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

SORPTION AND MOVEMENT OF IONIC AND NON-IONIC PESTICIDES IN SELECTED SOILS OF NEW ZEALAND

SUNDARAM BASKARAN

1994

SORPTION AND MOVEMENT OF IONIC AND NON-IONIC PESTICIDES IN SELECTED SOILS OF NEW ZEALAND

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

SUNDARAM BASKARAN

1994

Dedication

This thesis is
dedicated
to my late beloved *Grand-mother*

ABSTRACT

There is a growing concern about the persistence of pesticide residues in soils and their subsequent movement to groundwater and surface water. Sorption of pesticide by soil particles is one of the key processes affecting the fate of pesticides in soil. The overall objective of this research was to examine the sorption and movement of ionic (2,4-D, atrazine and metsulfuron methyl) and non-ionic (phorate and terbufos) pesticides in a range of allophanic and non-allophanic soil materials of New Zealand.

Firstly, the methods of measuring pesticide in the soil solution were evaluated. The results suggested that radiotracer techniques can be used to measure low concentrations of pesticide in the soil solution during sorption studies. Based on this, the sorption and movement of pesticides was examined using ^{14}C-labelled compounds. Complete recovery of ^{14}C pesticide residues in soils was achieved by direct extraction of soils with a scintillation cocktail, which contained an organic solvent.

The effect of drying soils on the sorption and leaching of an inorganic anion (phosphate; P) and organic pesticides (2,4-D and phorate) was examined using field-moist, freeze-dried, air-dried and oven-dried soil samples. Compared to field-moist and freeze-dried, both air-drying and oven-drying of soil increased the sorption of P, but decreased the sorption of pesticides. Solubilization of organic carbon during air-drying and oven-drying may have increased the accessibility of P to sorption sites on the mineral surfaces and thereby increased the sorption. In contrast, the addition of water soluble organic carbon bound onto pesticides in solution and decreased the apparent sorption onto the soil; thereby increasing leaching.

Pesticide sorption was measured in a range of allophanic and non-allophanic topsoil and subsoil samples using a batch equilibrium technique. In general, pesticide sorption, as measured by the distribution coefficient (K_d), increased with an increase in octanol-water partition coefficient (K_{ow}) of the pesticide and followed the order: terbufos > phorate > 2,4-D > atrazine > metsulfuron methyl. The K_d values increased with increasing organic carbon content of the soils and when the sorption was normalised to organic carbon (K_{oc}) there was less variation in K_{oc} values between the soils. Removal of organic carbon decreased the sorption of pesticides and the

effect was more pronounced with non-ionic than with the ionic pesticides. The results suggest that organic carbon is the principal sorbent for non-ionic pesticides, whereas clay is also contributing to the sorption of ionic pesticides. Multiple regression models were developed to predict pesticide sorption based on soil properties. The existing empirical equations based on K_{ow} values gave unsatisfactory predictions of pesticide sorption in the soils examined.

The contribution of different particle size fractions of soils to sorption and desorption of pesticides was examined using two soils with contrasting characteristics. The K_d values decreased in the order: clay > silt > sand. Organic carbon accounted for most of the variation in K_d values between the particle size fractions, and the removal of organic carbon decreased the K_d values of the pesticides. Following four successive extractions with 0.01 M $CaCl_2$, 65-90% and 22-75% of the initially sorbed ionic and non-ionic pesticides, respectively were released from the particle size fractions. Greater amounts of pesticides were released from the soil fractions from which organic carbon had been removed than from natural soil fractions and the difference was greater for the non-ionic than the ionic pesticides.

Experiments were conducted to examine the effects of different sources of added carbon (peat, sludge, mushroom compost, pig manure and poultry manure), and dissolved organic carbon (DOC) on the sorption and movement of pesticides in soils. Added carbon sources increased the sorption of pesticides and followed the order: peat > sludge > pig manure > mushroom compost > poultry manure. The differences in the effect of carbon addition on the sorption of pesticides may be related to the differences in their effect on DOC and pH of the soil. Premixing DOC with the pesticide solutions decreased the pesticide sorption whereas premixing DOC with soil increased the pesticide sorption. Column studies showed that pesticide mobility was enhanced by the presence of DOC.

Column leaching experiments were conducted to examine the movement of pesticides through repacked soil cores (step-function and pulse inputs) and intact cores (step-function input) using two soils with different pesticide sorption

capacities. In repacked soil columns, the step-function experiments showed a symmetrical breakthrough curve (BTC) for a non-sorbed solute (^3H_2O) with a sigmoidal shape, whereas there was an asymmetrical BTC with extensive tailing for a sorbed solute (2,4-D). In the pulse experiments the leaching of pesticides decreased with an increase in the K_d values and leaching decreased in the order: terbufos > phorate > 2,4-D > atrazine. The results from the intact core experiments suggested that both the sorbed (2,4-D) and non-sorbed (^3H_2O) solutes move preferentially through macropores such as worm holes and root channels.

