

CRANFIELD UNIVERSITY

Stephanie Pullan

Modelling of Pesticide Exposure in Ground and Surface Waters
Used for Public Water Supply

School of Applied Sciences

PhD
Academic Year: 2013 - 2014

Supervisors: Dr. Ian Holman and Dr. Mick Whelan

January 2014

[This page is left intentionally blank]

CRANFIELD UNIVERSITY

School of Applied Sciences

PhD

Academic Year 2013 - 2014

Stephanie Pullan

Modelling of Pesticide Exposure in Ground and Surface Waters
Used for Public Water Supply

Supervisors: Dr. Ian Holman and Dr. Mick Whelan

January 2014

This thesis is submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy

© Cranfield University 2014. All rights reserved. No part of this
publication may be reproduced without the written permission of the
copyright owner

[This page is left intentionally blank]

Abstract

Diffuse transfers of pesticides from agricultural land to ground and surface waters can lead to significant drinking water quality issues. This thesis describes the development and application of a parameter-efficient, numerical model to predict pesticide concentrations in raw water sources within an integrated hydrological framework. As such, it fills an unoccupied niche that exists in pesticide fate modelling for a computationally undemanding model that contains enough process complexity to be applicable in a wide range of catchments and hydrogeological settings in the UK and beyond.

The model represents the key processes involved in pesticide fate (linear sorption and first-order degradation) and transport (surface runoff, lateral throughflow, drain flow, percolation to the unsaturated zone, calculated using a soil water balance) in the soil at a daily time step. Soil properties are derived from the national soil database for England and Wales and are used to define the boundary conditions at the interface between the subsoil and the unsaturated zone. This is the basis of the integrated hydrological framework which enables the application of the model to both surface water catchments and groundwater resources. The unsaturated zone model accounts for solute transport through two flow domains (accounting for fracture flow and intergranular matrix flow) in three hydrogeological settings (considering the presence and permeability of superficial deposits).

The model was first applied to a small headwater sub-catchment in the upper Cherwell. Performance was good for drainflow predictions (Nash Sutcliffe Efficiency > 0.61) and performed better than the MACRO model and as well as the modified MACRO model.

Surface water model performance was evaluated for eight pesticides in five different catchments. Performance was generally good for flow prediction (Nash Sutcliffe Efficiency > 0.59 and percentage bias below 10 %, in the validation period for all but two catchments). The 90th percentile measured concentration was captured by the model in 62 % of catchment-pesticide combinations. In the

remaining cases predictions were within, at most, a factor of four of measured 90th percentile concentrations. The rank order of the frequency of pesticides detected over $0.1 \mu\text{g L}^{-1}$ was also predicted reasonably well (Spearman's rank coefficient > 0.75 ; $p < 0.05$ in three catchments). Pesticide transport in the unsaturated zone model was explored at the point scale in three aquifers (chalk, limestone and sandstone). The results demonstrate that representing the unsaturated zone processes can have a major effect on the timing and magnitude of pesticide transfers to the water table.

In comparison with the other catchment scale pesticide fate models that predict pesticide exposure at a daily time-step, the model developed stands out requiring only a small number of parameters for calibration and quick simulation times. The benefit of this is that the model can be used to predict pesticide exposure in multiple surface and groundwater resources relatively quickly which makes it a useful tool for water company risk assessment. The broad-scale approach to pesticide fate and transport modelling presented here can help to identify and prioritise pesticide monitoring strategies, to compare catchments in order to target catchment management and to highlight potential problems that could arise under different future scenarios.

Key Words: Model, Pesticide, Drinking Water, Catchment Scale, Unsaturated Zone, Diffuse Source.

Acknowledgments

First of all, I would like to thank my supervisors Ian Holman and Mick Whelan. To Ian, for your excellent guidance, supervision and support and to Mick, for your enthusiasm for the subject, constant flow of ideas, and patience in teaching me how to code, without either of you I would never have got this far.

I gratefully acknowledge the EPSRC, Anglian Water and Severn Trent Water for funding my PhD project. With particular thanks to Simon Eyre from Anglian Water and Jodie Whitehead and Katherine Cherry from Severn Trent Water. To the thesis committee: Sue White, Emma Goslan and Fred Coulon, thank you for your valuable insights.

To Ken Rushton, our discussions really enlivened my PhD with your experience and anecdotes from around the world, and closer to home, you helped me make the journey through the last three years an enjoyable exploration of new ideas and concepts.

