Polymer coated controlled release agrichemicals as mitigation tools in pastoral farming

A thesis presented in partial fulfilment of the requirements for
the degree of
Doctor of Philosophy in Soil Science
at Massey University, Palmerston North
New Zealand.

Peter Andrew Bishop

2010

Abstract

Controlled release coating technology and nitrification inhibitors offer potential mitigation options, for the reduction of pastoral nitrate leaching. Previous published research on this topic was reviewed indicating two potential areas of new research and development around two main hypotheses:

- That polymer coated urea can allow high urea N applications in winter reducing application costs, nitrate leaching, herbage N content and urine N return to pasture.

- That polymer coated nitrification inhibitor dicyandiamide (DCD) can increase the longevity of DCD in soil and effectively inhibit nitrification of dairy urine affected soils.

To facilitate this research a range of coated urea and nitrification inhibitor dicyandiamide (DCD) products were produced using low cost, reactive layer, polyurethane (RLP) and were assessed in laboratory and field studies.

The mechanism of urea release from modified RLP coated urea was investigated, leading to the development of a comprehensive model of release, based on the porous water repellent nature of the RLP coating. The “hydraulic convection” model was validated using water extraction and under field conditions for modified RLP coated urea.

In, field trials (June-Nov 2007) using Italian ryegrass, a single application of 150 kgN ha^{-1} of palmitic acid modified RLP coated urea (5UCU) reduced winter nitrate leaching by 7 kgN ha^{-1} compared to uncoated urea and reduced peak herbage N levels over this period (150 days). Using an empirical N partitioning model for grazing cows, the reduction in herbage N was predicted to reduce urine N return by 5 to 10 kgN ha^{-1} over the 150 day trial.

The effectiveness of laboratory prepared controlled release nitrification inhibitor dicyandiamide (PDCD) was tested as a surface application in repacked core studies on two soils contrasting in organic matter content and anion sorption capacity, Manawatu fine sandy silt and Dannevirke silt loam. The data from this trial was used to develop a model to explain DCD movement and degradation soils, which predicted that PDCD can potentially increase DCD longevity by 120 days at 20 ^{o}C over uncoated DCD.

Acknowledgements

I would like to acknowledge the assistance of my supervisors, Dr. M. Hedley, Dr. J. Jones and Dr. P. Loganathan for their guidance and support. The technical staff; Mr. I. Furkert, Mr. B. Toes from the Institute of Natural Resources, Mr. W. Johnson and Mrs. M. Tamehana from the Institute of Food, Nutrition and Human Health, for their assistance with laboratory work. I would also like to acknowledge the assistance of Mrs. H. Liu and Mrs. J. Bishop in the field work and sample preparation. This work was made possible by an INR scholarship.

Table of Contents

Polymer coated controlled release agrichemicals as mitigation tools in pastoral farming i

Abstract ii

Acknowledgements iv

Table of Contents v

Table of Figures xii

Table of Tables xxi

Nomenclature xxiv

Chapter 1 Review: Mitigation of pastoral nitrate leaching by nitrification inhibitors and polymer coated fertilisers - applications, release characteristics and production 1

1.1 Introduction 1

1.2 Controlled release coated fertilisers: their production and applications 3

1.2.1 Sulphur Coated Fertiliser 3
1.2.2 Polymer Coated Sulphur Coated Urea (PCSCU) 6
1.2.3 Alkyd Resin (Osmocote®) 7
1.2.4 Reactive isocynate coatings 10
1.2.5 Poly-Olefins coatings- Solvent based 14
1.2.6 Poly-Olefins coatings -Thermoplastic 16
1.2.7 Inorganic coatings 17

1.3 Release Mechanisms of Controlled Release Fertilisers 18

1.3.1 Rupture Model 20
1.3.2 Permeability Models 22
1.3.3 Osmotic pumping model 24
1.3.4 Orifice diffusion model 26
1.3.5 Combined models 27

1.3.6 Modelling parameters........29
Film Elasticity and Volume Change........29
Variable Permeability........30
Temperature effect........30
1.3.7 Modelling developments........32
1.4 Nitrification inhibitors........33
1.4.1 Types and Mode of Action........33
1.4.2 Agronomic impact of nitrification inhibitors........38
1.5 Conclusion:........40

Chapter 2 Modelling of nutrient release rate of modified Castor/MDI coated urea........42
2.1 Introduction........42
2.2 Hydraulic convection of solute from a coated granule........43
2.2.1 Lag time........44
2.2.2 Equilibrium release period........47
2.2.3 Constant equilibrium rate period........48
2.2.4 Falling rate period........49
2.2.5 Terminal period........51
2.2.6 Summary of spherical model........52
2.2.7 Non-spherical coated granules........52
2.3 Working model for reactive layer poly-urethane coated urea........53
2.3.1 Water extraction model........54
2.3.2 Field condition model........55
2.4 Objectives........56
2.5 Methods and Materials:........57
2.5.1 Preparation of film and coated urea........57