The convection-dispersion equation (CDE) either with an equilibrium or a bicontinuum non-equilibrium sorption process was used to simulate the measured effluent BTCs obtained by simultaneous displacement of ^3H_2O and 2,4-D. The CDE with an equilibrium sorption process failed to simulate the BTC for 2,4-D in repacked and intact soil columns; whereas the CDE with a bicontinuum non-equilibrium sorption process provided a good description of the experimental data. Both chemical (intraorganic matter diffusion) and physical (preferential flow) processes are involved in the non-equilibrium sorption during the movement of pesticides in soil.

ACKNOWLEDGEMENT

I wish to express my sincere thanks, heartfelt gratitude and appreciation to the following people for their contribution towards the completion of this thesis.

My chief supervisor, Dr. N.S. Bolan, for his valuable guidance, help, encouragement, patience, and friendship during my studies. My co-supervisors, Drs. R.W. Tillman, A. Rahman and A.N. Macgregor, for their supervision, suggestion, patience and friendship.

The past and present Heads and other staff members of the Department of Soil Science for their assistance and friendship. Dr.D.R. Scotter for his valuable guidance and suggestions in conducting leaching experiment and modelling the experimental data.

Dr.P.S.C. Rao, Professor of Soil Science, The University of Florida, USA, for his help in modelling the experimental data using the bicontinuum model. Dr. R. Naidu, Principal Research Scientist, CSIRO, Adelaide, Australia for organising the transmission electron microscope pictures of the clay samples.

Mr Lance Curie, Bob Toes and Ann West for their help in laboratory experiments, Mike Bretherton for his help in computing, Ms Nicola for drawing some figures and friendship, Malcolm Boag for his proof reading and Denise for her help and friendship.

All my fellow postgraduates for their help and friendship. Mr. Kapila Zoysa for proof reading some of the sections.

The Ministry of External Relations and Trade of New Zealand, for granting tuition fees, Massey University for awarding a Vice Chancellor's Ph.D study award and also Helen E. Akers scholarship.

The Tamil Nadu Agricultural University, Coimbatore, South India, for granting me study leave.

Ciba-Geigy New Zealand, DowElanco USA, American Cyanamid Company for supplying the radioactive pesticide compounds.

Dr. Leela Bolan for her love and friendship during our stay in New Zealand.

My parents Mr.A. Sundaram and Mrs. Sulochana Sundaram, for their love, encouragement, continual support and prayers. All my family members, including my uncle, Mr.L. Jothiramalingam, sister, Renuka, father-in-law, mother-in-law and brother-in-law for their love and encouragement.

Finally, but most importantly to my wife Aruna and my son Vivek for their love, patience, encouragement during my study.

TABLE OF CONTENTS

ABSTRACT ..... **i**
ACKNOWLEDGEMENTS ..... **iv**
TABLE OF CONTENTS ..... **vi**
LIST OF TABLES ..... **xvii**
LIST OF FIGURES ..... **xx**
LIST OF PLATES ..... **xxv**
LIST OF SYMBOLS ..... **xxvi**

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND 1
1.2 OBJECTIVES 2
1.3 STRUCTURE OF THE STUDY 3

CHAPTER 2

REVIEW OF LITERATURE

2.1 INTRODUCTION 4
2.2 PESTICIDE USAGE IN NEW ZEALAND 4
2.3 PESTICIDE CONTAMINATION OF SURFACE AND GROUNDWATER 6
2.4 PROCESSES AFFECTING THE FATE OF PESTICIDES IN SOIL .. 6
2.4.1 Sorption-desorption processes 8
2.4.1.1 Sorption 8
2.4.1.2 Desorption 9
2.4.2 Degradation 9
2.4.2.1 Chemical degradation 9
2.4.2.2 Biological degradation 10
2.4.3 Volatilization 10
2.4.4 Leaching 11
2.4.5 Surface runoff 11
2.4.6 Plant uptake 12
2.4.6.1 Uptake of foliage-applied herbicides 12
2.4.6.2 Uptake of soil-applied herbicides 12