And last, but by no means least, to my parents and grandparents, boyfriend (Matt), friends from Cranfield University (Marta, Jerome and everyone else I don't have room to mention), EEE girls from York Uni and friends from Leamington (particularly the Lady Lemmings), without your continued unwavering support I would not be where I am today and for that I will be eternally grateful.

Table of Contents

Abstract	iii
Acknowledgments	v
Table of Contents	vi
List of Figures	xiii
List of Tables	xviii
List of Abbreviations	xxii
List of Publications, Presentations and Awards	xxiv
Chapter 1. Introduction	1
1.1. Context of the thesis	1
1.1.1. Pesticides and drinking water resources.....	1
1.1.2. Limitations of current pesticide fate and transport models	3
1.2. Aim and objectives of the thesis.....	5
1.3. Structure of the thesis	6
Chapter 2. A review of Catchment Scale Pesticide Fate Models	9
2.1. Introduction	9
2.2. Pesticide fate and transport catchment scale models	10
2.2.1. Process representation	10
2.2.2. Data requirements	11
2.2.3. Examples of pesticide fate and transport models predicting pesticide transport to surface water resources	14
2.2.4. Examples of models predicting pesticide fate and transport to groundwater	16
2.3. Conclusions.....	18
Chapter 3. Pesticide Fate and Transport to Surface Water Resources: Model Conceptualisation and Development	19

3.1. Introduction	19
3.2. Soil water balance model	20
3.2.1. Precipitation	24
3.2.2. Evapotranspiration	24
3.2.2.1. Reference evapotranspiration.....	24
3.2.2.2. Potential evapotranspiration	25
3.2.2.3. Effect of water stress on evapotranspiration.....	26
3.2.2.4. Evapotranspiration from two soil stores	27
3.2.2.5. Bare soil evaporation	28
3.2.3. Drainage from the topsoil store to the subsoil store	29
3.2.4. Surface runoff	30
3.2.5. Artificial field drains	31
3.2.6. Lateral throughflow	32
3.2.7. Percolation into the unsaturated zone.....	33
3.2.8. Other pathways to surface water resources.....	35
3.3. Boundary conditions between the subsoil and the unsaturated zone.....	36
3.3.1. Unsaturated and free draining boundary condition	38
3.3.2. Low permeability boundary condition.....	38
3.3.3. Partially saturated subsoil boundary condition	40
3.3.4. Peat soils	41
3.4. Description and conceptual model of pesticide fate and transport processes in the soil.....	42
3.4.1. Pesticide application to the soil	43
3.4.2. Degradation in the soil	44
3.4.3. Sorption in the soil	45
3.4.4. Advective transport in the soil after application.....	46

3.4.5. Pesticide displacement at the time of a rainfall event	47
3.4.6. Pesticide transport from the soil at the time of a rainfall event.....	49
3.5. Pesticide fate and transport at the catchment scale.....	52
3.5.1. Baseflow	53
3.6. Edge-of-field application of the pesticide fate and transport model.....	54
3.6.1. Introduction to the upper Cherwell catchment.....	54
3.6.2. Set-up of the pesticide fate and transport model	55
3.6.3. Upper Cherwell results and discussion.....	56
3.7. Conclusions.....	60
Chapter 4. Calibration and Evaluation of the Pesticide Fate and Transport	
Model at the Catchment Scale.....	61
4.1. Introduction	61
4.2. Case-study catchments.....	62
4.2.1. River Lugg at Lugwardine	63
4.2.2. River Teme at Knightsford Bridge	64
4.2.3. River Waveney at Needham Mill.....	66
4.2.4. River Wensum at Costessey Mill	68
4.2.5. River Yare at Colney.....	70
4.2.6. Measured Data	72
4.3. Selection of input data.....	73
4.3.1. Rainfall and temperature input data.....	73
4.3.2 Evapotranspiration input data	74
4.3.2.1 Independent evaluation of Hargreaves K_T	75
4.3.3. Soils	76
4.3.4. Land use.....	78
4.3.5. Vegetation parameters.....	79

