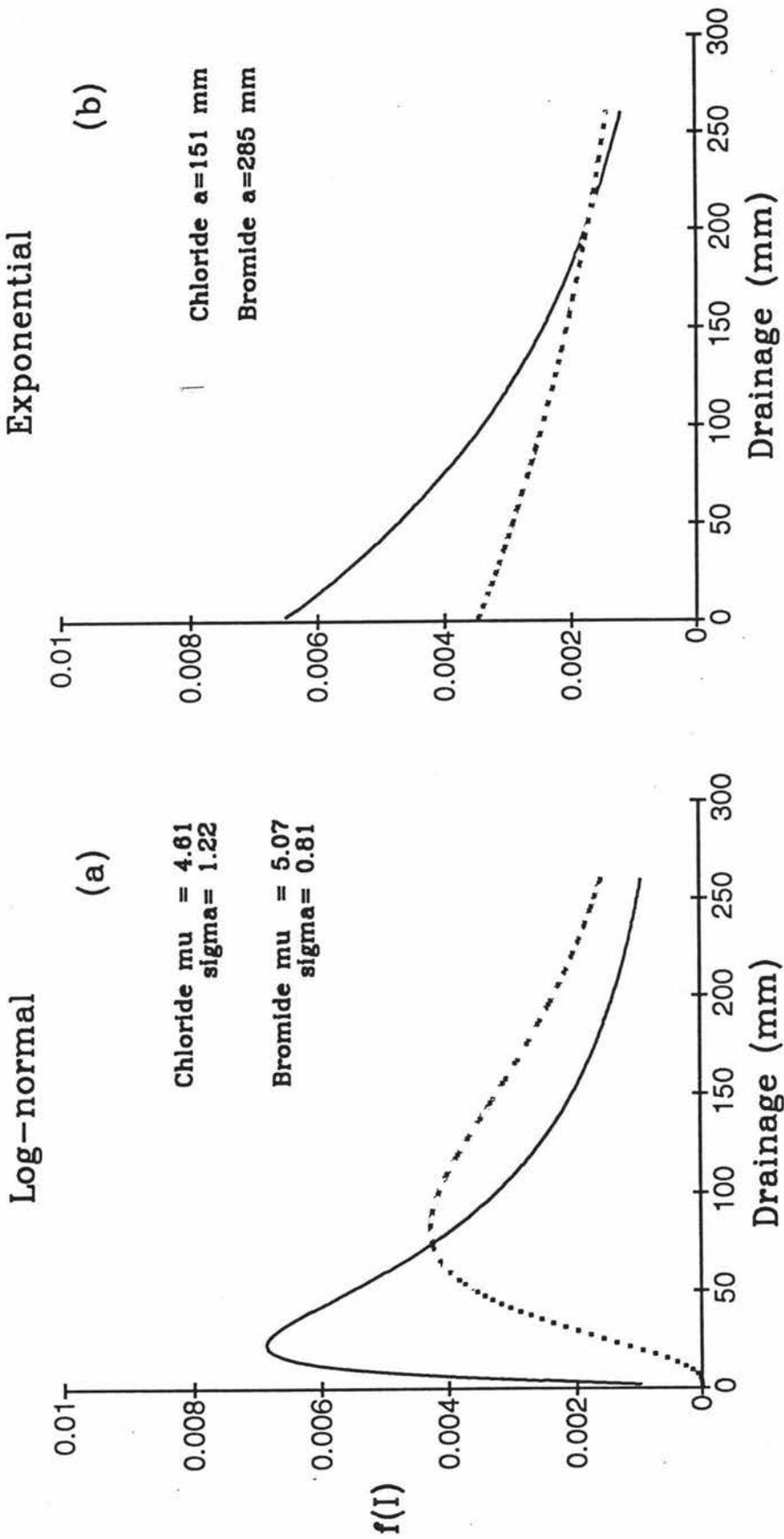


Fig. 7.6. Comparison of pdfs of bromide (---) and chloride (—) with (a) lognormal and (b) exponential

to note that they apparently have very different pdfs whichever analytical form is assumed. The exponential model did not fit the bromide data at all well, therefore there must be considerable uncertainty about the comparison between the exponential pdfs obtained for bromide and chloride (Figure 7.6b). Because four different pdfs are obtained, a natural question is 'Which of these pdfs is the "right" one?' We need to see why these pdfs are different and which of them should be used to predict nitrate leaching. The most likely reason for the difference relates to the assumed boundary condition for bromide. The surface application of solid sodium bromide was assumed to be a Dirac delta pulse in the input flux concentration, as assumed by White (1987) for nitrate and chloride, and Heng (1991) for chloride. This assumption was apparently not valid. Rather than being dissolved by the first rainfall after application, the sodium bromide was probably largely dissolved by hygroscopic condensation. The average volumetric water content of the soil was  $0.40 \text{ m}^3 \text{ m}^{-3}$  on the day before fertilizer application. But it should be noted that there was no rain for four days after the fertilizer was applied. When a salt is placed on moist soil, water moves into the salt predominantly in the vapour phase in response to a total potential gradient caused by the osmotic potential due to the salt (Wheeting, 1925). This water condenses in the salt, which dissolves. Liquid water with dissolved salt then moves back into the soil in response to the matric potential and gravitational gradient (Scotter and Raats, 1970). Once in the soil, molecular diffusion causes further salt movement. Thus the NaBr probably became fairly uniformly distributed throughout the soil solution (both mobile and immobile) in the surface soil. This is quite a different boundary condition to a Dirac delta pulse input in the applied water. However, if the rain or irrigation had occurred immediately after the NaBr was applied, then the Dirac delta flux input assumption may well have been more closely approximated.

Kluitenberg and Horton (1990) recently reported an effect of solute application method on the preferential transport of solutes in soil. They found that applying solute in the irrigation water resulted in an earlier and higher peak for the breakthrough of solute when compared with its incorporation into the surface soil. Steenhuis *et al.* (1990), using a numerical model for preferential solute movement in structured soils, predicted similar results. So the rate of movement from the input

surface to the exit surface depends on how the solute is applied. Another possibility is that the physicochemical behaviour in soil of bromide and chloride are not as similar as assumed. If the assumption of a surface application of solid sodium bromide being approximated by a Dirac delta pulse in the input flux concentration is not valid, the parameters estimated from the bromide data should not be used for prediction of other solutes with other boundary and for initial conditions. The parameters derived from the chloride data, which were not subject to this problem, were assumed to be the more valid ones. The parameters derived from the 1990 chloride data were used to predict leaching of chloride in 1991 and leaching of nitrate in 1990 and 1991.

#### 7.4.2. The stationarity of $f(I)$

The transfer function equation (7.1) is only useful if  $f(I)$  is relatively constant from year to year. Both lognormal and exponential pdfs with parameters derived from the 1990 chloride data were used to predict the leaching of chloride in 1991. A starting value for the initial soil solution concentration,  $C_a$ , in 1991 was also required to predict the solute concentrations in the drainage. The initial measured soil solution concentration was  $46 \pm 2 \text{ g Cl m}^{-3}$  and the source-sink term,  $C_b$ , was  $-1.5 \text{ g Cl m}^{-3}$ . The measured and predicted chloride concentrations in 1991 for paddocks A and B are given in Figures 7.7 and 7.8. In general, the 1990 chloride parameters predicted the leaching of chloride in 1991 reasonably well. Also, for both paddocks the exponential pdf predicted the data slightly better than the lognormal pdf. However, as observed by Heng (1991), neither pdf could model the variation in concentration occurring during individual flow events. As discussed in Chapter 6, this variation tends to be associated with marked changes in flow rate. Heng (1991) observed that a lognormal fit was better than an exponential fit for chloride in 1988 and vice versa in 1989. This could be due to different reasons. First, in their experiment chloride was applied as a solid to the soil surface in both years and a Dirac delta flux input was assumed for the surface applied chloride. As has been shown here this is not a reasonable assumption, although it should be acknowledged that it also depends on the year. If the KCl was dissolved quickly by rainfall, then a pulse flux input is a reasonable assumption. There was also resident chloride present in the soil. Thus, both applied chloride and resident chloride contributed towards leaching. Second, the

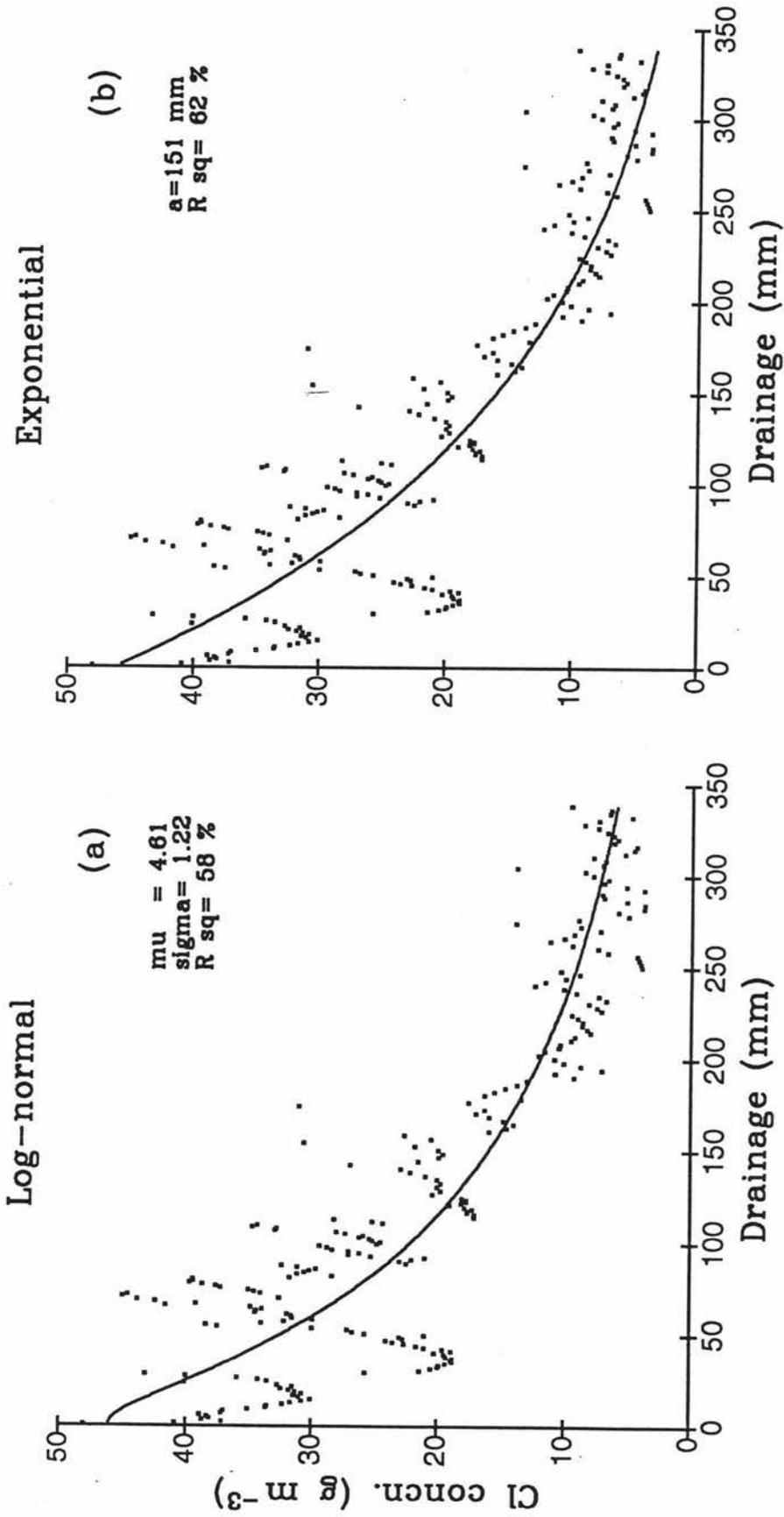


Fig. 7.7. Measured (■) and predicted (—) chloride concentrations in the drainage from paddock A for 1991 using 1990 chloride model parameters with (a) lognormal and (b) exponential pdf