2.5.2 Physical testing of polymer films for Young’s modulus and tensile strength 58
2.5.3 Water vapour permeability W’ of laboratory prepared polymer films 58
2.5.4 Release rate from coated urea in water 59
2.5.5 Digital analysis of particle size and volume change distributions 59
2.5.6 Film thickness distribution 60
2.5.7 Permeability of film with coating thickness 60
2.5.8 Hydraulic permeability H’ 60

2.6 Results and discussion: 62

2.6.1 Physical testing of polymer films for Young’s modulus and tensile strength 62
2.6.2 Water vapour permeability W’ of laboratory prepared films 63
2.6.3 Permeability of film with coating thickness (coated granular urea) 64
2.6.4 Critical Pressure and hydraulic conductivity 66
2.6.5 Estimation of equilibrium pressure P_{eq} 67
2.6.6 Volume change following extraction 67
2.6.7 Digital Analysis 68
2.6.8 Coating thickness distribution 69
2.6.9 Release rate in water 70

2.7 Modelling of release rates based on physical film and granular parameters 71

2.7.1 Effect of temperature on models 75
2.7.2 Field trial release rate data 75
2.7.3 Summary and Conclusions 75

Chapter 3 Evaluation of polymer coated urea in grazed pasture systems 78

3.1 Introduction 78

3.2 Materials and methods 79

3.2.1 Site 79

3.2.2 Design and treatments ... 79
3.2.3 Plant analysis ... 81
Drymatter ... 81
Herbage N ... 81
3.2.4 Soil Analysis ... 81
Soil bulk density and estimated field capacity ... 81
Total soil carbon and nitrogen ... 81
3.2.5 Statistics ... 81
3.3 Results and Discussion ... 82
3.3.1 Dry matter ... 82
3.3.2 Herbage N recovery ... 83
3.3.3 Drainage ... 85
3.3.4 Climatic conditions ... 86
3.3.5 Nitrogen use efficiency ... 86
3.3.6 Nitrogen recycling via grazing ... 88
3.4 Conclusion ... 89

Chapter 4 Distribution and fate of fertilizer N in the soil profile ... 91
4.1 Introduction ... 91
4.2 Materials and Methods ... 91
4.2.1 Experimental site ... 91
4.2.2 Soil analysis ... 91
Mineral N ... 92
4.2.3 Residual fertiliser N – amount and release characteristics ... 93
4.3 Results and Discussion ... 93
4.3.1 N Balance ... 100
4.3.2 Residual N in soil from UCU ... 101

4.3.3 Agronomic availability of residual N 102
4.4 Conclusion 103

Chapter 5 A model of nitrification inhibitor (DCD) movement in soil columns from conventional granular DCD and a new polymer coated granule: development and validation. 105

5.1 Introduction 105
5.2 Theory and experimental design 107
5.2.1 Diffusion of solute in soil 107
5.2.2 Boundary conditions for uncoated and coated granules 108
5.2.3 Summary of diffusion modelling factors 109
5.3 Equipment and methods 110
5.3.1 Soil microtone 110
5.3.2 Soil bulk density and volumetric field capacity 111
5.3.3 Total soil carbon and nitrogen 111
5.3.4 DCD analysis in soil and fertiliser 111
5.3.5 Mineral N 112
5.3.6 Preparation of Coated granular DCD 112
5.3.7 Soils 113
5.4 Methodology 113
5.4.1 Main experiment 113
Diffusion column study 113
DCD and urine redistribution and N transformations 114
5.4.2 Supporting experiments 114
DCD degradation rate 114
DCD adsorption isotherm 115
Release rate of DCD 116

5.5 Results - Supporting experiments 116

5.5.1 DCD degradation rate 116
5.5.2 DCD absorption isotherms 118
5.5.3 Release rate of coated DCD 120

5.6 Diffusion Column study- observations and model development 121

5.6.1 Total DCD in soil over time 121
5.6.2 DCD concentrations at each soil depth over time 124

5.7 Model application to predict DCD profiles 126

5.7.1 Uncoated DCD 126
5.7.2 Coated PDCDs 130

5.8 Application of model to determine longevity of PDCD release over DCD 134

5.9 Conclusion: 136

Chapter 6 Nitrification inhibitory effect of polymer coated DCD in two contrasting New Zealand soils. 138