4.3.6. Pesticide properties	80
4.3.7. Pesticide usage.....	81
4.4. Model Execution.....	84
4.4.1 Description of model implementation	84
4.4.2 Calibration, validation and sensitivity analysis of the hydrograph	86
4.4.3. Evaluation of model performance on predicting pesticide exposure	89
4.5. Results and discussion	91
4.5.1. Hydrograph results.....	91
4.5.1.1. West Midlands catchments (Lugg and Teme)	92
4.5.1.2. East Anglian catchments (Waveney, Wensum, Yare)	94
4.5.1.3. Discussion of hydrograph results.....	98
4.5.1.4. Conclusions of hydrograph results	99
4.5.2. Modelled pesticide concentrations	100
4.5.2.1. Model performance with respect to prediction of 90 th percentile concentration	102
4.5.2.2. Model performance with respect to prediction of frequency of concentrations greater than 0.1 µg L ⁻¹	104
4.5.2.3. Discussion of pesticide concentration results	106
4.6. Time series results of pesticide concentrations at the catchment outlet and contribution of hydrological pathways	109
4.6.1. Discussion of hydrological pathways and pesticide concentrations	111
4.7. Conclusions.....	113
Chapter 5. Conceptual Model of Pesticide Fate and Transport in the Unsaturated Zone.....	115
5.1. Introduction	115
5.2. Hydrogeological settings, transport pathways and pesticide fate	116
5.2.1. Aquifer at outcrop.....	117

5.2.1.1. Intergranular matrix flow	118
5.2.1.2. Fracture flow	120
5.2.1.3. Dual permeability	121
5.2.2. Aquifer overlain by permeable superficial deposits	123
5.2.3. Pesticide fate in the unsaturated zone	125
5.4. Conclusions.....	126

Chapter 6. Application of the Unsaturated Zone Pesticide Fate and Transport Model 127

6.1. Introduction	127
6.2. Methodology for unsaturated zone model setup	128
6.2.1. Weather, soil and land use	128
6.2.2. Pesticide properties	131
6.2.3. Unsaturated zone parameter values	131
6.3. Results for pesticide concentration and travel time to the water table..	134
6.3.1. Peak pesticide concentrations and travel time to the water table in a limestone aquifer	135
6.3.1.1. Limestone aquifer at outcrop	135
6.3.1.2. Limestone aquifer overlain by superficial deposits	135
6.3.2. Peak pesticide concentrations and travel time to the water table in a sandstone aquifer	137
6.3.2.1. Sandstone aquifer at outcrop.....	137
6.3.2.2. Sandstone aquifer overlain by superficial deposits.....	138
6.3.3. Peak pesticide concentrations and travel time to the water table in a chalk aquifer	142
6.3.3.1. Chalk aquifer at outcrop.....	142
6.3.3.2. Chalk aquifer overlain by superficial deposits.....	144
6.4. Discussion.....	146

6.4.1. The role of fractures in the unsaturated zone	146
6.4.2. Travel time to the water table via the intergranular matrix	148
6.4.2.1. Intergranular matrix hydraulic conductivity.....	148
6.4.2.2. Organic carbon content and sorption.....	149
6.4.2.3. Unsaturated zone thickness	150
6.4.3. Degradation in the unsaturated zone	150
6.4.4 Superficial deposits.....	151
6.5. Conclusions.....	152
Chapter 7. Scenario Modelling at the Catchment Scale in Surface Water	
Resources	153
7.1. Introduction	153
7.2. Methodology.....	154
7.2.1. Temporal restrictions of application	154
7.2.2. Spatial targeting of pesticide application.....	155
7.2.3. Change in area of winter oilseed rape grown.....	155
7.2.4. Input data.....	156
7.3. Mitigation scenario results.....	158
7.3.1. Temporal restrictions on the timing of application.....	158
7.3.1.1. Restricting propyzamide application when drains are flowing..	158
7.3.1.2. September only propyzamide application	162
7.3.2. Spatial targeting of pesticide application.....	164
7.3.3. Changing crop area and treated crop area	167
7.4. Discussion.....	171
7.4.1. Temporal restrictions of application	171
7.4.2. Spatial targeting of application on vulnerable soils	172
7.4.3. Switching to spring oilseed rape	173

7.4.4. Drivers and constraints of pesticide application	173
7.4.5. Utility of the pesticide fate and transport model in scenario modelling	174
7.5. Conclusions.....	175
Chapter 8. General Discussion and Conclusions.....	177
8.1. Meeting the aim and objectives.....	177
8.2. Implications of model results of pesticide exposure in surface and groundwater in relation to public water supplies	183
8.2.1. Implications of model results for surface water drinking water resources.....	183
8.2.2. Implications of model results for groundwater drinking water resources.....	185
8.3. Recommendations for further work	185
8.4. Conclusions.....	187
References	189
Appendix A. Model Symbols	224
Appendix B. Catchment Maps.....	230
Appendix C. Rainfall and Temperature Regression Graphs.....	235
Appendix D. CORINE Land Cover Classes	241
Appendix E. Pesticide Application Rate and Timing.....	242
Appendix F. Hydrographs for Calibration and Validation Period and Sensitivity Analysis.....	247
Appendix G. Pesticide Cumulative Frequency	255
Appendix H. Pesticide Time Series Results.....	262