2.5 SORPTION OF PESTICIDES IN SOILS 12
2.5.1 Methods for measuring pesticide sorption 13
2.5.2 Sorption isotherm models 13
2.5.2.1 Freundlich equation 14
2.5.2.2 Linear equation 14
2.5.2.3 Langmuir equation 14
2.5.2.4 Linear vs nonlinear equations 15
2.5.3 Factors influencing sorption 16
2.5.3.1 Pesticide properties 16
(i) Octanol-water partition coefficient 16
(ii) Water solubility 18
(iii) Ionization 18
2.5.3.2 Soil properties 18
(i) Organic matter 18
(ii) Clay 20
(iii) Amorphous minerals 20
(iv) pH 21
(v) Soil depth 21
2.5.4 Techniques used to relate soil constituents to pesticide sorption 22
2.5.4.1 Correlation/regression 22
2.5.4.2 Subtraction 24
2.5.5 Distribution coefficient based on organic carbon 24
2.6 EFFECT OF ORGANO-MINERAL FRACTIONS OF SOILS ON PESTICIDE SORPTION-DESORPTION 25
2.6.1 Soil particle size fractionation 27
2.6.2 Chemical characteristics of particle size fractions 27
2.6.3 Contribution of organo-mineral fractions of soils to sorption of pesticides 27
2.7 EFFECT OF DISSOLVED ORGANIC CARBON (DOC) ON SORPTION AND MOVEMENT OF PESTICIDES 30
2.7.1 Sources of DOC 34
2.7.1.1 Endogenous DOC 34

2.7.1.2 Exogenous DOC 34
2.7.2 Measurement of DOC 35
2.7.3 Effect of DOC on sorption of pesticides 35
2.7.4 Effect of DOC on movement of pesticides 36
2.8 MOVEMENT OF PESTICIDES IN SOIL 37
2.8.1 Modelling solute leaching 37
2.8.1.1 Uses of simulation models 38
2.8.1.2 Type of simulation models 38
2.8.2 Convection-Dispersion equation 38
2.8.2.1 Non-sorbing solutes 39
2.8.2.2 Sorbing solutes 39
2.8.3 Equilibrium sorption model 40
2.8.4 Non-equilibrium sorption models 41
2.8.4.1 One-site first-order model 41
2.8.4.2 Bicontinuum model 42
2.9 SUMMARY 44

CHAPTER 3
AN EVALUATION OF METHODS OF MEASUREMENT OF PESTICIDES IN SORPTION STUDIES

3.1 INTRODUCTION 46
3.2 OBJECTIVES 47
3.3 METHODS AND MATERIALS 47
3.3.1 Pesticides 47
3.3.1.1 Metsulfuron methyl 48
3.3.1.2 Atrazine 48
3.3.1.3 2,4-D 48
3.3.1.4 Phorate 51
3.3.1.5 Terbufos 51
3.3.2 Methods for pesticide analysis 51
3.3.2.1 UV spectrophotometer 51

3.3.2.2 *Gas liquid chromatography (GLC) and High performance liquid chromatography (HPLC)* . . 52
(i) Atrazine 52
(ii) 2,4-D 52
(iii) Phorate and Terbufos 52
3.3.2.3 *Radiotracer technique* 53
(i) Principles of radiotracer technique 53
(ii) Liquid Scintillation Counting 54
(iii) Quenching 54
3.3.3 Measurement of ^{14}C labelled pesticides in soil 55
3.3.3.1 *Direct extraction with scintillation cocktail* 55
3.3.3.2 *Dry combustion* 55
3.3.4 Sorption of the pesticides by centrifuge tubes 56
3.4 RESULTS AND DISCUSSION 56
3.4.1 UV spectrophotometer 56
3.4.1.1 *Scanning* 56
3.4.1.2 *Standard preparation* 58
3.4.2 Gas liquid and High performance liquid chromatography 58
3.4.3 Radiotracer technique 59
3.4.4 Comparison of UV, GLC/HPLC and radiotracer techniques . . . 59
3.4.5 Recovery of ^{14}C labelled pesticides in soil 62
3.4.5.1 *Direct extraction with scintillation cocktail* 62
3.4.5.2 *Dry combustion* 63
3.4.6 Sorption of the pesticides by centrifuge tubes 63
3.5 CONCLUSIONS 65

CHAPTER 4

EFFECTS OF THE DRYING OF SOILS ON SORPTION AND LEACHING OF AN INORGANIC PHOSPHATE ION AND ORGANIC PESTICIDES

4.1 INTRODUCTION 66
4.2 OBJECTIVES 68

4.3 MATERIALS AND METHODS 68
4.3.1 Soils 68
4.3.2 Pesticides 70
4.3.3 Phosphate sorption 70
4.3.4 Pesticide sorption 70
4.3.5 Kinetics of phosphate and pesticide sorption 71
4.3.6 Leaching experiments 71
4.3.7 Statistical analysis 72
4.4 RESULTS AND DISCUSSION 72
4.4.1 Effect of drying on soil properties 72
4.4.2 Phosphate sorption 74
4.4.3 Pesticide sorption 76
4.4.4 Kinetics of phosphate and pesticide sorption 81
4.4.5 Leaching of phosphate and pesticides 83
4.4.6 Drying effects on soil properties in relation to phosphate and pesticide sorption 85
4.5 CONCLUSIONS 87