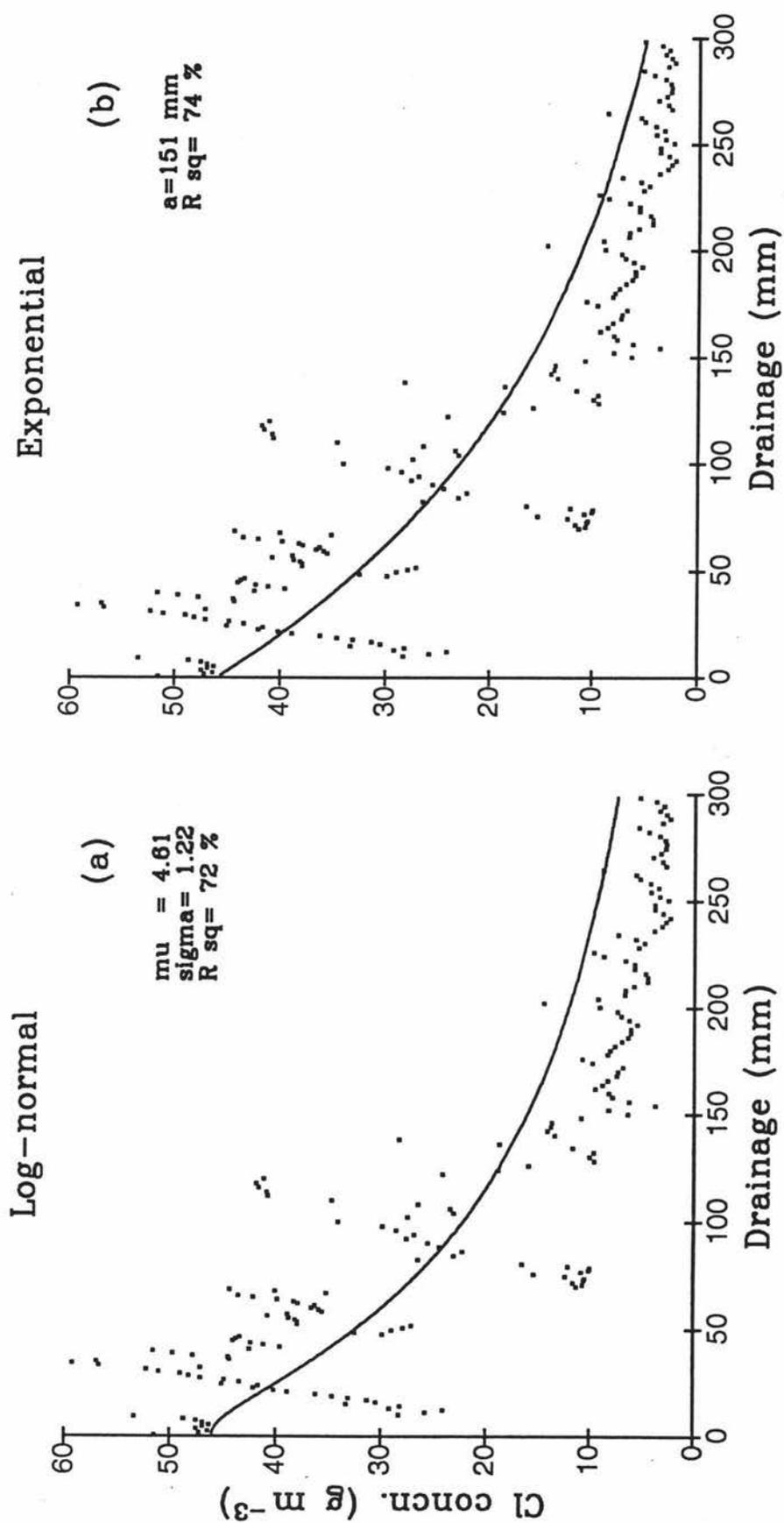


Fig. 7.8. Measured (■) and predicted (—) chloride concentrations in the drainage from paddock B for 1991 using 1990 chloride model parameters with (a) lognormal and (b) exponential pdf

model parameters may not have been stationary. This might have been due to different soil water flow patterns in different rainfall events, and the very different amounts of drainage collected in the two years.

Because the exponential form of the pdf for chloride of 1990 predicted leaching of chloride in 1991 reasonably well, this pdf will be used to predict nitrate leaching in 1990 and 1991 in the next chapter.

## 7.5. FRACTIONAL SOLUTE TRANSPORT VOLUME

Solute transport volumes for bromide and chloride were estimated using equation (4.8). The results are given in Table 7.1. At first mean and median pathway lengths were calculated and then transport volumes were estimated.

**Table 7.1.** Estimation of the fractional transport volume

Solute	Pathway length (mm)		Transport volume ( $\theta_{st}$ )	
	Mean	Median	Mean	Median
Bromide	221	159	0.49	0.35
Chloride	212	101	0.47	0.22

Some observations from Table 7.1 are (1) in general, the mean pathway length and mean transport volume were greater than the median pathway length and median transport volume. The results are similar to those obtained with undisturbed soil cores (Chapter 4); (2) both bromide and chloride had similar mean pathway lengths and hence mean transport volumes, whereas the median travel pathway lengths were different.

## 7.6. CONCLUSIONS

The main implications of the results presented are:

- (a) Assuming a Dirac delta flux input for a surface-applied solid salt was found

not to be a valid assumption.

- (b) The model parameters derived from the 1990 chloride leaching data predicted 1991 chloride leaching reasonably well. Thus the pdf for solute travel appeared to be stationary from one drainage season to the next, when the total drainage for the two seasons did not vary too much (i.e. 260 vs 330 mm), although Heng (1991) found this did not apply so well when the two seasons had markedly different drainage.
- (c) An exponential pdf produced predictions which fitted the data slightly better than a lognormal pdf. Therefore, on the basis of parsimony, the exponential model should be preferred (a one parameter model vs a two parameter model).

## CHAPTER 8

### MODELLING NITRATE LEACHING UNDER FIELD CONDITIONS

#### 8.1. INTRODUCTION

In Chapter 7, the theory for analytical solution of the Transfer Function model was described. There the source-sink term was considered to be linear with drainage. This was a reasonable assumption for non-reactive solutes. The same assumption may not be appropriate for nitrogen because it is a biologically active solute. To incorporate the mineralization process and the effects of grazing, a numerical approach is described below. In the numerical solution, the source-sink term is treated as non-linear with drainage. It was shown in Chapter 7 that an exponential pdf was either as good as, or better than, a lognormal pdf in predicting solute leaching for a given drainage season. So in this chapter an exponential pdf is assumed. The pdf assumed is that obtained from the chloride data. Nitrate leaching data obtained in the field for the 1990 and 1991 drainage seasons (see Chapter 6) are modelled. A comparison is made between the results of the analytical solution and a numerical solution of the transfer function equation.

A numerical solution has two advantages over an analytical solution of the transfer function equation. Firstly, any source-sink term (or surface input) can serve as an input for the numerical solution, whereas for the analytical solution the source-sink term needs to be assumed linear with drainage over the drainage season. Fertilizer and urine additions and mineralization are treated as sources, while plant uptake and immobilization are treated as sinks for nitrate. Secondly, any pdf can be analyzed, not just those for which analytical functions such as the log normal or exponential distribution are assumed. Thus, there is no need to make an assumption about the parametric form of the pdf.

#### 8.2. THEORY

For flow of a conservative non-reactive solute through soil from an input to an output surface, the "net applied water" form of the transfer function equation is, as

already mentioned

$$C_{ex} = \int_0^I C_{ent} (I-I') f(I') dI' \quad (8.1)$$

where  $C_{ex}$  and  $C_{ent}$  are the output and the input concentrations [ $M L^{-3}$ ] respectively,  $I$  is cumulative drainage [L], and  $f(I)$  is the probability density function (pdf) [ $L^{-1}$ ] for solute travel through the soil expressed as a function of  $I$ . This assumes there is no solute in the soil when  $t = 0$ . For the leaching of solute already present uniformly in the soil, the transfer function equation is

$$C_{ex} = C_a \left[ 1 - \int_0^I f(I') dI' \right] \quad (8.2)$$

where  $C_a$  is the average initial value of the soil solution concentration.

Superimposing equations (8.1) and (8.2), the resultant output concentration is

$$C_{ex} = \int_0^I C_{ent} (I-I') f(I') dI + C_a \left[ 1 - \int_0^I f(I') dI' \right]. \quad (8.3)$$

The finite difference form of equation (8.3) is

$$C_{ex}(m) = \sum_{n=1}^m C_{ent}(m-n+1) f(n) \Delta I + C_a \left[ 1 - \sum_{n=1}^m f(n) \Delta I \right] \quad (8.4)$$

where  $n$  and  $m$  are integers, and  $m$  is defined by

$$m = [I/\Delta I] \quad (8.5)$$

$I$  is the cumulative drainage and,  $\Delta I$  is the finite difference interval chosen. Given  $C_{ent}$ ,  $C_a$  and  $f(I)$ , equation (8.4) gives  $C_{ex}$  directly.

There are many situations where source-sink terms at the surface are not linear with drainage. For example, if rotational grazing occurs, input from urine and faeces will

be spasmodic. If there is a dry period during winter, the plant uptake would not be linear with drainage. In the case of nitrogen, mineralization of organic N takes place. In these situations, Equation (8.4) could be used, with sources and sinks in the surface soil being taken into account by including them in  $C_{ent}(I)$ . Notional negative concentrations can be used for sinks.