6.1 Introduction 138

6.2 Methodology 139

6.2.1 Measurement of soil mineral N 139
6.2.2 Estimation of nitrification rate with depth 139
6.2.3 Measurement of soil DCD concentration 139
6.2.4 Measurement of inhibitory effect of DCD on nitrification 140
6.2.5 Mass flow of solute 140
6.2.6 Urine NH_4^+ -N isotherm 141
6.2.7 Modelling 141

6.3 Results 142

6.3.1 Urine NH_4^+ -N isotherm 142
6.3.2 Nitrification rate with depth 143
6.3.3 Soil core incubation with urine application 146

6.3.4 Nitrification with depth..149
6.3.5 Inhibitor constant for Manawatu and Dannevirke soils........................152
6.3.6 Soil pH profiles and electrical conductivity..154
6.4 Modelling urine movement and conversion...156
6.5 Conclusion...158

Chapter 7 Conclusions and recommendations for future work....................................160
7.1 Conclusions...160
7.1.1 Mechanism of release from UCU 160
7.1.2 Field trials of modified RLP coated urea 5UCU and 7UCU 161
7.1.3 Evaluation of PDCD in repacked soil core studies..............................161
7.2 Further work..162
Appendix 1 Model of release of urea from reactive layer polyurethane coated urea...164
A1.1 Field conditions...168
Appendix 2 Model of diffusion, sorption and degradation of DCD in soil................172
Appendix 3 Model of diffusion, sorption and Nitrification of dairy urine in soil...177
References 182

Table of Figures

Figure 1.1 Schematic of TVA pilot plant for sulphur coated urea, using twin fluid sulphur spray. Redrawn from Rindt et al.,(1968)................................ 4

Figure 1.2 Comparative dry matter yields of Bumarda grass in glasshouse pot trials grown with the addition of 160 kgNha^{-1}of 9%(■) and 15% (▲)sulphur coated urea, urea(♦) and a blend of 40% urea and 60% SUC(x). Data from (Rindt et al. 1968) 6

Figure 1.3 Cumulative release of urea from Soya-cyclopentadiene resin coated urea, with coating expressed as % initial fertilizer weight, data from (Hansen, 1965) 8

Figure 1.4 Effect of leaching volume on electrical conductivity of a 1:1.5 extract of potting media exposed to high temperatures in summer 31.8±2.6 ^{o}C. Data from Huett (1997). 10

Figure 1.5 Schematic of continuous reactive urethane coating process derived from Detrick and Carney (1994).. 12

Figure 1.6 Schematic of Spouted bed coater for the application of poly-olefin coatings. Derived from Fujita et al. (1977). 15

Figure 1.7 Release characteristics of 3 % low density polyethylene coatings with the addition of 0 to 15% surfactant (octaoxyethylene nonylphenyl ether) in the coating. Data from Fujita et al. (1977). 16

Figure 1.8 Summary of factors contributing to release of nutrients from a coated controlled release fertiliser 20

Figure 1.9 Biological oxidation of ammonia to nitrite by membrane bound ammonium monooxygenase (AMO) and hydroxylamine oxidoreductase (HAO)... 34

Figure 1.10 Structure of the nitrification inhibitors cyanamide and dicyandiamide. 36

Figure 1.11 Effectiveness of heterocyclic nitrogen compounds, as nitrification inhibitors with % inhibition in soil with (high and low) organic matter contents. (McCarty and Bremner 1989) 37

Figure 1.12 Structures of highly effective heterocyclic nitrogen containing nitrification inhibitors (commercial name)(McCarty 1999). 37

Figure 2.1 Transformation of digital image to spherical equivalent model granule for estimation of potential volume change γ. 53

Figure 2.2 Membrane diffusion and permeability apparatus. 61

Figure 2.3 Pressure calibration curve for dead weight syringe system 62

Figure 2.4 Release rate profiles for RLP coated urea with film thickness, Δ 0.00104, ◊ 0.00156, □ 0.00206, × 0.0026, ○ 0.0036 and ● 0.0052 cm. 65

Figure 2.5 Relationship between water vapour permeability (W') and mean coating thickness of RLP coated urea (control, MDI) Dashed line represents model $W' = 2.68 \times 10^{-8} + 4.05\times10^{-6}\, e^{-2800lo}$ 65

Figure 2.6 Flow rate of urea solution (50% w/w) through laboratory prepared coating films as the result of applied pressure, control (○) and 20% Palmitic acid (+) amended polymer films. Solid lines represent linear regressions for control membrane and dashed lines 20% Palmitic acid 66

Figure 2.7 Granule image morphology of urea prior to coating. 68

Figure 2.8 Proportional urea release with time in water at 20 ^{o}C, for urea coated with ♦ RLP and RLP modified with ,■ Canola oil,▲ Palmitic acid and ● Soya oil at levels of 10% (hollow), 15% (gray) and 20% (solid). 70