CHAPTER 5
PESTICIDE SORPTION BY ALLOPHANIC AND NON-ALLOPHANIC SOILS

5.1 INTRODUCTION 88
5.2 OBJECTIVES 89
5.3 MATERIALS AND METHODS 89
5.3.1 Soils 89
5.3.2 Soil characteristics 91
5.3.3 Pesticides 91
5.3.4 Pesticide sorption 92
5.3.5 Effect of organic carbon removal on pesticide sorption 93
5.3.6 Statistical analysis 93
5.4 RESULTS AND DISCUSSION 94
5.4.1 Soil Characteristics 94

5.4.1.1 *Allophanic* 94
(i) Andesitic 94
(ii) Basaltic 94
(iii) Rhyolitic 96
5.4.1.2 *Non-allophanic* 96
5.4.2 Pesticide Sorption Isotherms 96
5.4.2.1 *Sorption isotherms* 96
5.4.2.2 *Linear vs non-linear sorption isotherms* 98
5.4.2.3 *Distribution coefficient (K_d) of pesticides...* 100
5.4.2.4 Influence of soil depth on the distribution coefficient (K_d) 103
5.4.3 Relationship between pesticide sorption and soil properties ... 104
5.4.3.1 *Simple correlation studies* 104
5.4.3.2 *Multiple regression equations* 106
5.4.4 Sorption dependence on soil organic carbon 108
5.4.5 Effect of removal of organic carbon on pesticide sorption 109
5.4.6 Prediction of pesticide sorption 112
5.4.7 Sensitivity analysis of the prediction equations 116
5.5 CONCLUSIONS 117

CHAPTER 6

CONTRIBUTION OF ORGANO-MINERAL FRACTIONS OF SOILS TO SORPTION AND DESORPTION OF IONIC AND NON-IONIC PESTICIDES

6.1 INTRODUCTION 118
6.2 OBJECTIVES 118
6.3 MATERIALS AND METHODS 119
6.3.1 Soils 119
6.3.2 Pesticides 119
6.3.3 Particle size fractionation 119
6.3.4 Characterisation of particle size fractions 121

6.3.4.1 *Chemical analysis* 121
6.3.4.2 *Clay mineralogy* 121
(i) X-ray diffraction 121
(ii) Transmission Electron Microscopy 121
(iii) Infrared spectroscopy 122
6.3.5 Pesticide sorption 122
6.3.6 Prediction of K_d values of whole soil 122
6.3.7 Pesticide desorption 123
6.3.8 Effect of organic carbon on sorption and desorption of pesticides123
6.3.9 Prediction of pesticides in surface runoff 124
6.3.9.1 *Pesticide concentration in the sediment* 124
6.3.9.2 *Sediment loss* 125
6.4 RESULTS AND DISCUSSION 127
6.4.1 Distribution of particle size fraction 127
6.4.2 Characteristics of particle size fractions 128
6.4.3 Clay mineralogy 128
6.4.3.1 *X-ray diffraction* 128
6.4.3.2 *Transmission electron microscopy* 131
6.4.3.3 Infrared spectroscopy 133
6.4.4 Sorption of pesticides by whole soil and particle size fractions . 133
6.4.5 Relative contribution of particle size fractions to the distribution coefficient (K_d) of the whole soil 136
6.4.6 Relationship between pesticide sorption and organic carbon content 138
6.4.7 Sorption of ionic and non-ionic pesticides in oxidised soil and particle size fractions 143
6.4.8 Desorption 147
6.4.9 Predicted pesticide losses in surface runoff 150
6.5 CONCLUSIONS 154

CHAPTER 7
IMPORTANCE OF CARBON ADDITION ON SORPTION AND MOVEMENT OF PESTICIDES IN SOIL

7.1 INTRODUCTION 155
7.2 OBJECTIVES 156
7.3 MATERIALS AND METHODS 156
7.3.1 Soils 156
7.3.2 Sources of carbon material 157
7.3.3 Pesticides 157
7.3.4 Incubation 158
7.3.5 Preparation of dissolved organic carbon 158
7.3.6 Pesticide sorption 158
7.3.7 Effect of DOC on pesticide sorption 159
7.3.7.1 Preincubating DOC with pesticide 159
7.3.7.2 Preincubating DOC with soil 159
7.3.8 Effect of pH on sorption 160
7.3.9 Effect of DOC on the movement of pesticides 160
7.3.9.1 Soil column studies 160
7.3.9.2 Movement of organic chemicals in the presence of DOC and the retardation factor 161
7.3.10 Interaction of pesticides with DOC 162
7.3.11 Chemical analysis 163
7.3.12 Statistical analysis 163
7.4 RESULTS AND DISCUSSION 163
7.4.1 Characteristics of the soils 163
7.4.2 Characteristics of carbon materials 163
7.4.3 Sorption of pesticides by soils 164
7.4.4 Effect of carbon additions on the distribution coefficients (K_d) of pesticides 164