A uniform initial soil solution concentration must be assumed, because the transfer function model cannot take account of a non-uniform distribution of initial soil solution concentration explicitly. However, if the topsoil initially has a different soil solution concentration from the rest of the soil profile, this may be approximated by partitioning the initial solute between an assumed uniform initial soil solution concentration and an assumed value of  $C_{ent}$  over the first 50 mm drainage (as discussed later). The whole soil solution is taken as the "transport volume" in calculating  $C_a$ , as if enough drainage occurred eventually all the solute would be flushed out of the soil to drain depth. "Immobile" solute is just assumed to be in very "long" flow tubes which do not get "flushed out" during an average winter.

Figure 8.1 shows one way of visualizing equation (8.4). The output concentration is the sum of the products of the output concentration from each flow tube and the flow tube's contribution to the area under the pdf. After each drainage interval, the concentrations cascade down one row in the array.

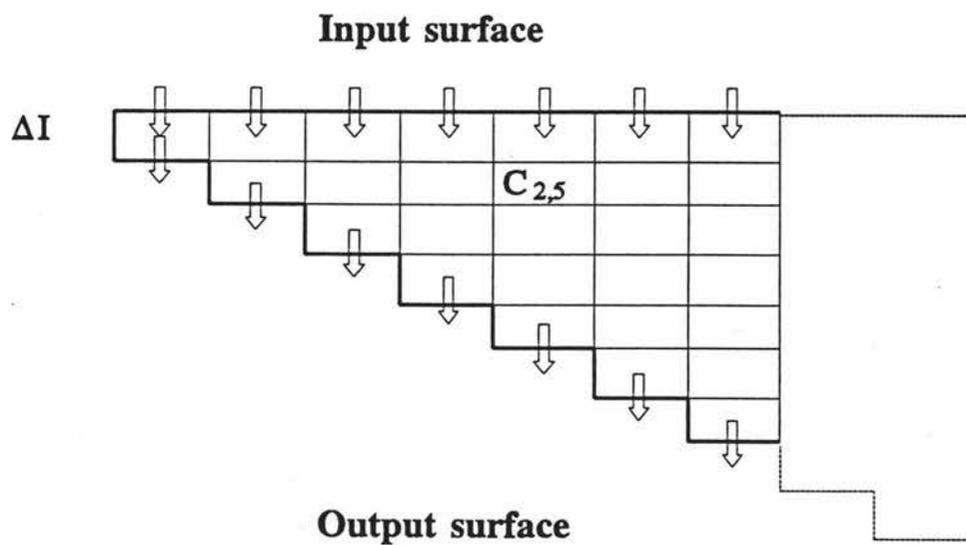
Equation (8.4) represents the numerical solution. For the sake of convenience, equation (7.5) is repeated here as equation (8.6). It represents the analytical solution. An exponential pdf (Equation 7.8) was assumed, for the reason mentioned earlier.

$$C_{ex}(I) = M_o f(I) + C_a + (C_b - C_a) P(I) . \quad (8.6)$$

where  $C_b$  is a source-sink term.

### 8.3. MODEL PARAMETER ESTIMATION

Soil nitrate measurements made just before fertilizer application were used to calculate the initial values of the soil solution concentration ( $C_a$ ). Because the nitrate



**Fig. 8.1. Schematic diagram of travel pathways used in numerical solution of the Transfer Function Model**

concentration in the soil profile was not uniform, as mentioned above, the soil nitrate present in the soil was divided into a uniform initial soil solution concentration, and the remainder was assumed to be present in the surface layer. This is a reasonable assumption because it is often found that the nitrate concentration in the surface layer is higher than in lower layers. The amount of nitrate present in the soil on 28 May 1990, a day before fertilizer application, was 87 kg N/ha to 450 mm depth. The average volumetric water content of the profile was  $0.4 \text{ m}^3 \text{ m}^{-3}$ , and thus the amount of water present in the top 450 mm of the soil profile was 180 mm ( $0.4 \times 450 \text{ mm}$ ). The amount of nitrate was partitioned into two components. The first component was a uniform initial resident soil solution concentration of nitrate throughout the profile to mole drain depth (c.  $35 \text{ g N m}^{-3}$  in 1990). This particular concentration value was assumed because it was almost equal to the initial drainage nitrate concentration. So, 63 kg N/ha of the available nitrate was distributed uniformly in the soil profile. The remaining nitrate ( $87 - 63 = 24 \text{ kg N/ha}$ ) was taken as the second component which contributed  $M_0$ . For the analytical solution (equation 8.6),  $M_0$  was given at just one instant at the start of the season. For the numerical solution (equation 8.4),  $M_0$  was assumed to be a uniform rectangular pulse which was incorporated in  $C_{in}$  for the first 50 mm of drainage. Dividing  $M_0$  by 50 mm drainage gives the value per unit drainage.

On 29 May 1990 urea equivalent to  $120 \text{ kg N ha}^{-1}$  was applied to paddock B. A mass balance calculation (Table 6.2) indicated that in spite of the urea application in paddock B, there was only a small difference in the changes in soil mineral N between the two paddocks. This suggests that most of the unaccounted for N in paddock B was rapidly immobilized. It was assumed that 85 kg N/ha of applied N was rapidly immobilized and the contribution from the fertilizer towards  $M_0$  was taken as 35 kg N/ha (discussion is given in next section). So the total  $M_0$  for paddock A was 24 kg N/ha, and for paddock B was 59 kg N/ha (24 kg N/ha from the soil, plus 35 kg N/ha from the fertilizer).

### 8.3.1. *Analytical solution to the TFM*

For the analytical solution, the procedure followed was similar to the one described in Chapter 7. The prediction was made using Equation 8.6 with an exponential pdf.

The best estimated model parameter,  $a = 151$  mm, obtained from the chloride data was used. In the analytical solution the source-sink component,  $C_b$ , was only took account of the herbage uptake and mineralization. The contribution from atmospheric input was negligible and the effect of the grazing event in 1990 was ignored because it occurred almost at the end of the drainage season. Also as mentioned in Chapter 6, the influence of grazing on nitrate concentrations in the drainage water was not apparent. Cumulative mineralization was assumed proportional to drainage over the winter period.

The total plant uptake during the 1990 drainage season was 51 kg N/ha for paddock A and 77 kg N/ha for paddock B (Figure 8.2). The average herbage uptake contributions of nitrogen to the source-sink term,  $C_b$ , was calculated by dividing these values by the amount of drainage. Assuming uptake was linear with drainage, the contributions were  $-19.5$  g N m<sup>-3</sup> for paddock A and  $-29.5$  g N m<sup>-3</sup> for paddock B.

Net mineralization,  $M_n$ , was calculated for the drainage season as the discrepancy in the inorganic N mass balance. It was assumed equal to the change in soil inorganic N between the first and last day of the drainage season, plus total plant uptake, plus total leaching, minus the fertilizer contribution to soil inorganic N. Thus for paddock A,  $M_n = -72 + 52 + 35 - 0 = 15$  kg N/ha, which is equal to 0.17 kg N/ha/day. In the case of paddock B, however, it was not possible to calculate exactly the amount of N contributed from the fertilizer. But it could be estimated by assuming the same the mineralization rate (0.17 kg N/ha/day) of indigenous N as in paddock A. It can be estimated from the amounts of N leached (43 kg N/ha), plant uptake (79 kg N/ha), soil N changes (-72 kg N/ha) and assuming the same mineralization as in paddock A (15 kg N/ha), that the amount of inorganic N contributed from the fertilizer source was 35 kg N/ha ( $43 + 79 - 72 - 15$ ). This indicates that in paddock B, 85 kg N/ha of the applied 120 kg N/ha was immobilized. When the amount of mineralization (15 kg N/ha or 1.5 g m<sup>-2</sup>) is divided by total drainage the average contribution is equal to 6.5 g N m<sup>-3</sup> for both paddocks.

So the net source-sink term,  $C_b$ , comprising the plant uptake and net mineralization components, was equal to  $-13$  g N m<sup>-3</sup> for paddock A and  $-23$  g N m<sup>-3</sup> for paddock B.

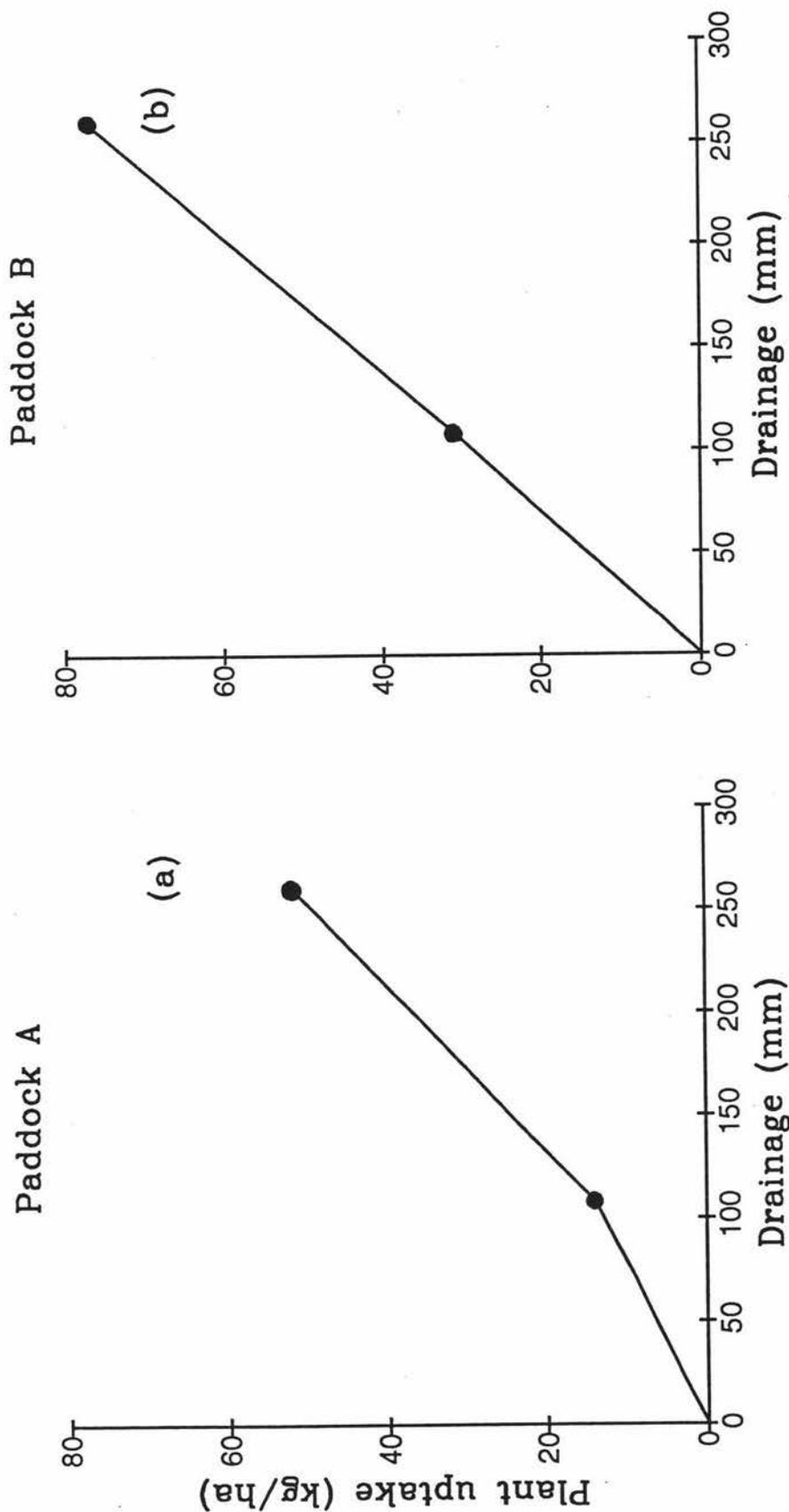


Fig. 8.2. Nitrogen uptake as a function of drainage for the 1990 drainage season

### 8.3.2. *Numerical Solution to the TFM*

In the numerical solution, the effect of grazing was included. For the numerical solution Equation 8.4 was used, with the same pdf as for the analytical solution (equation 8.6).