List of Figures

Figure 1.1. Thesis outline by chapter.....	6
Figure 2.1. Schematic representation of example pesticide fate models with respect to process representation and typical scale of application.....	11
Figure 2.2. Schematic representation of example pesticide fate models with respect to process representation and typical data requirements.....	12
Figure 2.3. Schematic representation of example pesticide fate models with respect to typical data requirements and typical scale of application.....	15
Figure 3.1. Conceptual diagram of key transport pathways from the topsoil store.....	22
Figure 3.2. Conceptual diagram of the key transport pathways from the subsoil.....	23
Figure 3.3. Linear interpolation of K_c values for winter wheat in one year growth cycle.....	26
Figure 3.4. Root growth for winter wheat between planting and harvest.....	28
Figure 3.5. Schematic illustration of the generation of lateral throughflow in the soil.....	32
Figure 3.6. Schematic diagram of the three boundary conditions at the interface between the soil and the unsaturated zone considered in the model.....	37
Figure 3.7. Schematic diagram of boundary condition A between the soil and the unsaturated zone.....	38
Figure 3.8. Schematic diagram of the interface between the subsoil and the unsaturated zone for the low permeability boundary condition, without drains (left) and with drains (right).....	39

Figure 3.9. Schematic diagram of the interface between the subsoil and the unsaturated zone for the partially saturated subsoil boundary condition, with drains.....	41
Figure 3.10. Schematic diagram for pesticide fate processes in the soil between application and a rainfall event.....	43
Figure 3.11. Schematic diagram of the key processes generating pesticide transport in the soil zone.....	48
Figure 3.12. Conceptual diagram the upper Cherwell sub-catchment and the key hydrological pathways to surface water and groundwater resources.....	55
Figure 3.13. Rainfall in the upper Cherwell (a) and observed and predicted drain flow with observed and predicted propyzamide concentration in drain flow in the upper Cherwell during the calibration period (b).....	57
Figure 3.14. Rainfall in the upper Cherwell (a) and observed and predicted drain flow with observed and predicted carbetamide concentration in drain flow in the upper Cherwell during the validation period (b).....	57
Figure 4.1. Location of case-study catchments.....	62
Figure 4.2. Map of the Lugg catchment for the gauging station and the pesticide monitoring point.....	63
Figure 4.3. Map of the Teme catchment for the gauging station and the pesticide monitoring point.....	65
Figure 4.4. Map of the Waveney catchment for the gauging station and the pesticide monitoring point.....	67
Figure 4.5. Map of the Wensum catchment for the gauging station and the pesticide monitoring point.....	69
Figure 4.6. Map of the Yare catchment for the gauging station and the pesticide monitoring point.....	71

Figure 4.7. Sensitivity analysis of the catchment calibration parameters for total flow between 1991 – 2010 in the Yare catchment.....	89
Figure 4.8. Measured rainfall and measured and predicted flow from October 2006 to September 2009 in (a) the river Lugg at Lugwardine and (b) the river Teme at Knightsford Bridge.....	93
Figure 4.9. Observed and predicted cumulative flow in (a) the river Lugg and Lugwardine and (b) the river Teme at Knightsford Bridge.....	94
Figure 4.10. Measured rainfall and measured and predicted flow from October 2006 to September 2009 in (a) the river Waveney at Needham Mill (b) the river Wensum at Cottessey Mill and (c) the river Yare at Colney.....	96
Figure 4.11. Observed and predicted cumulative flow in (a) the river Waveney at Needham Mill (b) the river Wensum at Cottessey Mill and (c) the river Yare at Colney.....	97
Figure 4.12. Example cumulative frequency distributions for measured carbetamide concentrations with predicted best case and worst case concentrations at the catchment outlet in the (a) Lugg, (b) Teme, (c), Waveney, (d) Wensum, (e) Yare.....	101
Figure 4.13. Ratio of unsaturated hydraulic conductivity (K_{θ}) to the saturated hydraulic conductivity (K_{sat}) for a representative soil in the Lugg (Brickfield) and Waveney (Beccles) during the pesticide model run period (2006 – 2009).....	108
Figure 4.14. Comparison of predicted and measured propyzamide concentrations and predicted flow between September 2006 and September 2007 in the (a) Lugg (b) Teme (c) Waveney (d) Wensum and (e) Yare catchments.....	110
Figure 5.1. Schematic diagram of the three broad hydrogeological settings considered in the unsaturated zone model.....	117