Figure 2.9 Proportional urea release with time in water at 10 °C , for urea coated with ♦ RLP and RLP modified with ,■ Canola oil,▲ Palmitic acid and ● Soya oil at levels of 10% (hollow), 15% (gray) and 20% (solid). 71

Figure 2.10 Correlation plot of modelled and measured urea release for 5(●), 7(+) and 10% (X) coating levels of the control polymer MDI: Castor oil: TEA in water at 20°C with lag period calculated.......... 72

Figure 2.11 Correlation plot of modelled and measured urea release for 5(●), 7(+) and 10% (X) coating levels of the control polymer (MDI: castor oil: TEA) in water at 20°C with no lag period calculated 73

Figure 2.12 Plot of the measured proportion of urea released at 20°C in water extraction of 5% coating level of 20% Palmitic acid amended coated urea(▲), compared to modelled results using hydraulic convection model, with (solid) and without lag period (dashed) line.......... 74

Figure 2.13 Plot of the measured proportion of urea released at 10°C in water extraction of 5% coating level of 20% Palmitic acid amended coated urea(▲), compared to modelled results using hydraulic convection model, with (solid) and without lag period (dashed) line.......... 74

Figure 2.14 Proportional herbage N recovery for surface applications 5UCU(▲) and 7UCU (●) at 150 kg N ha^{-1} on Italian ryegrass crop (Bishop et al. 2008) with release of urea modelled using Hydraulic convection model (black dashed line) using mean daily temperature(black line) and soil volumetric water content (gray line).......... 76

Figure 3.1 Randomized block layout for RLP coated urea field trial at Massey University Palmerston North. Gray blocks treatments applied at 50 kgN ha^{-1} while black blocks recovered treatments at 150 kgN ha^{-1}.......... 80

Figure 3.2 Estimated nitrate-N leaching from 150 kg N ha^{-1} treatments during drainage events. Significance of difference between treatments expressed as LSD (P=0.05) for each leaching event. 85

Figure 3.3 Monthly dry matter production to herbage N recovery over the trial period for all treatments. Showing N use efficiency increasing from winter to summer 87

Figure 3.4 Monthly herbage N contents of pasture at harvest for 150 Ntreatments. Vertical bars indicate LSD (P=0.05). 87

Figure 4.1 Soil pits used for bulk density and field water capacity measured in the trial plots on Tokomaru silt loam, Massey University, Palmerston North, New Zealand. 94

Figure 4.2 Initial mineral N profile of soil cores in 5 cm sections (19/06/2007). Error bars represent standard error of mean for n = 7. 95

Figure 4.3 Mineral N soil profiles on 28th June 2007, 10 days following treatment applications. 97

Figure 4.4 Measured soil exchangeable NH_4^+-N (kgN ha^{-1}) to a depth of 25 cm, for the 150 kgN ha^{-1} treatments (◊ U, ■ DCDU, ▲ 5UCU, × 7UCU, ○ control (nil-N)). The vertical error bars represent the least significant difference between treatments on each date. 98

Figure 4.5 Measured soil exchangeable NH_4^+-N (kgN ha^{-1}) to a depth of 25 cm, for the 50 kgN ha^{-1} treatments (◊ U, ■ DCDU, ▲ 5UCU, × 7UCU, ○ control (nil-N)). The vertical error bars represent the least significant difference between treatments on each date. 98

Figure 4.6 Measured soil exchangeable NO_3^- -N (kgN ha^{-1}) to a depth of 25 cm, for the 150 kgN ha^{-1} treatments (◊ U, ■ DCDU, ▲ 5UCU, × 7UCU, ○ control (nil-N)). The vertical error bars represent the least significant difference between treatments on each date. 99

Figure 4.7 Measured soil exchangeable NO_3^- -N (kgN ha^{-1}) to a depth of 25 cm, for the 50 kgN ha^{-1} treatments (◊ U, ■ DCDU, ▲ 5UCU, × 7UCU, ○ control (nil-N)). The vertical error bars represent the least significant difference between treatments on each date. 99

Figure 5.1 The PVC pipe packed with soil used to study the diffusion of DCD and urine-N into soil and subsequent N transformations. 110

Figure 5.2 Degradation rates of DCD in Manawatu (○) and Dannevirke (□) soils incubated at 20°C and 75% FC. 117

Figure 5.3 Change in extractable NO_3^- -N in Manawatu (○) and Dannevirke (□) soils incubated at 20°C and 75% FC following treatment DCD and urea solution (30 mg DCD kg^{-1} soil and urea as 27 mgN kg^{-1} soil). 118