For the numerical solution the source/sink term was calculated for every 10 mm of drainage predicted from the water balance for the 1990 drainage season. The method used was similar to that described by Scotter *et al.* (1991). For the 1991 drainage season measured drainage data was used. Plant uptake was assumed to be proportional to evaporation. Plant uptake between two herbage sampling dates, divided by the total evaporation during that interval, gave the plant uptake per unit evaporation. This estimated value was converted to plant uptake per day, by multiplying it by the average daily evaporation for each month. Then this value, multiplied by the number of days for every 10 mm drainage to occur, gave the plant uptake during that 10 mm drainage interval. The mineralization rate per day was calculated as described earlier, and calculations of mineralization for each 10 mm drainage interval were made. 36 % of the N taken up by the pasture between grazing was assumed to be readily available for leaching after it was deposited back on the soil in excreta during grazing (Walker *et al.*, 1954; Quin, 1977). Also, instead of the grazing input being a Dirac delta input, it was spread over the 50 mm of drainage occurring after grazing. The grazing input was incorporated into  $C_{ent}$  as was done for  $M_o$ . This was because it was shown in Chapter 7 that solutes applied at the surface do not behave as a pulse flux input to the transport volume.

## 8.4. RESULTS AND DISCUSSION

### 8.4.1. *Analytical solution*

The measured and predicted drainage nitrate concentrations from paddocks A and B for the 1990 drainage season are given in Figures 8.3 and 8.4. Two  $C_b$  values were used. The first value is the one as calculated above, with the results shown in Figures 8.3 (a) and 8.4 (a). The dashed line shows the prediction with the analytical solution. At the start of the drainage season the model over-predicted the nitrate concentration in the drainage. The results are similar to those obtained by Scotter *et*

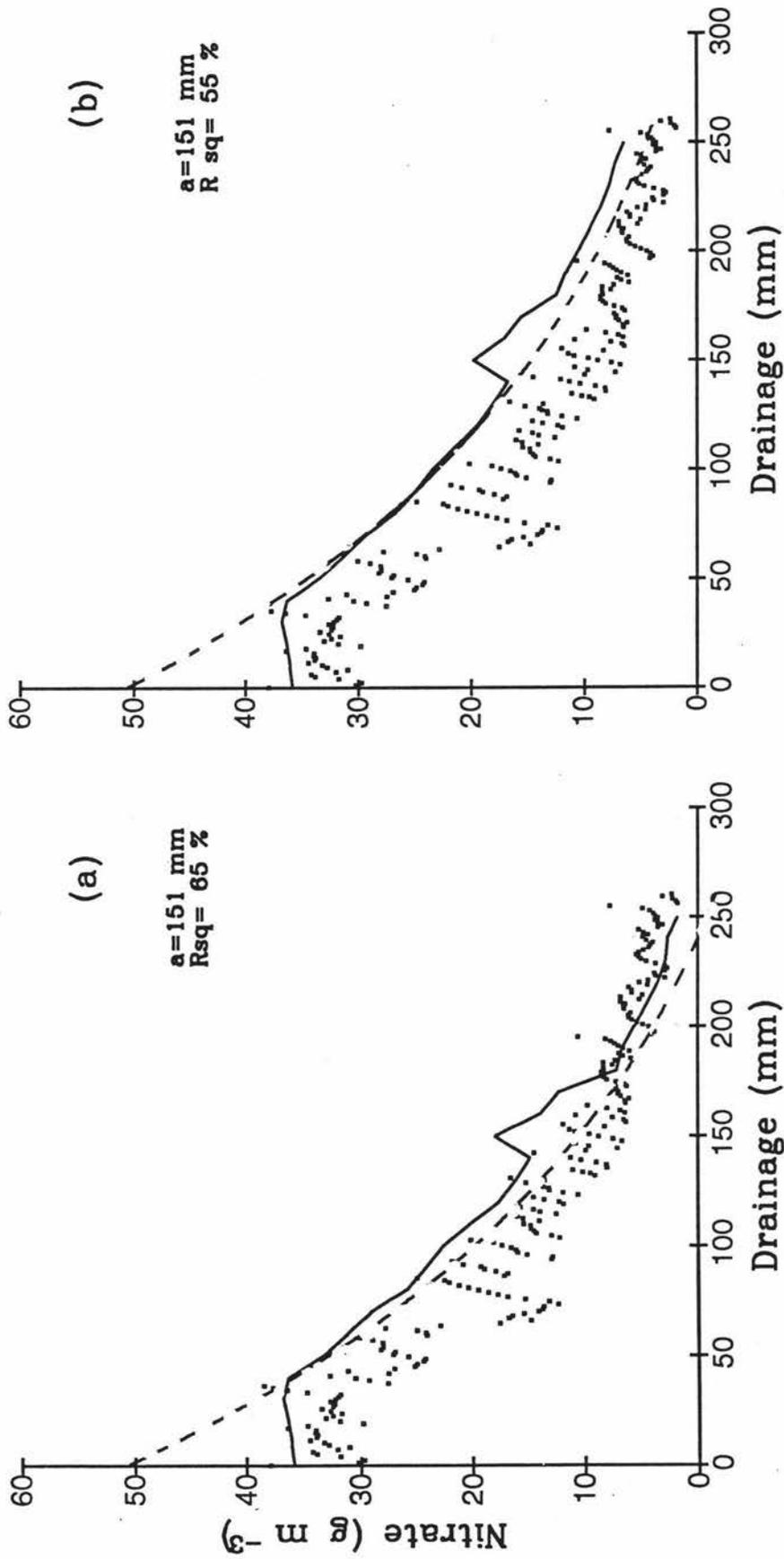


Fig. 8.3. Measured (■) and predicted, using analytical (---) and numerical solutions (—), nitrate concentrations for paddock A for the 1990 drainage season. (a) assumes the plant N uptake is as nitrate and (b) assumes plant uptake is half as nitrate and half as ammonium

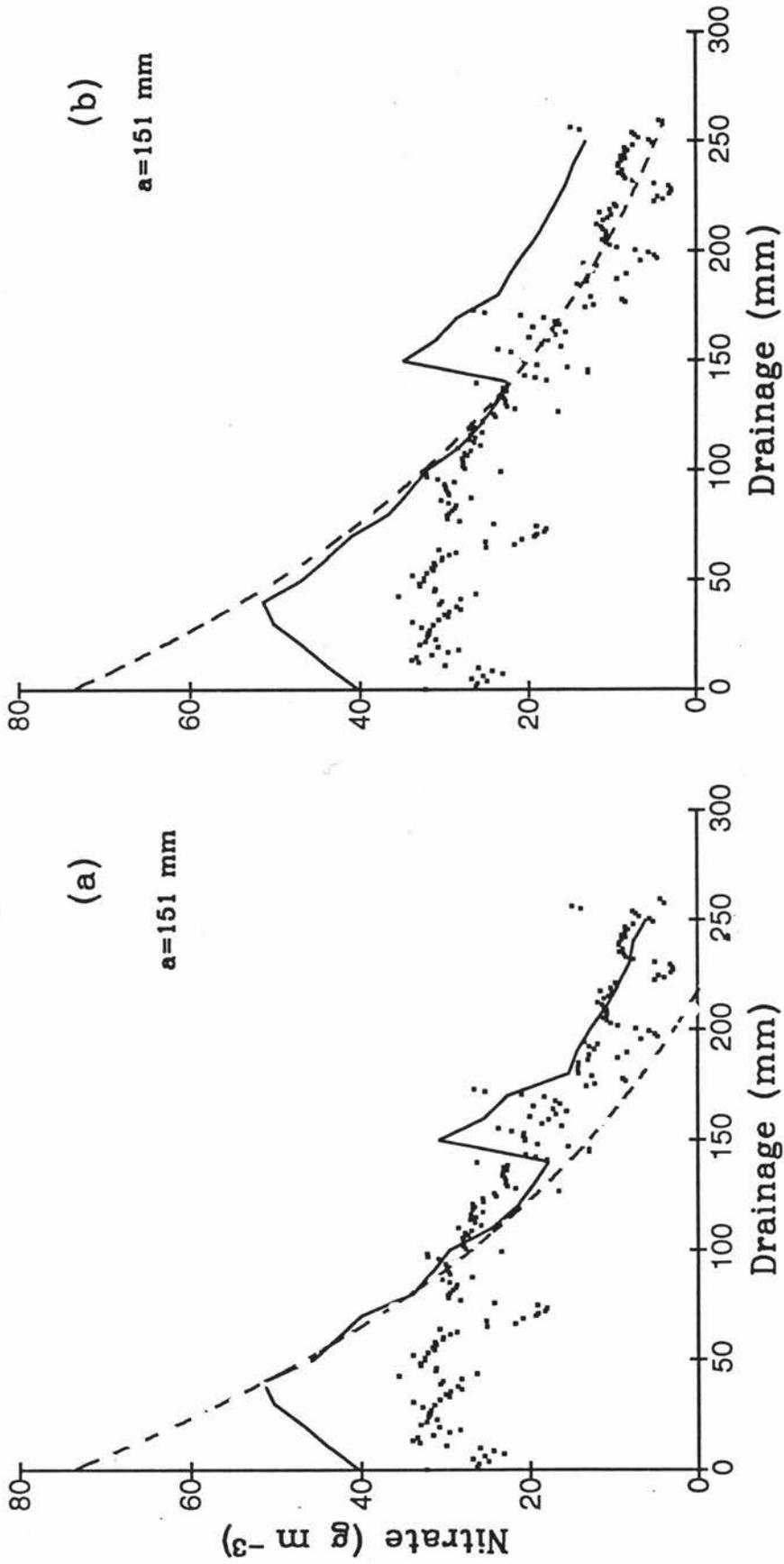


Fig. 8.4. Measured ( $\blacksquare$ ) and predicted, using analytical (---) and numerical solutions (—), nitrate concentrations for paddock B for the 1990 drainage season. (a) assumes the plant uptake is as nitrate and (b) assumes plant uptake is half as nitrate and half as ammonium

*al.* (1991) with their "well-mixed" model for chloride, which is described in Chapter 1. The mole-tile drained soil system can be assumed to behave as a "well-mixed" system (Scotter *et al.*, 1991) when the solute concentration in the drain flow, which applies for vertically uniform horizontal flow towards the drain (Raats, 1978). Scotter *et al.* (1991) predicted chloride concentrations reasonably well early in the drainage season using the first model, but could not predict concentrations well using the second model. One reason for this difference was that in the first model, rain had to move chloride from an upper to lower layer in the soil before it was predicted to affect the drainage concentration significantly. Whereas in the second model, the surface-applied chloride was predicted to have an immediate effect on solute concentration in the drainage, due to the "apparently well-mixed soil solution" assumption, even though in the surface soil above the water table this assumption is not valid (Scotter *et al.*, 1991). In this study, for the analytical solution (Equation 8.6),  $M_0$  was assumed to be applied at the surface soil at one instant, which is similar to their chloride application.