7.4.5 Effect of DOC on pesticide sorption 171
7.4.5.1 Preincubating DOC with pesticide 171
7.4.5.2 Preincubating DOC with soil 171
7.4.6 Effect of pH on pesticide sorption 173
7.4.7 Effect of DOC on the movement of pesticides 180
7.4.7.1 Column breakthrough experiments 180
7.4.7.2 Effect of DOC in column leaching 184
7.4.7.3 Soil column characteristics and the retardation factor 188
7.4.8 Infrared Spectroscopy 191
7.4.8.1 Spectra of DOC (Figure 7.17) 191
7.4.8.2 Spectra of pure pesticides (Figure 7.18) 191
7.4.8.3 Spectra of DOC-pesticide complexes (Figure 7.19-7.23) 194
7.5 CONCLUSIONS 200

CHAPTER 8
EFFECT OF SORPTION ON THE MOVEMENT OF PESTICIDES IN SOILS

8.1 INTRODUCTION 202
8.2 OBJECTIVES 203
8.3 MATERIALS AND METHODS 204
8.3.1 Soils 204
8.3.2 Column experiments 204
8.3.2.1 Repacked soil column experiments 205
(i) Step-function experiment 205
(ii) Pulse experiment 207
8.3.2.2 Intact (undisturbed) soil core experiment 209
(i) Core collection 209
(ii) Step-function experiment 210
8.3.3 Dual label counting 210
8.3.4 Modelling the non-sorbing and sorbing solutes in soil column studies 212

8.3.4.1 *Theoretical consideration and numerical methods* . 212
8.3.4.2 *Model parameter estimation* 215
8.4 RESULTS AND DISCUSSION 216
8.4.1 Repacked soil column experiment 216
8.4.1.1 *Step-function experiment* 216
8.4.1.2 *Pulse experiment* 219
8.4.2 Intact soil core experiment 222
8.4.3 Repacked versus intact soil core experiments 226
8.4.4 Model simulation 229
8.4.4.1 *Equilibrium CDE model* 229
(i) Repacked soil column 229
(ii) Intact soil core experiment 231
8.4.4.2 *Bicontinuum sorption model* 231
(i) Repacked soil column 233
(ii) Intact soil core experiment 233
8.4.5 Significance of model parameters 235
(i) Peclet number (P) 235
(ii) Retardation factor (R) 235
(iii) β and ω 235
(iv) Rate constant (Q_2) 236
8.5 CONCLUSIONS 237

CHAPTER 9
SUMMARY AND CONCLUSION

9.1 Review of literature 239
9.2 Measurement of pesticides in sorption studies 242
9.3 The effect of drying of soils on pesticide sorption 242
9.4 Equilibrium sorption of pesticides in soils 243
9.5 Organo-mineral contribution to pesticide sorption-desorption 244
9.6 Effect of carbon addition on pesticide sorption and movement in soils 246

9.7 Effect of sorption on movement of pesticides in soils 247
9.8 Suggestions for future research 248

REFERENCES 251

LIST OF TABLES

Table **Page**

CHAPTER 2

2.1 Correlation and subtraction techniques used to relate soil properties to pesticide sorption 23

2.2 Prediction equations for estimating distribution coefficient based on organic carbon (K_{oc}) of pesticides from the octanol-water partition coefficient (K_{ow}) values 26

2.3 Summary of literature on the chemical characteristics of particle size fractions 28

2.4 Summary of literature on the particle size contributions to pesticide sorption-desorption by soils and sediments 31

2.5 Summary of literature on the runoff losses of pesticides from natural and simulated rainfall 33

CHAPTER 3

3.1 Some important properties of the pesticides 49

3.2 Effect of increasing amount of soil extract on the recovery of ^{14}C pesticides (33 Bq of ^{14}C was added) 60

3.3 Linear range, minimum concentration and soil solution concentration of pesticides as measured by different methods 61

3.4 Recovery of ^{14}C labelled pesticides by a direct extraction technique . . . 62

3.5 Percent recovery of ^{14}C labelled pesticide using a combustion technique 63

3.6 Pesticide sorption to centrifuge tubes 64

CHAPTER 4

4.1 Summary of literature on the effects of drying on soil properties 67

4.2 Some characteristics of the soils used 69

4.3 Effect of drying on some of the soil properties 73

4.4 Effect of drying on the Freundlich sorption coefficients (K, N) and retardation factor (R) for Phosphate and pesticides 80