Figure 5.4 Freundlich absorption isotherm plots for DCD in Manawatu (Δ), Dannevirke (◊) top soil (3-10 cm) and the DCD soil carbon isotherm for both soils(solid fill) on the secondary axis. 119

Figure 5.5 DCD release rate from polymer coated products in water, ♦ PDCD3,■ PDCD4. 120

Figure 5.6 Measured degradation of DCD (mg (soil column) $^{-1}$) in cores of Manawatu (Δ) and Dannevirke (○) soils following the application of uncoated DCD (9.5 mg) at day 1 and fresh cow urine (44ml) added at day 28, incubated at 20°C and 75% of field capacity for a total of 99 days. Initial decay function to day 21 (solid lines) and post urination decay function from day 41 (dashed lines)(Error bars +/- $P<0.05$). 122

Figure 5.7 Measured and modelled results for DCD (mg (soil column) $^{-1}$) accumulation in Manawatu (▲) and Dannevirke (●) soil columns treated with 9.5 mg of DCD in the form of PDCD4. The black lines represents the release rate of DCD by water, gray lines the estimated rate in soil based on the $\theta = 0.39$ and dashed lines simultaneous release and degradation of DCD using the two rate functions (Error bars LSD (P<0.05)). 123

Figure 5.8 Concentration of DCD at different soil depths in the Dannevirke and Manawatu soil at increasing time following the application of uncoated DCD (DCD) and RLP Coated DCD (PDCD) to the core surface (♦ day 7, ■ day 15, ▲ day 21, × day 34,* day 41, ●day 55 and + day 99). 125

Figure 5.9 Correlation of modelled and measured amounts of DCD at different depths in the Dannevirke soil (♦ day 7, ■ day 15, ▲ day 21, × day * day 41, ●day 55 and + day 99; Model parameters are given Table 5.6)... 127

Figure 5.10 Concentration of DCD in the Dannevirke soil core profile with modelled DCD profile(dashed lines) at each sampling period (♦ day 7, ■ day 15, ▲ day 21, × day 34, * day 41, ●day 55 and + day 99; Model parameters are given Table 5.6). 128

Figure 5.11 Correlation of modelled and measured amounts of DCD at different depths in the Manawatu soil (♦ day 7, ■ day 15, ▲ day 21, × day 34, * day 41, ●day 55 and + day 99; Model parameters are given Table 5.6). 129

Figure 5.12 Concentrations of DCD in Manawatu soil core profiles with modelled DCD profile(dashed lines) at each sampling period (♦ day 7, ■ day 15, ▲ day 21, × day 34, * day 41, ●day 55 and + day 99; Model parameters Table 5.6). 129

Figure 5.13 Correlation of modelled and measured amounts of DCD at different depths in the Dannevirke soil treated with PDCD (♦ day 7, ■ day 15, ▲ day 21, × day 34, * day 41, ●day 55 and + day 99;Model parameters are given in Table 5.5 & 5.6). 130

Figure 5.14 Correlation of modelled and measured amounts of DCD at different depths in the Manawatu soil treated with PDCD (♦ day 7, ■ day 15, ▲ day 21, × day 34, * day 41, ●day 55 and + day 99; Model parameters are given in Table 5.5 & 5.6) 131

Figure 5.15 Correlation of modelled and measured amounts of DCD at different depths in the Manawatu soil treated with PDCD. (♦ day 7, ■ day 15, ▲ day 21, × day 34, * day 41, ● day 55 and + day 99; Model parameters are given in Table 5.6 & 5.7) 133

Figure 5.16 Correlation of modelled and measured amounts of DCD at different depths in the Dannevirke soil treated with PDCD. (♦ day 7, ■ day 15, ▲ day 21, × day 34, * day 41, ● day 55 and + day 99; Model parameters are given in Table 5.6 & 5.7) 133

Figure 5.17 Modelled soil DCD concentrations in soil columns 150mm deep for DCD and PDCD applied to Manawatu silt loam over 300 days (♦ day 15, ■ day 30, ▲ day 60, × day 120, * day 180, ● day 240 and + day 300; Model parameters are given in Table 5.7 & 5.8) 135

Figure 5.18 Modelled soil DCD concentrations in soil columns 150mm deep for combination of PDCD:DCD (80:20) applied to Manawatu silt loam at 25 kgDCD ha^{-1} over 300 day (♦ day 15, ■ day 30, ▲ day 60, × day 120, * day 180, ●day 240 and + day 300; Model parameters are given in Table 5.7 & 5.8). 136

Figure 6.1 NH_4^+ -N Freundlich isotherm plots for urine treated Manawatu Silt loam (+) and Dannevirke loam (×). 143