Figure 5.2. Schematic diagram of solute transport pathways in hydrogeological setting (i) aquifer at outcrop.....	118
Figure 5.3. Schematic diagram of solute transport pathways in hydrogeological settings (ii) permeable superficial deposits and (iii) low permeability superficial deposits.....	123
Figure 6.1. Unsaturated zone model hydrogeological settings diagrams including the representative soil for each setting: (i) aquifer at outcrop; (ii) aquifer overlain by permeable superficial deposits; and (iii) aquifer overlain by low permeability deposits, for three principal aquifers: chalk; limestone; and sandstone.....	129
Figure 6.2. Example of hydrogeological unit thicknesses assumed in the unsaturated zone model in a chalk aquifer, for a water table depth of 4 mbgl and 20 mbgl.....	134
Figure 6.3. Predicted peak concentrations at the water table (4 mbgl) for three hydrogeological settings in a limestone aquifer.....	137
Figure 6.4. Predicted peak concentrations at the water table (4 mbgl) for three hydrogeological settings assuming a sandstone aquifer.....	140
Figure 6.5. Predicted peak concentrations at the water table (20 mbgl) for two hydrogeological settings assuming a sandstone aquifer.....	141
Figure 6.6. Predicted pesticide concentration at the water table when the water table is 4 mbgl and 20 mbgl, calculated with the advection dispersion equation assuming a sandstone aquifer at outcrop.....	142
Figure 6.7. Predicted peak concentrations with the water table 4 mbgl assuming a chalk aquifer at outcrop and two flow pathways: intergranular matrix flow and fracture flow.....	143
Figure 6.8. Predicted peak concentrations when the water table is 20 mbgl when the sands and gravels are overlying an unsaturated chalk aquifer and two flow pathways: intergranular matrix flow and fracture flow.....	145

Figure 6.9. Illustrative predicted peak pesticide concentrations and travel time to the water table using the advection-dispersion equation for three different intergranular matrix hydraulic conductivities.....	149
Figure 7.1. Predicted propyzamide concentrations in the baseline scenario and predicted concentrations when restricting application when drain flow is greater than 0.5 mm day ⁻¹ in the Yare catchment between October 2006 and January 2007.....	162
Figure 7.2. Predicted propyzamide concentrations in the baseline scenario and predicted concentrations with a September-only application window in the Yare catchment between September 2006 and January 2007. Also shown is predicted drain flow from the Beccles soil type.....	163
Figure 7.3. Predicted total frequency of propyzamide and metazachlor greater than 0.1 µg L ⁻¹ at the catchment outlet in the Lugg catchment (a) Year 1 (2006/2007), (b) Year 2 (2007/2008) and (c) Year 3 (2008/2009).....	168
Figure 7.4. Predicted total frequency of propyzamide and metazachlor greater than 0.1 µg L ⁻¹ at the catchment outlet in the Yare catchment (a) Year 1 (2006/2007), (b) Year 2 (2007/2008) and (c) Year 3 (2008/2009).....	169
Figure 7.5. Monthly rainfall in (a) the Lugg catchment and (b) the Yare catchment for: Year 1 (2006/2007), Year 2 (2007/2008) and Year 3 (2008/2009).....	170
Figure 8.1. Schematic overview of hydrological and hydrogeological pathways included in the soil water balance model and the unsaturated zone model....	178