In a sense, the simple model of Scotter *et al.* (1991) discussed in chapter one, and the analytical solution given in this chapter, are similar. The model used for the prediction of nitrate leaching under field conditions (White, 1987) is also similar in some ways to the above two simple models.

Probable reasons for the discrepancy between measured and modelled values early in the drainage season are:

- (a) the use of the wrong boundary conditions. In Chapter 7, we have shown that treating a surface-applied solid fertilizer as a Dirac delta input may not be a valid assumption. Instead, it is more realistically considered as a uniform resident solute in the surface soil. More discussion of this is given in a later section on the numerical solution;
- (b) Due to preferential flow which occurred during heavy rainfall in Autumn. Scotter *et al.* (1979) observed the soil water profile during autumn recharge following a dry summer. They found that some of the rain had penetrated to a metre depth while only partially rewetting the soil above, and a wetting front was not discernible. They explained this in terms of rapid preferential

flow. During such intense rain in autumn it is likely that different flow pathways are involved from those active later in the drainage season, and this cannot be taken account of by the constant  $a$  value (Heng, 1991).

The predicted concentration values for the analytical solution became negative as the drainage progressed because of the negative  $C_b$  term. In fact the source-sink term is a balance between plant uptake and mineralization-immobilization. As the rate of mineralization during the drainage period was less than that of plant uptake, plant uptake contributed more to the  $C_b$  term. Because the first value of  $C_b$  predicted negative concentrations at the end of the drainage season, a second  $C_b$  value was used. In this study, the plant uptake was assumed to be from both ammonium-N and nitrate-N (total N). Following the example of Selim and Iskander (1981), ammonium and nitrate were assumed to be equally available for plant uptake. A similar approach was followed by Scotter *et al.* (1984) when modelling the fate of urea applied to barley. The resulting  $C_b$  values are approximately half of the  $C_b$  values given earlier. The predicted and measured concentrations are given in Figures 8.3(b) and 8.4(b). It is interesting to note that while the first  $C_b$  values predicted negative concentrations as the drainage progressed, the second pair of values did not.

It should be noted that a constant  $a$  value was used. The value was  $a = 151$  mm. The estimated total soil water in Tokomaru silt loam soil down to 450 mm depth during winter was 210 mm. But there can be only one  $a$  which can give the "right" area under the curve. The amount of water in the top 300 mm depth was 146 mm which is near to the value used. Similar assumptions were also made by Heng (1991). They mentioned that although the drain depth was 450 mm, the amount of flow through the subsoil (>300 mm) to the mole drain was assumed to be small because of the much lower saturated hydraulic conductivity in the subsoil (estimated to be  $37 \text{ mm d}^{-1}$ ) (Scotter *et al.*, 1991) between 300 and 450 mm, compared to the topsoil ( $370 \text{ mm d}^{-1}$ ). Preferential flow from 300 mm depth to the moles would interact little with the subsoil. Therefore, they assumed an operational soil depth of 300 mm for parameterization of the models.

There was no grazing in the 1991 drainage season. Again using the  $a$  value obtained

from the 1990 chloride data, nitrate leaching data of 1991 season was predicted (Figure 8.5). Drainage occurred not only during winter but also during autumn and spring. As mentioned in Chapter 6, drainage occurred in March and then there was a dry period which lasted over a month. During this period not only mineralization occurred because of soil rewetting in Autumn (White *et al.*, 1983), but also vigorous pasture growth. When the drainage restarted in April, the nitrate concentrations in the drainage were only about half the concentration of the previous event which occurred before the dry period. In the analytical solution, such temporal variation cannot be simulated. However, the general seasonal trend in the data is reasonably well modelled.

Some demerits of the analytical solution are

- (1) it could not predict well the solute concentrations early in the drainage period,
- (2) the predicted concentrations became negative as the drainage season progressed,
- (3) it could not predict the change in solute concentration either during the heavy rainfall events or following the dry period, and
- (4) the effect of mineralization during the dry period could not be predicted well.

#### 8.4.2. *Numerical solution*

The solid lines in Figures 8.3 (a) and (b) show the predicted values, for paddock A in 1990, of nitrate concentration using the numerical approach. While Fig 8.3(a) gives the prediction using the first  $C_b$  value, Fig 8.3(b) gives the prediction using the second  $C_b$  value. It can be observed that early in the drainage period the nitrate concentrations were predicted reasonably well in paddock A when compared to the analytical approach. After 50 mm drainage the numerical solution predicted slightly higher concentrations than that predicted by analytical solution, when the first  $C_b$  value was used. Moreover, the analytical solution predicted negative concentrations during later period of the drainage season. However, when the second  $C_b$  value was used, both numerical and analytical solutions predicted similar concentration values between 50 mm and 150 mm drainage. After 150 mm drainage the numerical solution predicted slightly higher concentrations than the analytical solution due to grazing effect. Similarly, Figures 8.4 (a) and (b) give the predictions for paddock B.

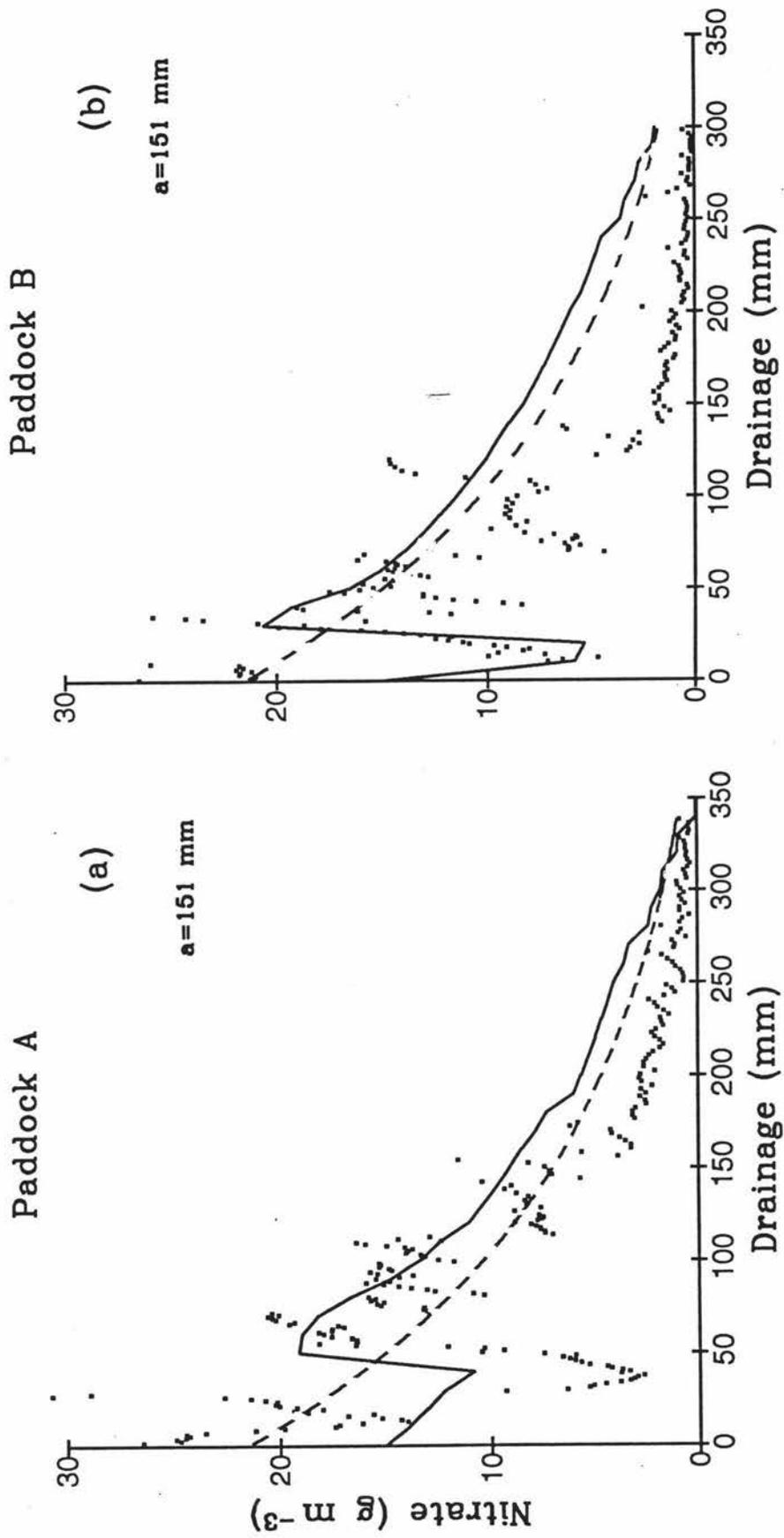


Fig. 8.5. Measured (■) and predicted, using analytical (---) and numerical (—) solutions, nitrate concentrations for paddocks A (a) and B (b) for the 1991 drainage season

The prediction of nitrate concentration by the numerical solution in paddock B, where urea was applied, was not good early in the drainage period, although it was better than that predicted by the analytical solution. In the numerical approach, instead of the Dirac delta input,  $M_0$  was spread over the first 50 mm of drainage input. This is because we have shown in Chapter 7 that even if soluble fertilizer is applied to the soil surface as a solid, it cannot be assumed to contribute all its solute for leaching from the start.

The results for the 1991 drainage season are given in Figure 8.5. The plant uptake and mineralization, in particular, during the dry period soon after the first drainage event were modelled reasonably well using the numerical solution. However, the numerical solution could not take account of the high rainfall event which produced the first drainage event in Figure 8.5. Neither model predicted well the nitrate concentrations later in the drainage season. In general, the demerits of the analytical solution mentioned earlier were overcome by the numerical solution, except that the leaching of nitrate in paddock B to which urea was applied in 1990 was not well modelled. The predicted and measured leaching losses of nitrate for the 1990 and 1991 drainage seasons are given in the Table 8.1.