Figure 6.2 The change in soil extractable NH_4^+-N concentrations in Dannevirke soil layers over time following dairy urine application (□ 0-0.2 cm, ◊ 0.2-0.6 cm, Δ 0.6-1.4 cm, × 1.4-2.5 cm, + 2.5-3.5 cm and ○ 3.5-4.5 cm depths; Lines of best (fit slope Table 6.2); vertical error bars LSD (P=0.05)). 144

Figure 6.3 The change in soil extractable NH_4^+-N concentrations in Manawatu soil layers over time following dairy urine application (□ 0-0.2 cm,◊ 0.2-0.6 cm, Δ 0.6-1.4 cm, × 1.4-2.5 cm, + 2.5-3.5 cm and ○ 3.5-4.5 cm depths; lines of best fit (slopes Table 6.2); vertical error bars LSD (P=0.05)). 145

Figure 6.4 Change in extractable NH_4^+ -N (mean core concentrations) over time (relative to control) following urine application. Error bars 95% confidence interval (○ Dannevirke, Δ Manawatu, no fill is DCD, Black is PDCD and grey is no DCD). 147

Figure 6.5 Change in extractable NO_3^- -N (mean core concentration) over time (relative to control) following urine application. Error bars 95% confidence interval (○ Dannevirke Δ Manawatu, no fill is DCD, Black is PDCD and grey is no DCD). 148

Figure 6.6 The change with time of extractable NH_4^+-N concentrations in Dannevirke soil treated with DCD and dairy urine (□ 0-0.2 cm,◊ 0.2-0.6 cm, Δ 0.6-1.4 cm, × 1.4-2.5 cm, + 2.5-3.5 cm and ○ 3.5-4.5 cm depths; vertical error bars LSD (P=0.05)).................................. 149

Figure 6.7 The change with time of extractable NH_4^+-N concentrations in Dannevirke soil treated with PDCD and dairy urine (□ 0-0.2 cm,◊ 0.2-0.6 cm, Δ 0.6-1.4 cm, × 1.4-2.5 cm, + 2.5-3.5 cm and ○ 3.5-4.5 cm depths; Vertical error bars LSD (P=0.05)). 150

Figure 6.8 The change with time in extractable NH_4^+-N concentrations in Manawatu soil treated with DCD (□ 0-0.2 cm,◊ 0.2-0.6 cm, Δ 0.6-1.4 cm, × 1.4-2.5 cm, + 2.5-3.5 cm and ○ 3.5-4.5 cm depths; vertical error bars LSD (P=0.05)). 151

Figure 6.9 The change with time of extractable NH_4^+-N concentrations in Manawatu soil treated with PDCD and dairy urine (□ 0-0.2 cm,◊ 0.2-0.6 cm, Δ 0.6-1.4 cm, × 1.4-2.5 cm, + 2.5-3.5 cm and ○ 3.5-4.5 cm depths; vertical error bars LSD (P=0.05)).................................. 152

Figure 6.10 Inhibitor effect plot of DCD concentration in soil vs. relative nitrification velocity in Manawatu soils (Δ silt loam and ○ fine sandy loam data J. Asing) and initial DCD degradation incubation trials (● Manawatu and ■ Dannevirke soils) 153

Figure 6.11 Soil core pH profile Manawatu soil 7 days following urine addition, ▲ PDCD, ▲DCD and Δ control with no urine. 155

Figure 6.12 Soil core pH profile of Dannevirke soil 7days following urine addition, ● PDCD, ● DCD and ○ is the control with no urine. 155

Figure 6.13 Correlation plots of modelled and measured amounts of soil NH_4^+ -N in soil sections for Manawatu soil cores treated with dairy urine over 68 day (● soil + DCD, ● soil + PDCD, ○ soil alone, × excluded data; Modelling parameters Tables 6.1, 6.2 and 6.4 and K =0.035)... 157

Figure 6.14 Correlation plots of modelled and measured amounts of soil NH_4^+ -N in soil sections for Dannevirke soil cores treated with dairy urine over 65 days (● soil + DCD, ● soil + PDCD and ○ soil alone; Modelling parameters Tables 6.1, 6.2 and 6.4 and K =0). 158

Figure A1 Layout of input parameters and output fields for the Hydraulic convection model in Excel 2007.. 164

Figure A1.1 Layout of input parameters and output fields for Hydraulic convection model with daily field data in Excel 2007............................ 168

Figure A2. Worksheet layout for DCD release, diffusion, adsorption and degradation in soil at 20°C.. 172

Figure A3 Worksheet layout for modelled urine N nitrification and movement in soil cores at 20°C. 177