Table		Page
4.5	Effect of drying on the percent distribution of added P or pesticides in the soil column and leachate	84

CHAPTER 5

5.1	Soil descriptions	90
5.2	Some important characteristics of the soil samples	95
5.3	Freundlich sorption coefficients (K, N) of pesticides in soils	99
5.4	Distribution coefficients (K_d, K_{oc}) of pesticides for the soils	102
5.5	Simple correlation coefficients (r) between K_d of pesticides and soil properties	105
5.6	Multiple regression equation between K_d of pesticides and soil properties	107
5.7	Distribution coefficients (K_d, K_{oc}) of pesticides in H_2O_2 treated soils	111
5.8	Comparison of experimental K_{oc} values of five pesticides with literature values and values estimated using prediction equations from Table 2.2	113
5.9	Effect of change in slope of the prediction equation on K_{oc} of pesticides	116

CHAPTER 6

6.1	Classification and chemical characteristics of soils	120
6.2	Soil, pesticide and sediment data for prediction of pesticide losses in runoff	126
6.3	Comparison of the particle size distribution of the soils by (A) the conventional pipette and (B) the ultrasonic dispersion method	127
6.4	Some important characteristics of particle size fractions	129
6.5	Distribution of minerals in clay fractions of the Egmont and the Tokomaru soils as indicated by X-ray diffraction analysis	131
6.6	Distribution coefficients (K_d and K_{oc}) of ionic (atrazine and 2,4-D) and non-ionic pesticides (phorate and terbufos) in whole soils and particle size fractions	142
6.7	Distribution coefficients (K_d and K_{oc}) of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides in oxidised soil and particle size fractions	144

Table		Page
6.8	Some important characteristics of oxidised particle size fractions	146
6.9	Recovery of ^{14}C pesticides during desorption from the Tokomaru soil	148
6.10	Distribution coefficient (K_d) values of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides during sorption and desorption in the Egmont and the Tokomaru natural and oxidised soil and particle size fractions	152
6.11	Predicted pesticide losses with sediment runoff resulting from a 65 mm rainfall event	153

CHAPTER 7

7.1	Important characteristics of the soil materials	157
7.2	Some important characteristics of carbon materials	157
7.3	Distribution coefficient (K_d) of pesticides for each soil	164
7.4	Effect of additions of Carbon materials on the pH and the DOC in the tailings and the Tokomaru and the Egmont soils	165
7.5	Distribution of pesticides in the leachate at different pore volumes during leaching with either $CaCl_2$ or DOC	183
7.6	Column breakthrough data and retardation factor	189

CHAPTER 8

8.1	Types of column leaching experiments conducted	204
8.2	Experimental parameters for the repacked and intact soil column studies	208
8.3	Model parameter values for the step-function experiment	217
8.4	Mass balance of ^{14}C pesticides in the column experiment and the distribution coefficient (K_d) values obtained in the batch experiment .	221

LIST OF FIGURES

Fig — Page

CHAPTER 2

2.1 Trends in Pesticide sales in New Zealand 5

2.2 Relative contribution of herbicide, fungicide and insecticide to pesticide sales in New Zealand 5

2.3 Processes involved in the fate of pesticides in soil 7

2.4 Deviation from nonlinear isotherm introduced by the linear sorption isotherm. (The numbers near the lines are the values of the Freundlich coefficient, N) 17

CHAPTER 3

3.1 Structural formulae of the pesticides 50

3.2a Spectrophotometric scan of atrazine and 2,4-D 57

3.2b Spectrophotometric scan of (B) 2,4-D in aqueous (0.01 M $CaCl_2$), (A) 0.01 M $CaCl_2$ soil extract and (C) 2,4-D in 0.01 M $CaCl_2$ extract . . 57

CHAPTER 4

4.1 Effect of drying on phosphate sorption 75

4.2 Effect of drying on 2,4-D sorption 77

4.3 Effect of drying on Phorate sorption 78

4.4 Effect of drying on sorption kinetics of phosphate (—), 2,4-D (- - -) and phorate (— —) in Patua soil 82

CHAPTER 5

5.1 Pesticide sorption isotherms in allophanic (—) and non-allophanic (- -) soils 97

5.2 Deviation from nonlinear isotherm introduced by the linear sorption isotherm. (The numbers near the lines are the values of Freundlich coefficient, N obtained in this experiment) 101

Fig | Page

5.3 Relationship between the distribution coefficient of pesticides based on organic carbon (K_{oc}) and octanol-water partition coefficient (K_{ow}). The range of K_{oc} values for the various pesticides used in this study is also presented 115

CHAPTER 6

6.1 Relationship between organic carbon and particle size in the Egmont and the Tokomaru soils. (Vertical bars represent standard error of mean) 130