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

Year	Paddock A			Paddock B		
	Measured	Predicted analytical	Predicted Numerical	Measured	Predicted Analytical	Predicted Numerical
1990	39	45	50	54	61	69
1990 *	39	54	55	54	76	79
1991	23	26	28	17	25	25

\* For the 1990 data with second  $C_0$  value.

In general, both the analytical and numerical solutions of the TFM predicted higher amounts of nitrate leached than the measured amounts. Although Figures 8.3, 8.4 and 8.5 showed that the numerical solution simulated the change in nitrate concentration with drainage better than the analytical solution, the amounts predicted by the numerical solution were higher than by the analytical solution.

## 8.5. CONCLUSIONS

Important conclusions derived from this chapter are:

- (a) The chloride model parameters predicted nitrate leaching reasonably well, but not in 1990 for paddock B (to which urea was applied), nor very well in 1991 when there were some marked fluctuations in drainage early in the season.
- (b) The numerical solution of the transfer function equation had advantages over the analytical solution in modelling the leaching data. It could take account of temporal variations in drainage, plant uptake and mineralization rates.

## **CHAPTER 9**

### **GENERAL DISCUSSION, CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH WORK**

#### **9.1. INTRODUCTION**

In this study leaching experiments were carried out both under laboratory and field conditions. The extent of the leaching of both non-reactive (bromide, chloride) and biologically reactive (nitrate) solutes was measured. Subsequently, modelling of the leaching data was carried out to gain a better knowledge and understanding of the movement of solutes in mole-tile drained soils under pasture. This final chapter provides a general discussion in which the conclusions from the work described in Chapters 2 to 8 are summarized, and some of the implications of the findings are discussed.

#### **9.2. GENERAL DISCUSSION AND CONCLUSIONS OF LABORATORY EXPERIMENTS**

##### **9.2.1. Spatial distribution of soil nitrate and chloride**

Leaching experiments were carried out using large intact soil cores which were taken in close proximity to each other from the field site where field measurements of leaching were made. Soil samples taken from within a few cm of the large cores were used to estimate the initial average solute concentration before leaching. But it was found that the average concentration in those samples was different from the initial concentration in the leachate. Large differences in leachate concentrations between the large cores were also noted. This was apparently due to spatial variability of the solute concentration in the soil, and sheep grazing is probably the major cause of this variability. So estimates of the initial solute concentration using small soil cores taken from around large cores under grazed conditions have considerable uncertainty, which may result in large errors in leaching calculations. In such cases the concentration of solute in the first effluent might enable a reasonably accurate, prediction of the leaching losses of a resident solute to be made. When a uniform solute distribution with depth was achieved by repeatedly preleaching the

soil with the solute of interest, accurate predictions of leaching could be made using an average initial concentration obtained from small, independent samples.

### 9.2.2. Effect of long time storage

Soil samples were stored at 4 °C prior to the extraction of solutes. Long term storage of a pair of soil large cores for nearly 22 months at 4 °C before leaching had an effect on soil water content and on nitrate leaching. The volumetric water content decreased by 5 % (from 0.35 to 0.30 m<sup>3</sup> m<sup>-3</sup>) during storage, and the average soil solution nitrate concentration in the soil increased markedly to about 18 times the initial value (from 10 g N m<sup>-3</sup> to 180 g N m<sup>-3</sup>). Most of this nitrate was in the top layer, with an exponential decrease with depth. This shows the importance of biological activity in the surface soil, even at very low temperatures. That nitrification could occur in this pasture soil at 4 °C is consistent with Macduff and White's (1985) field observations on an Evesham clay loam soil under pasture in the U.K. during winter.

### 9.2.3. Preferential flow

Early breakthrough of applied solute anions can occur either due to macropore flow or anion exclusion. The emergence of peak concentrations of a pulse input before one liquid-filled pore volume of drainage indicated the preferential flow of water and solutes through soil macropores. The soil solution concentrations of nitrate at different depths of cores after leaching were found to be much higher than those in the final effluent, providing further evidence of preferential flow. This involves the concept of a transport and non-transport volume, and dynamic differences in concentration of a labile solute such as nitrate between them. Comparing the breakthrough curves of step-change inputs, the relative concentration of chloride approached 1.0 earlier than for tritium, and this could be due to anion exclusion and/or different mean input rates. Tokomaru silt loam soil has high negative charge and low positive charge (Bolan *et al.*, 1986) which is likely to cause the negative adsorption of anions. The application of Nile blue dye to the soil surface after the solute movement experiments indicated that worm holes and root channels were the main preferential pathways for water and solute movement through the soil.

#### **9.2.4. Edge flow**

Cameron *et al.* (1990) mentioned that edge flow between soil monoliths and their casings is common. In this study, in most cases, some conducting channels were cut off by the core wall, causing blue staining on the side of the soil core, but there was no indication of solution leaking down between the soil and the corer. However, on one occasion a small stone was pushed ahead of the cutting edge of the cylinder and cut a groove which allowed some edge-flow. It appears that in this soil, and with the techniques used, edge flow is not a significant problem.

#### **9.2.5. Denitrification**

In the core experiments approximately 15 % of the applied N was not accounted for either in the leachate or in the soil. This could have been lost by denitrification, especially from the surface soil layer. The silica sand, which was applied to the soil surface to help to distribute the applied solution uniformly, could have reduced the oxygen supply thus making the topsoil anaerobic. This, plus a ready supply of nitrate and organic carbon in the topsoil, could have allowed denitrification to occur. Recently, it has been shown that under waterlogged conditions denitrification occurs in the top layer of Tokomaru silt loam soil (J.Luo - Personal communication). This also shows the importance of biological transformations of N in soil in changing the source strength of nitrate available for leaching.

#### **9.2.6. Modelling laboratory leaching data**

The transfer function approach was used to model the leaching data. In general, model parameters derived from tritiated water could be used successfully to simulate the movement of resident chloride when chloride was almost uniform throughout the soil. However, it was not possible to predict nitrate leaching successfully using these parameters. This was probably due to several complicating factors associated with the non-uniform distribution and biological transformations of nitrate in soil.

### 9.3. GENERAL DISCUSSION AND CONCLUSIONS ON FIELD EXPERIMENTS

#### 9.3.1. Deep percolation

In a mole-tile drained field it is often assumed that almost all water and solutes that move through the soil are intercepted by the moles. So in this study monthly soil sampling was carried out to study the movement of bromide, chloride and nitrate through the soil. Soil sampling down to 1m at the end of drainage season showed that about 12 % of the applied bromide went below mole depth.

#### 9.3.2. Effect of grazing

The influence of periodic sheep grazing on solute concentrations in soil and drainage was studied, because many earlier studies have shown an effect on drainage concentrations. The soil samples taken from the field after grazing showed an increase in the concentrations of mineral N ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) and chloride in the surface layer. The high concentrations of mineral N and chloride observed down to 450 mm (mole depth) at some locations were assumed to be due to grazing and preferential flow of water and solutes below urine patches. The high variability in solute concentrations found in the topsoil after grazing was probably due in part to the uneven distribution of animal excreta. An effect on drainage concentrations due to grazing by sheep was not observed in this study.

#### 9.3.3. Drainage and leaching

Drainage was collected and analyzed for solute concentrations during the 1990 and 1991 drainage seasons. The amounts of rain received in 1990 and 1991 were almost equal but the drainage collected during these two years was quite different. This was due to the difference in the seasonal distribution of the rain between the two years.

The concentration of nitrate and chloride in the drainage were high at the start of each drainage season and decreased subsequently. From the viewpoint of water quality control, separating the early drainage from later drainage could reduce surface water nitrate loading. The concentrations of nitrate in the drainage in 1991 were lower than in 1990. Although cumulative drainflow was greater in 1991 than 1990,

the amount of nitrate leached in 1991 was almost 50 % less than that in 1990. This was apparently due to a smaller amount of nitrate being present in the soil at the start of drainage season, and illustrates that the source strength of nitrate in the soil is the major determinant of total N loadings in the drainage water. The difference illustrates the dangers inherent in assuming one year's data is typical of all years. The nitrate concentration was greater than the concentration levels recommended for potable water ( $10 \text{ g NO}_3\text{-N m}^{-3}$ ) for most of the 1990 drainage season, irrespective of whether urea was applied or not.

Comparing the amounts of nitrate leached from the paddocks, it appeared that only 8 % of the fertilizer applied was leached during the drainage period. However, about 52 % of bromide applied was leached during the same period although urea and bromide were applied on the same day. This shows the importance of the nature of the solute applied. It can be speculated that if nitrate was applied in a very soluble form, such as potassium nitrate, more nitrate could be leached. But the fact that N from urea could undergo immobilization, plant uptake and denitrification is possibly a more important cause of this difference in solute leaching loss. Application of urea in Spring 1989 did not cause any substantial increase in the nitrate concentration in the drainage. This could be due to more plant uptake occurring during spring.

When both chloride and nitrate were indigenous, as in the 1991 drainage season, the leaching patterns were similar. This indicates that during this drainage season only leaching and plant uptake were major factors, because if biological transformations such as immobilization and mineralization were very important, they would have affected nitrate but not chloride. As a result the leaching patterns of nitrate and chloride would have been different.

#### **9.3.4. Suction cup sampling**

Both soil and suction cup samples were collected regularly throughout the drainage season. The concentration of applied solutes (e.g. bromide) in suction cups placed at two depths increased from a very low value to a peak and then decreased. The deeper suction cups responded more slowly than the shallower ones. There was a differential time delay in the rise in concentration between the upper and lower

depths. The concentration of indigenous chloride decreased with time at the upper depth, whereas it remained fairly constant at the lower depth for most of the season. This indicates more effective leaching of indigenous solutes from the surface layers than the deeper layers. The concentration of indigenous nitrate in both upper and lower layers decreased during the drainage season.

### **9.3.5. Comparison of soil solute concentrations**

The soil solution concentration measured by soil extraction was compared with the suction cup sample concentration. For an externally applied solute, such as bromide, the suction cup concentration was greater than the volume-averaged solution concentration. In contrast for an indigenous solute such as chloride, the volume-averaged soil solution concentration was greater than the suction cup concentration during the drainage season.

In general, it was difficult to relate the solute concentration in the drainage to that in the soil solution. For both applied and indigenous non-reactive solutes, the drainage concentration was closely related to the suction cup concentration throughout the drainage season. In the case of nitrate, however, there was no consistent relationship between drainage concentration and either suction cup or soil extraction concentration. This obviously poses problems for the quantitative estimation of nitrate leaching based on indirect soil measurements.