Table of Tables

Table 1.1 Operating conditions for the Pursell Process 13

Table 1.2 Expected yields increases for Maize grown in the US Corn belt based on data from (Blaylock et al. 2005) 13

Table 2.1 Physical properties of laboratory polymer films........ 63

Table 2.2 Water vapour permeability of laboratory prepared polymer films 64

Table 2.3 Critical pressure ($P_{critical}$) and hydraulic permeability (H') of the control and 20% Palmitic acid amended films. 67

Table 2.4 Measured mean volume change of coated granules following 100 days of extraction in water 68

Table 2.5 Modelled volume change of granule population based on measures spheroid shape parameters r_{max}, e and Feret radii for the transition from equivalent spherical volume (ESV) to oblate sphreriod. 69

Table 2.6 Polymer film thickness means and standard deviation’s for the control coated and palmitic acid amended coatings 69

Table 2.7 Polymer film thickness and distribution within products to be modelled........ 72

Table 3.1 Soil properties at the trial site 79

Table 3.2 (a) Cumulative additional dry matter (DM) (cumulative treatment DM minus cumulative Nil-N control DM) in kg DM/ha for 50 and 150 kg N/ha treatments and (b) Cumulative control yields on different harvest dates. 83

Table 3.3 (a) Additional herbage N recovered from treatments (treatment minus nil-N control (b)) (kg N/ha) on different harvest dates after N applications at 50 and 150 kg/ha. 84

Table 3.4 Summary of climatic data over harvest periods from NIWA[a] and Site[b] 86

Table 3.5 Urine-N return to pasture following grazing based on 87

Table 4.1 Soil profile properties after cultivation just prior to treatment application 93

Table 4.2 Measured soil moisture deficit in soil profile relative to field capacity at 0.05 bar suction with standard error of means. 96

Table 4.3 Soil nitrogen balance from the pre-trial condition to following the third harvest at 94 days, for 150 kgN ha^{-1} treatment applications 97

Table 4.4 Soil nitrogen balance from the pre-trial condition to following the third harvest at 94 days, for 50 kgN ha^{-1} treatment applications 98

Table 4.5 Residual N unreleased from coated urea after 158 days in winter field trial 98

Table 4.6 Effect of soil core moisture content on the release of residual N from polymer coated urea granules. 99

Table 4.7 Herbage nitrogen and dry matter recovered from the residual polymer coated fertiliser core study under dry and wet conditions 103

Table 5.1 DCD content of polymer coated DCD granules and estimated coat thickness 112

Table 5.2 Physical and chemical properties of soils 113

Table 5.3 First order decay rate *k* (d^{-1}) constants and half life of DCD in soils incubated at 20^{o}C and 75% FC 117

Table 5.4 Freundlich coefficients derived from the isotherm plot for Manawatu and Dannevirke top soil 3-10 cm and soil carbon ($C_{ad} = a\ C_l^b$) 119

Table 5.5 Cumulative release rate function of polymer coated DCD in water and 20°C for coating levels of 3 and 4. 121

Table 5.6 Model parameters for DCD diffusion and degradation in Manawatu and Dannevirke soils 126

Table 5.7 Modelled release rate of DCD from polymer coated DCD in soil at 75% FC and 20°C 132

Table 6.1 Freundlich isotherm coefficients for NH_4^+-N adsorption in urine treated Manawatu and Dannevirke soils. 143

Table 6.2 Nitrification velocity U (mol g^{-1} day^{-1}) in Manawatu and Dannevirke soil cores as a function of soil depth in cm. 146

Table 6.3 % Inhibition of nitrification in total soil cores over 68 days of incubation 148

Table 6.4 Inhibitor response constant (K) for Manawatu, Dannevirke and Iowa soils, Harps, Webster and Storden (McCarty and Bremner 1989) 153