6.2 Transmission Electron Micrographs of (A) Egmont (Ah) clay showing allophane and (B) Tokomaru (Ah1) clay showing illite 132

6.3 Infrared spectra of Egmont Ah and Bw3 horizon clay 134

6.4 Distribution coefficient (K_d) of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides in whole soil and particle size fractions. (Vertical bars represent LSD (0.05)). 135

6.5 Relative contribution of particle size fractions to distribution coefficient (K_d) of pesticides 137

6.6 Relationship between measured and predicted distribution coefficient (K_d) of pesticides on a whole soil basis 139

6.7 Relationship between organic carbon and distribution coefficient (K_d) of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides in particle size fractions 140

6.8 Comparison of K_{oc} of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides in (A) Egmont and (B) Tokomaru natural and oxidised soil and particle size fractions. (Vertical bars represent LSD (0.05)) 145

6.9 Desorption of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides from whole soil and particle size fractions 149

6.10 Desorption of ionic (atrazine and 2,4-D) and non-ionic (phorate and terbufos) pesticides from oxidised whole soil and particle size fractions 151

Fig Page

CHAPTER 7

7.1 Effect of addition of carbon on the distribution coefficient (K_d) of pesticides in the tailings. (Vertical bars represent standard error of mean). 166

7.2 Effect of addition of carbon on the distribution coefficient (K_d) of pesticides in the Tokomaru soil. (Vertical bars represent standard error of mean) 167

7.3 Effect of addition of carbon on the distribution coefficient (K_d) of pesticides in the Egmont soil. (Vertical bars represent standard error of mean) 168

7.4 Effect of additions of (A) peat and (B) poultry manure on the distribution coefficient based on organic carbon (K_{oc}) in the Tokomaru soil 169

7.5 Effect of DOC on the sorption of pesticides by the tailings due to (A) preincubation of DOC with pesticides and (B) preincubation of DOC with soil. (The results are expressed as percent increase or decrease in sorption) 172

7.6 Soil pH modification with HCl or $Ca(OH)_2$ for the Egmont (A) and the Tokomaru soil (B) soils 174

7.7 Effect of pH on the distribution coefficient (K_d) of pesticides in the Egmont (A) and the Tokomaru (B) soils incubated with HCl or $Ca(OH)_2$ 175

7.8 Effect of pH on the distribution coefficient (K_d) of pesticides in the Egmont (A) and the Tokomaru (B) soils incubated with $Ca(OH)_2$ (—) or NaOH (- -) 176

7.9 Effect of pH on dissolved organic carbon (DOC) of the Egmont (A) and the Tokomaru (B) soils incubated with $Ca(OH)_2$ or NaOH 178

Fig		Page
7.10	Relationship between difference in dissolved organic carbon (DOC) and the distribution coefficient (K_d) between the NaOH and $Ca(OH)_2$ amended Egmont soil	179
7.11	Breakthrough curves for pesticides leached with either $CaCl_2$ or dissolved organic carbon (DOC) in the tailings	181
7.12	Breakthrough curves for pesticides leached with either $CaCl_2$ or dissolved organic carbon (DOC) in the Egmont soil	182
7.13	Percent organic carbon of the solid phase following leaching with either $CaCl_2$ or dissolved organic carbon (DOC) in the tailings	185
7.14	Dissolved organic carbon (DOC) concentration in the column leachate in the tailings and the Egmont soil. (Dashed line indicates the concentration of DOC used to leach the pesticides in the soil column)	186
7.15	Phorate concentration of the soil column following leaching with either $CaCl_2$ or dissolved organic carbon (DOC) in the Egmont soil. (Horizontal bars represent standard error of mean)	187
7.16	Relationship between the predicted and the observed retardation factor (R) in soil column leaching	190
7.17	Infrared spectra of DOC extracted from (A) sludge, (B) peat, (C) pig manure, (D) mushroom compost and (E) poultry manure	192
7.18	Infrared spectra of pesticides (A) Atrazine, (B) 2,4-D, (C) Phorate and (D) Terbufos	193
7.19	Infrared spectra of (A) sludge DOC, (B) DOC-atrazine, (C) DOC-2,4-D, (D) DOC-phorate and (E) DOC-terbufos	195
7.20	Infrared spectra of (A) peat DOC, (B) DOC-atrazine, (C) DOC-2,4-D, (D) DOC-phorate and (E) DOC-terbufos	196
7.21	Infrared spectra of (A) pig manure DOC, (B) DOC-atrazine, (C) DOC-2,4-D, (D) DOC-phorate and (E) DOC-terbufos	197
7.22	Infrared spectra of (A) mushroom compost DOC, (B) DOC-atrazine, (C) DOC-2,4-D, (D) DOC-phorate and (E) DOC-terbufos	198
7.23	Infrared spectra of (A) poultry manure DOC, (B) DOC-atrazine, (C) DOC-2,4-D, (D) DOC-phorate and (E) DOC-terbufos	199