### **9.3.6. Drainage flow rates and solute concentrations**

The solute concentrations in the drainage water varied with the flow rate. Early in the drainage season the concentration of applied solute tended to increase with flow rate. This is an effect of the pulse inputs of bromide and urea combined with preferential flow. The concentration of indigenous solutes in the drainage tended to be inversely related to flow rate. At high flow rates the input water moves through the soil more rapidly, resulting in less mixing with the accessible (mobile) soil solution and consequently lower concentrations in the drainage water. This behaviour was observed both early and late in the drainage season. Over time, applied and indigenous solutes behaved similarly, with a dilution of the mobile soil solution by rain water occurring.

### 9.3.7. Modelling field leaching data

Bromide, chloride and nitrate leaching data obtained in the field were modelled using transfer functions. Analytical and numerical solutions of the transfer function equation were used. Source-sink terms were treated as linear with drainage in the analytical solution, but as non-linear in the numerical solution. There are many situations where source-sink terms at the soil surface are not linear with drainage.

The chloride and bromide data were used to infer the probability density function (pdf) of solute travel times, which was tested for stationarity from one drainage season to the next. The pdf is only useful for predictive modelling if it is relatively constant from year to year. Two experimental situations were used to evaluate the pdf. Surface application of solid sodium bromide was assumed to be a Dirac delta pulse input, and the leaching of indigenous chloride was taken as a step change in input concentration. In all cases, analytical forms of the pdf for solute travel, either log-normal or exponential, were assumed. For bromide, the log-normal pdf fitted the drainage data much better than the exponential pdf. For chloride, the exponential pdf fitted the data slightly better than or equal to the lognormal pdf, despite having only one rather than two fitted parameters. Although both bromide and chloride are conservative and non-reactive solutes, it was interesting to note that they apparently had very different pdfs. The most likely reason for the difference was the assumed different boundary conditions not being met experimentally. The surface application of solid potassium bromide was assumed to be a Dirac delta pulse in the input flux concentration, which was apparently not valid. Thus the exponential pdf obtained from the chloride data is the better of the two estimates.

The pdf for solute travel appeared to be stationary from one drainage season to the next. The transfer function approach could model the variation in concentration occurring during individual flow events, and this variation tends to be associated with marked changes in flow rate.

Numerical solution of the transfer function equation has two advantages over an analytical solution in modelling the leaching data. Firstly, any source-sink term or surface solute flux can serve as an input for the numerical solution. Fertilizer and

urine additions and mineralization are treated as sources, while plant uptake and immobilization are treated as sinks for nitrate. Thus there is no need to make an assumption about the shape of the pdf. Thus temporal variations in drainage, plant uptake and mineralization rates can be taken into account. Secondly, any pdf can be analyzed, not just analytical ones such as the log normal and exponential distribution.

#### 9.4. SUGGESTIONS FOR FUTURE RESEARCH WORK

In both the laboratory and field experiments when non-reactive solutes were used for leaching their behaviour could be predicted reasonably well. But this was not the case with nitrate. In the short term laboratory experiments, nitrate was treated as a non-reactive solute. But the results of the field experiments confirm that biological transformations of N (mineralization and denitrification) play an important role which affects nitrate leaching. So in future studies, experimental and theoretical, these transformations should be taken into consideration in more detail.

It is a usual practice to store the soil samples at 4 °C. Certainly it is not good to store the samples for too long, as one of the experiments has shown, because nitrate concentrations can change tremendously. Experiments could be designed to study the effect of storage on soil nitrate, and on processes such as mineralization.

The two paddocks used for the field experiments were almost identical in terms of drained area as well as hydrological behaviour. They could be used as a "test" site for further experiments; e.g. experiments on the influence of land application of agricultural wastes (e.g. dairy effluents) on solute concentrations in the soil and drainage. Because dairy effluents and other wastes have high organic N, it would be interesting to study the biological transformations of N, such as immobilization and denitrification, in these experiments.

In the field experiments carried out the effect of sheep grazing on the drainage concentrations was not obvious. However, other studies (e.g. Sharpley and Syers, 1979) have shown a great influence of cattle grazing on the drainage concentrations. It would be interesting to see if these two paddocks (one for sheep and the other for cattle) can be used for experiments on the effects of different grazing on nitrate leaching.

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## APPENDIX 1

' This program calculates the model parameters ( $\mu$  and  $\sigma$ ) for solutes applied as step-change in input concentration by least sum of squares optimization using Equation 4.5

CLS

INPUT " Enter solute data filename : ", Inputfile\$  
INPUT " Enter solute output filename: ", Outputfile\$

OPEN Inputfile\$ FOR INPUT AS #1  
OPEN Outputfile\$ FOR OUTPUT AS #2

' INITIAL SECTION

' m is the number of points for which computation is carried out  
' Initial mu and sigma values are given below for the iteration

m = 79

Mu = 4.103: Sigma = 1.111

' D = drainage (mm); NC = measured solute concentration ( $\text{g m}^{-3}$ ); Cex =  
Predicted solute concentration ( $\text{g m}^{-3}$ )

DIM D(m), NC(m), Cex(m, 3, 3), SumSq(3, 3)

LSumSq = 1E+10

pi = 3.14159

p = .47047

a1 = .34802

a2 = -.09588

a3 = .74786

Co = 420

delta = .001

' where p, a1, a2 and a3 are constants used to find the values of error function approximately.

, Co is the concentration of solute applied

FOR n = 1 TO m  
INPUT #1, D(n), NC(n)  
NEXT

' DYNAMIC SECTION

DO UNTIL ABS(Mu - Mu(1)) = 0 AND ABS(Sigma - Sigma(1)) = 0

Mu(1) = Mu

Mu(2) = Mu + delta

Mu(3) = Mu - delta

Sigma(1) = Sigma

Sigma(2) = Sigma + delta

Sigma(3) = Sigma - delta

```

FOR u = 1 TO 3
  FOR v = 1 TO 3
    SumSq(u, v) = 0

    FOR n = 1 TO m
      i = 1
      x = (LOG(D(n)) - Mu(u)) / (SQR(2) * Sigma(v))
      IF x < 0 THEN x = -x: i = -1
      t = 1 / (1 + p * x)
      erfx = 1 - (a1 * t + a2 * t * t + a3 * t * t * t) * EXP(-x * x)
      erfx = erfx * i
      Cex(n,u,v) = Co / 2 * (1 + erfx)
      SumSq(u, v) = SumSq(u, v) + (NC(n) - Cex(n, u, v)) *
                    (NC(n) - Cex(n, u, v))
    NEXT

    IF SumSq(u, v) < LSumSq THEN
      LSumSq = SumSq(u, v)
      Mu = Mu(u)
      Sigma = Sigma(v)
    END IF
  NEXT
NEXT

PRINT USING "#####.###"; LSumSq, Mu, Sigma
LOOP
' PRINT " D "; " Measured N "; " Predicted N "
FOR n = 1 TO m
  PRINT USING "###.##"; D(n), NC(n), Cex(n, 1, 1)
  PRINT #2, USING "###.##"; D(n), NC(n), Cex(n, 1, 1)
NEXT
PRINT USING "#####.#####"; LSumSq, Mu, Sigma

```

## APPENDIX 2

' This program calculates the model parameters ( $\mu$  and  $\sigma$ ) for solutes applied as pulse input by least sum of squares method using Equation 4.6.

CLS

INPUT " Enter solute data filename : ", Inputfile\$

INPUT " Enter solute output filename: ", Outputfile\$

OPEN Inputfile\$ FOR INPUT AS #1

OPEN Outputfile\$ FOR OUTPUT AS #2

' INITIAL SECTION

' m is the number of points for which computation is carried out

' D = drainage in mm; NC = pulse solute concentration; Cex = Predicted concentration

m = 79

Mu = 4.103: Sigma = 1.111

DIM D(m), NC(m), Cex(m, 3, 3), SumSq(3, 3)

LSumSq = 1E+10

pi = 3.14159

p = .47047

a1 = .34802

a2 = -.09588

a3 = .74786

Co = 420

delta = .001

FOR n = 1 TO m

    INPUT #1, D(n), NC(n)

NEXT

' DYNAMIC SECTION

DO UNTIL ABS(Mu - Mu(1)) = 0 AND ABS(Sigma - Sigma(1)) = 0

    Mu(1) = Mu

    Mu(2) = Mu + delta

    Mu(3) = Mu - delta

    Sigma(1) = Sigma

    Sigma(2) = Sigma + delta

    Sigma(3) = Sigma - delta

FOR u = 1 TO 3

    FOR v = 1 TO 3

        SumSq(u, v) = 0

            FOR n = 1 TO m

                i = 1

                    x = (LOG(D(n)) - Mu(u)) / (SQR(2) \* Sigma(v))

                    IF x < 0 THEN x = -x: i = -1

```

t = 1 / (1 + p * x)
erfx = 1 - (a1 * t + a2 * t * t + a3 * t * t * t) * EXP(-x * x)
erfx = erfx * i
Cex1 = Co / 2 * (1 + erfx)

Cex2 = 0
IF D(n) > 20 THEN
  i = 1
  x = (LOG(D(n) - 20) - Mu(u)) / (SQR(2) * Sigma(v))
  IF x < 0 THEN x = -x: i = -1
  t = 1 / (1 + p * x)
  erfx = 1 - (a1 * t + a2 * t * t + a3 * t * t * t) * EXP(-x
  * x)
  erfx = erfx * i
  Cex2 = Co / 2 * (1 + erfx)
END IF

Cex(n, u, v) = Cex1 - Cex2
SumSq(u, v) =      SumSq(u, v) + (NC(n) - Cex(n, u, v)) *
                (NC(n) - Cex(n, u, v))

NEXT

IF SumSq(u, v) < LSumSq THEN
  LSumSq = SumSq(u, v)
  Mu = Mu(u)
  Sigma = Sigma(v)
END IF

NEXT
NEXT

PRINT USING "#####.###"; LSumSq, Mu, Sigma
LOOP
'   PRINT " D "; " Measured N "; " Predicted N "
FOR n = 1 TO m
  PRINT USING "###.##"; D(n), NC(n), Cex(n, 1, 1)
  PRINT #2, USING "###.##"; D(n), NC(n), Cex(n, 1, 1)
NEXT
PRINT USING "#####.#####"; LSumSq, Mu, Sigma

```

## APPENDIX 3

- ' This program predicts the resident solute concentration in drainage using Equation 4.7.
- ' Inputfile name is 'eclrc.dat' and Outputfile name is 'eclrc.out'

CLS

INPUT " Enter solute data filename : ", Inputfile\$  
 INPUT " Enter solute output filename: ", Outputfile\$

OPEN Inputfile\$ FOR INPUT AS #1  
 OPEN Outputfile\$ FOR OUTPUT AS #2

- ' INITIAL SECTION
- ' m is the number of points for which computation is carried out
- ' Ci = resident solute concentration in the soil solution ( $\text{g m}^{-3}$ )
- ' D = drainage in mm; MeasC = measured concentration in drainage; and PredC= predicted drainage concentration

m = 79

Ci = 120

Mu = 4.103; Sigma = 1.111

DIM D(m), MeasC(m), PredC(m)