Nomenclature

Symbol	units	description
a	mg kg^{-1} dry soil	Freundlich coefficient
A_p	cm^2	area of pores
A_t	cm^2	total film/granule surface area
a_w	------	activity of water
A_{wp}	cm^2	area of water filled pores
B	-----	activity coefficient
$C_{(ext)}$	g cm^{-3}	external solute concentration
$C_{(int)}$	g cm^{-3}	internal solute concentration
C_s	g cm^{-3}	solute concentration
$C_{s(t)}$	g cm^{-3}	concentration of solute at time t
C_{sat}	g cm^{-3}	concentration saturated solute
C_u	g cm^{-3}	concentration urea solution
D	cm^{2}d^{-1}	diffusion coefficient
d_{eqv}	cm	diameter of equivalent spherical volume
dP/dt	Pa d^{-1}	change in pressure with respects to time
ΔP_{wv}	Pa	deference in water vapour pressure
D_s	cm^2 d^{-1}	diffusion coefficient of solute in water
D'_s	cm^2 d^{-1}	diffusion coefficient of solute in film
dV_{water}/dt	cm^{3}d^{-1}	change in volume with respects to time
D_{wv}	cm^2 d^{-1}	diffusion coefficient of water vapour in air
E_a	kJ mol^{-1}	activation energy of water membrane transport
f	-----	tortuosity coefficient
F	cm^{3}d^{-1}	volumetric water flux
F'	------	dimensionless volumetric water flux
$F_{(t)}$	cm^{3}d^{-1}	volumetric water flux at time t
F_{sat}	cm^{3}d^{-1}	volumetric water flux saturated solution
H'	cm^2 d^{-1} Pa^{-1}	specific hydraulic resistance
K	μmol g^{-1}	inhibitor response constant
k	d^{-1}	first order decay constant
k'	cm^{3}d^{-1}	volumetric release rate of solution
$l_{(t)}$	cm	film thickness at time t
l_e	cm	film thickness at equilibrium
l_o	cm	initial film thickness
L_p	cm^2	mechanical permeability coefficient
m	g	mass released
M_o	g	initial mass
$M_{wt(s)}$	g mol^{-1}	molar wt of solute

N	mol^{-1}	Avogadro's number
$P_{coating}$	Pa	coating stress
$P_{critical}$	Pa	critical pressure required for flow
P_{eq}	Pa	Internal equilibrium pressure
P_h	cm^{2}d^{-1}Pa^{-1}	film water vapour permeability
$P_{internal}$	Pa	internal granule pressure
P^o_{wv}	Pa	vapour pressure of water above pure water
$P_{rupture}$	Pa	rupture pressure
P_s	cm^{2}d^{-1}	film solute permeability
$P_{s(T)}$	cm^{2}d^{-1}	film solute permeability as a function of temperature
$P_{wv(ext)}$	Pa	external water vapour pressure
$P_{wv(int)}$	Pa	internal water vapour pressure
$P_{wv(soln)}$	Pa	water vapour pressure of solution
$Q_{(t)}$	-----	cumulative fractional release of solute at time t
Q_c	-----	cumulative fractional release of solute at end of constant rate period
R	J mol^{-1} K^{-1}	gas constant
R_f	cm	Feret radius
r_{max}	cm	maximum radius of spheroid
r_{min}	cm	minimum radius of spheroid
r_o	cm	radius time zero
S_y	Pa	tensile yield strength
t'	d	time required prior to solute release occurs at constant rate
t^*	d	time at which constant rate ends and falling rate starts
t_o	d	time zero
U	mol cm^{-1}d^{-1}	nitrification velocity
U_m	cm s^{-1}	mean fluid velocity
U_{max}	mol cm^{-1}d^{-1}	maximum nitrification velocity
V	cm^3	volume
$V_{critical}$	cm^3	Volume of granule at critical pressure
V_{eq}	cm^3	volume of granule at equilibrium pressure
V_{soln}	cm^3	volume of solution
V_w	cm^3	volume of water
w	g d^{-1}	weight change per day
W'	cm^{2}d^{-1}Pa^{-1}	specific water vapour permeability
W'_{min}	cm^{2}d^{-1}Pa^{-1}	minimum specific water vapour permeability
Y	Pa	Youngs Modulas

Greek Symbols

Symbol	units	description
ΔC	g cm^{-3}	concentration difference across film
$\Delta \pi$	Pa	osmotic pressure difference across film
ΔP	Pa	hydrostatic pressure difference across film
ΔP_{wv}	Pa	water vapour pressure difference across film
ΔE_{vis}	kJ mol^{-1}	activation energy of viscous flow
ΔV	cm^3	volume change
$\Delta V_{critical}$	cm^3	critical volume change
ΔV_g	cm^3	granule volume change
Δl	-----	coating strain
$\Delta \pi$	Pa	osmotic pressure
$\Delta \pi_{sat}$	Pa	osmotic pressure of saturated solution
ε_f	-----	voidage film
ε_{fmax}	-----	voidage
ε_g	-----	voidage granule
ε_w	-----	
γ	-----	proportional granule volume change
η	Pa s	viscosity
$\varnothing$	cm	diameter of permeability of membrane cell
θ	cm^3 cm^{-3}	volumetric water content
ρ_s	g cm^{-3}	density of solid
β_e	------	water activity coefficient
δ	Pa^{-1}d^{-1}	hydraulic resistance coefficient to flow
μ	Pa s	viscosity
φ	P	viscosity constant
η	P	viscosity
θ	cm^3 cm^{-3}	volumetric water content