Fig Page

CHAPTER 8

8.1 Breakthrough curve (BTC) for ^3H_2O and 2,4-D in the Tokomaru (A) and the Patua (B) soils - Step-function experiment 218

8.2 Leaching of ^{14}C pesticides through the Tokomaru and the Patua soil columns - Pulse experiment 220

8.3 Distribution of pesticides in the Patua and the Tokomaru soil column. (Horizontal bars represent standard error of mean) 223

8.4 Relationship between the distribution coefficient (K_d) and the percent of pesticide leached 224

8.5 Breakthrough curve (BTC) for ^3H_2O and 2,4-D in the Tokomaru soil - undisturbed soil core experiment 225

8.6 Breakthrough curve (BTC) for ^3H_2O and 2,4-D in repacked and undisturbed soil core experiments. (The arrows indicate a change in input from ^3H_2O and 2,4-D to $CaCl_2$). 227

8.7 Measured (o ^3H_2O ; ● 2,4-D) and simulated (line) breakthrough curve (BTC) using equilibrium CDE model for ^3H_2O and 2,4-D in soil columns of (A) repacked Tokomaru, (B) repacked Patua, and (C) intact Tokomaru soil column 230

8.8 Measured (o ^3H_2O ; ● 2,4-D) and simulated (line) breakthrough curve (BTC) using non-equilibrium bicontinuum model for ^3H_2O and 2,4-D in soil columns of (A) repacked Tokomaru, (B) repacked Patua, and (C) intact Tokomaru soil column 232

8.9 Measured and simulated (line) breakthrough curve (BTC) for 2,4-D in the Tokomaru and the Patua soil. Comparison of a linear (- -) and nonlinear (—) isotherm are shown 234

CHAPTER 9

9.1 Effect of sorption on the fate of pesticides in soils 240

LIST OF PLATES

CHAPTER 8

8.1 Experimental setup - Repacked soil column experiment 206

8.2 Preferential flow of dye through root channel and earthworm channel 228

APPENDIX

Appendix 1 Channel settings for dual label counting 250

LIST OF SYMBOLS

A =amount of pesticide added (kg ha^{-1})

a =Langmuir sorption coefficient (binding constant)

C =equilibrium solution concentration (μmol L^{-1})

C_e =leachate concentration (μmol L^{-1})

C_o =input concentration (μmol L^{-1})

C_{DOC} =concentration of dissolved organic carbon (mg L^{-1})

D =dispersion coefficient (mm^2 hr^{-1})

Er_i =enrichment ratio of the (i) th particle size fraction

F =fraction of equilibrium site

f(i) =fraction of the total mass represented by (i) th particle size fraction

i =(i) th particle size fraction

K =Freundlich sorption coefficient (sorption at unit concentration)

K_d =distribution coefficient (L kg^{-1})

K_s =sorption rate coefficient (hr^{-1}) (non-equilibrium first-order model)

K_1 =Freundlich sorption coefficient in equilibrium site

K_2 =Freundlich sorption coefficient in kinetic site

K_{de} =desorption rate coefficient (hr^{-1}) (non-equilibrium first-order model)

K_{ds} =distribution coefficient of the pesticide in the sediment

K_{oc} =distribution coefficient based on organic carbon (L kg^{-1})

K_{om} =distribution coefficient based on organic matter (L kg^{-1})

K_{ow} =Octanol-water partition coefficient

K_{DOC} =distribution coefficient of pesticide in dissolved organic carbon (DOC)

$K_d(i)$ =K_d of pesticides in (i) th particle size fraction

L =column length (mm)

N =Freundlich sorption coefficient

n_1 =rate constant (Freundlich kinetic sorption)

P =Peclet number

p =liquid-filled pore volume

Q_1 =Freundlich kinetic sorption coefficient (sorption at unit time)

Q_2 =rate constant (bicontinuum non-equilibrium model)

R =retardation factor

S =sorbed concentration (μmol kg^{-1})

S_m =Langmuir sorption coefficient (sorption maximum)

S_s =amount of pesticide sorbed onto the sediment

S_1 =sorbed phase concentration in equilibrium site

S_2 =sorbed phase concentration in kinetic site

t =time (hr)

v =average pore water velocity (mm hr^{-1})

W_s =water solubility of pesticide

x =distance in the direction of flow (mm)

Y =relative contribution of K_d from sand, silt or clay on the whole soil basis

ρ =soil bulk density (g cm^{-1})

θ =volumetric water content (mm^3 mm^{-3})

β =fraction of instantaneous retardation (bicontinuum non-equilibrium model

ω =Damkohler number