FOR n = 1 TO m  
     INPUT #1, D(n), MeasC(n)  
 NEXT

FOR n = 1 TO m  
     p = .47047  
     a1 = .34802  
     a2 = -.09588  
     a3 = .74786  
  
     i = 1  
     x = (LOG(D(n)) - Mu) / (SQR(2) \* Sigma)  
     IF x < 0 THEN x = -x: i = -1  
     t = 1 / (1 + p \* x)  
     erfx = 1 - (a1 \* t + a2 \* t \* t + a3 \* t \* t \* t) \* EXP(-x \* x)  
     erfx = erfx \* i  
     PredC(n) = Ci / 2 \* (1 - erfx)  
 NEXT

' LPRINT " D "; " MeasC "; " PredC "  
 FOR n = 1 TO m  
     PRINT USING "###.##"; D(n), MeasC(n), PredC(n)  
     PRINT #2, USING "#####.###"; D(n), MeasC(n), PredC(n)  
 NEXT

## APPENDIX 4

- ' This program calculates the Mu and Sigma by least sum of squares method using Equation 7.5.
- ' Inputfile is 'FAClexp.dat' and Outputfile is 'FACllogn.out'

CLS

INPUT " Enter solute data filename : ", Inputfile\$  
 INPUT " Enter solute output filename: ", Outputfile\$

OPEN Inputfile\$ FOR INPUT AS #1  
 OPEN Outputfile\$ FOR OUTPUT AS #2

' INITIAL SECTION

- ' m is the number of points for which computation is carried out
- ' D = drainage in mm; ClC = measured solute concentration ( $\text{g m}^{-3}$ ) and Cex = predicted solute concentration ( $\text{g m}^{-3}$ )

m = 241  
 mu = 4.654: sigma = 1.319  
 DIM D(m), ClC(m), Cex(m, 3, 3), SumSq(3, 3)  
 LSumSq = 1E+10  
 TSS = 0

pi = 3.14159  
 p = .47047  
 a1 = .34802  
 a2 = -.09588  
 a3 = .74786  
 Mo = 0  
 Ca = 72  
 Cb = -1.5  
 delta = .001  
 Total = 0

FOR n = 1 TO m  
 INPUT #1, D(n), ClC(n)  
 Total = Total + ClC(n)  
 Average = Total / m  
 NEXT

FOR n = 1 TO m  
 TSS = TSS + ((ClC(n) - Average) \* (ClC(n) - Average))  
 NEXT

' DYNAMIC SECTION  
 DO UNTIL ABS(mu - mu(1)) = 0 AND ABS(sigma - sigma(1)) = 0  
 mu(1) = mu  
 mu(2) = mu + delta  
 mu(3) = mu - delta

```

sigma(1) = sigma
sigma(2) = sigma + delta
sigma(3) = sigma - delta

```

```

FOR u = 1 TO 3

```

```

  FOR v = 1 TO 3

```

```

    SumSq(u, v) = 0

```

```

      FOR n = 1 TO m

```

```

        Cex1 = Mo * (EXP(-(LOG(D(n)) - mu(u)) ^ 2 / (2 * sigma(v) *
sigma(v))) / (SQR(2 * pi) * sigma(v) * D(n)))

```

```

        i = 1

```

```

        x = (LOG(D(n)) - mu(u)) / (SQR(2) * sigma(v))

```

```

        IF x < 0 THEN x = -x: i = -1

```

```

        t = 1 / (1 + p * x)

```

```

        erfx = 1 - (a1 * t + a2 * t * t + a3 * t * t * t) * EXP(-x * x)

```

```

        erfx = erfx * i

```

```

        Cex2 = (Cb - Ca) * 1 / 2 * (1 + erfx)

```

```

        Cex(n, u, v) = Cex1 + Ca + Cex2

```

```

        SumSq(u, v) = SumSq(u, v) + (CIC(n) - Cex(n, u, v)) * (CIC(n)
- Cex(n, u, v))

```

```

      NEXT

```

```

    IF SumSq(u, v) < LSumSq THEN

```

```

      LSumSq = SumSq(u, v)

```

```

      mu = mu(u)

```

```

      sigma = sigma(v)

```

```

    END IF

```

```

  NEXT

```

```

NEXT

```

```

RSq = 1 - (LSumSq / TSS)

```

```

PRINT USING "#####.###"; LSumSq, mu, sigma

```

```

LOOP

```

```

^ PRINT " D "; " Measured Cl "; " Predicted Cl "

```

```

FOR n = 1 TO m

```

```

  PRINT USING "###.##"; D(n), CIC(n), Cex(n, 1, 1)

```

```

  PRINT #2, USING "#####.###"; D(n), CIC(n), Cex(n, 1, 1)

```

```

NEXT

```

```

PRINT USING "#####.#####"; LSumSq, mu, sigma, RSq

```

## APPENDIX 5

' This program calculates the parameter "a" by least sum of squares method.  
' Inputfile is 'FAClexp.dat' and Outputfile is 'FAClexp.out'

CLS

INPUT " Enter chloride data filename : ", Inputfile\$  
INPUT " Enter chloride output filename: ", Outputfile\$

OPEN Inputfile\$ FOR INPUT AS #1  
OPEN Outputfile\$ FOR OUTPUT AS #2

' INITIAL SECTION

' m is the number of points for which computation is carried out

m = 241

a = 144

DIM D(m), ClC(m), Cex(m, 3), SumSq(3)

LSumSq = 1E+10

TSS = 0

Mo = 0

Ca = 72

Cb = -1.5

delta = .001

Total = 0

FOR n = 1 TO m

INPUT #1, D(n), ClC(n)

Total = Total + ClC(n)

Average = Total / m

NEXT

FOR n = 1 TO m

TSS = TSS + ((ClC(n) - Average) \* (ClC(n) - Average))

NEXT

' DYNAMIC SECTION

DO UNTIL ABS(a - a(1)) = 0

a(1) = a

a(2) = a + delta

a(3) = a - delta

FOR u = 1 TO 3

SumSq(u) = 0

FOR n = 1 TO m

Cex1 = Mo \* ((1 / a(u)) \* EXP(-D(n) / a(u)))

Cex2 = (Cb - Ca) \* (1 - EXP(-D(n) / a(u)))

Cex(n, u) = Cex1 + Ca + Cex2

SumSq(u) = SumSq(u) + (ClC(n) - Cex(n, u)) \* (ClC(n) - Cex(n, u))

NEXT

```
IF SumSq(u) < LSumSq THEN
    LSumSq = SumSq(u)
    a = a(u)
END IF

NEXT
Rsq = 1 - (LSumSq / TSS)
PRINT USING "#####.###"; LSumSq, a
LOOP
'    PRINT " D "; " Measured Cl "; " Predicted Cl "
FOR n = 1 TO m
    PRINT USING "###.##"; D(n), ClC(n), Cex(n, 1)
    PRINT #2, USING "#####.###"; D(n), ClC(n), Cex(n, 1)
NEXT
PRINT USING "#####.#####"; LSumSq, a, Rsq
```

## APPENDIX 6

- ' This program predicts solute concentration in the drainage using lognormal distribution
- ' Inputfile name is 'acl91.dat' and Outputfile name is 'acl91log.out'

CLS

INPUT " Enter chloride data filename : ", Inputfile\$  
 INPUT " Enter chloride output filename: ", Outputfile\$

OPEN Inputfile\$ FOR INPUT AS #1  
 OPEN Outputfile\$ FOR OUTPUT AS #2

'INITIAL SECTION

' m is the number of points for which computation is carried out

m = 237

mu = 4.606: Sigma = 1.222

Ca = 46

Cb = -1.5

LSumSq = 0

TSS = 0

Total = 0

DIM D(m), MeasC(m), PredC(m)

FOR n = 1 TO m

INPUT #1, D(n), MeasC(n)

Total = Total + MeasC(n)

Average = Total / m

NEXT

FOR n = 1 TO m

TSS = TSS + ((MeasC(n) - Average) \* (MeasC(n) - Average))

NEXT

FOR n = 1 TO m

p = .47047

a1 = .34802

a2 = -.09588

a3 = .74786

i = 1

x = (LOG(D(n)) - mu) / (SQR(2) \* Sigma)

IF x < 0 THEN x = -x: i = -1

t = 1 / (1 + p \* x)

erfx = 1 - (a1 \* t + a2 \* t \* t + a3 \* t \* t \* t) \* EXP(-x \* x)

erfx = erfx \* i

PredC(n) = Ca + (Cb - Ca) \* (1 / 2 \* (1 + erfx))

LSumSq = LSumSq + ((MeasC(n) - PredC(n)) \* (MeasC(n) - PredC(n)))

NEXT

Rsq = 1 - (LSumSq / TSS)

```
PRINT " D "; " MeasC "; " PredC "  
FOR n = 1 TO m  
    PRINT USING "###.##"; D(n), MeasC(n), PredC(n)  
    PRINT #2, USING "#####.###"; D(n), MeasC(n), PredC(n)  
NEXT  
PRINT USING "#####.###"; LSumSq, TSS, Rsq
```

## APPENDIX 7

' This program calculates outputC for given inputC and pdf. This is used for numerical solution of transfer function model.

' units ng, mm; NOTE 100 ng/mm\*2 = 1 kg/ha and 1 ng/mm\*3 = 1 ug/ml

' nn = number of flow paths exiting during drainage

' finite difference interval of pred. cum drainage assumed is deltaI (mm)

nn = 26; deltaI = 10

DIM cumI(nn + 1), probd(nn + 1), cumprob(nn + 1), inputC(nn), outputC(nn)

PRINT " n ", " cumI ", " inputC ", " outputC ", " probd "

initialC = 42

'mu = 4.552

'sigma = 1.138

'pi = 3.14159

a = .00694

cumI(0) = -deltaI / 2

FOR n = 1 TO nn

READ inputC(n)

' D A T A  
196,-15,-12,-8,-30,-20,0,0,-35,0,0,-25,-27,-8,-5,59.2,-60,-15,-92,0,-14,-14,-15,-1  
0,0,-15,

NEXT

FOR n = 1 TO nn

cumI(n) = cumI(n - 1) + deltaI

' probd(n) = EXP(-(LOG(cumI(n)) - mu) ^ 2 / (2 \* sigma \* sigma)) / (SQR(2  
\* pi) \* sigma \* cumI(n))

probd(n) = a \* EXP(-cumI(n) \* a)

cumprob(n) = cumprob(n - 1) + deltaI \* probd(n)

PRINT USING "###.#####"; cumI(n), probd(n), cumprob(n)

NEXT

FOR n = 1 TO nn

outputC(n) = initialC \* (1 - cumprob(n))

FOR m = 1 TO n

outputC(n) = outputC(n) + probd(m) \* inputC(n + 1 - m)

NEXT

PRINT " "; n, cumI(n), inputC(n), outputC(n), probd(n)

NEXT

PRINT " cumprob=", cumprob(nn)

STOP