List of Tables

Table 3.1. Boundary conditions at the interface between the subsoil and the unsaturated zone and related HOST classifications.....	37
Table 3.2. Maximum saturated hydraulic conductivity values at the interface between the subsoil and unsaturated zone based on HOST class.....	40
Table 3.3. Model performance statistics for predicted drain flow in the upper Cherwell catchment in the calibration period and validation period for the pesticide fate and transport model, MACRO model and MACRO + contribution from Northampton sands.....	58
Table 4.1. Summary statistics for the Lugg catchment at Lugwardine gauging station and the pesticide monitoring point at Mordiford Bridge.....	64
Table 4.2. Summary statistics for the Teme catchment at Knightsford Bridge gauging station and the pesticide monitoring point at Powick.....	66
Table 4.3. Summary statistics for the Waveney catchment at Needham Mill gauging station and the pesticide monitoring point at Ellingham Mill.....	68
Table 4.4. Summary statistics for the Wensum catchment at Costessey Mill gauging station and the pesticide monitoring point at Sweet Briar Road Bridge.....	70
Table 4.5. Summary statistics for the Yare catchment at Colney gauging station and the pesticide monitoring point at Trowse Mill.....	72
Table 4.6. Chosen weather stations measuring rainfall and temperature in each catchment.....	74
Table 4.7. Comparison of average annual ET_O (1990-2009) from the Hargreaves equation ($K_T=0.17$ and $K_T=0.15$) with MORECS ET_O (calculated from a modified Penman-Monteith equation for grass cover) for the case-study catchments.....	76

Table 4.8. Topsoil and subsoil input data requirements for the model.....	77
Table 4.9. Crop parameters and crop dates for grass, winter wheat and winter oilseed rape.....	79
Table 4.10. Pesticide properties, analytical limit of quantification reported by the EA and main uses in the UK of the pesticides in the model.....	80
Table 4.11. Estimated percentage of treated area in the UK and maximum application rate.....	83
Table 4.12. Estimated application windows for the pesticide land use combinations considered in the model.....	84
Table 4.13. Overall model performance based on two goodness-of-fit statistics, Nash Sutcliffe Efficiency and Percent Bias.....	88
Table 4.14. Calibrated parameter values for each study catchment.....	88
Table 4.15. Model performance statistics for the prediction of flow at the catchment outlet in five case -study catchments.....	91
Table 4.16. Overall model performance for five case-study catchments, based on Nash Sutcliffe Efficiency and Percent Bias.....	91
Table 4.17. Measured and modelled 90 th percentile concentration for each pesticide catchment combination. Predicted values show the range of best case and worst case K_{OC} and DT_{50} combinations.....	103
Table 4.18. Measured and modelled frequency of detections greater than 0.1 $\mu\text{g L}^{-1}$ for each pesticide catchment combination. Predicted values shown the range of best case and worst case K_{OC} and DT_{50} combinations.....	105
Table 4.19. Model performance with respect to relative rank order of measured frequencies greater than 0.1 $\mu\text{g L}^{-1}$ and modelled predictions, using Spearman's rank correlation.....	106

Table 4.20. Percentage of the total catchment assumed to be treated with chlorotoluron in the model.....	106
Table 6.1. Soil properties of the representative soils used in the unsaturated zone model.....	130
Table 6.2. Parameter values used for each geological unit considered in the unsaturated zone model.....	132
Table 6.3. Maximum and minimum predicted travel time to peak concentration for the full range of K_{OC} and DT_{50} combinations, for water tables at 4 mbgl and 20 mbgl, and for three hydrogeological settings, assuming a limestone aquifer.....	136
Table 6.4. Maximum and minimum predicted travel time to peak concentration for the full range of K_{OC} and DT_{50} combinations, for water tables at 4 mbgl and 20 mbgl, and for three hydrogeological settings, assuming a sandstone aquifer.....	138
Table 6.5. Maximum and minimum predicted travel time to peak concentration in the intergranular matrix and fracture for the full range of K_{OC} and DT_{50} combinations, for the water table 4 mbgl and 20 mbgl, and for three hydrogeological settings, assuming a chalk aquifer.....	146
Table 7.1. Percentages of arable land in the Lugg and Yare catchment growing winter OSR and spring OSR for the case study mitigation scenario exploring the effect of change in cropping, considering a step-wise approach.....	156
Table 7.2. Crop parameters and crop dates assumed for spring oilseed rape.....	157

Table 7.3. Predicted 90th percentile concentrations and frequency of detections greater than 0.1 µg L⁻¹ at the catchment outlet in the Yare catchment for the baseline and three temporal restriction mitigation scenarios, by crop year from September 2006 to August 2009.....160

Table 7.4. Predicted 90th percentile concentrations and frequency of detections greater than 0.1 µg L⁻¹ at the catchment outlet in the Lugg catchment for the baseline and three temporal restriction mitigation scenarios, by crop year from September 2006 to August 2009.....161

Table 7.5. Predicted 90th percentile propyzamide concentrations and the frequency of detections greater than 0.1 µg L⁻¹ in the Yare for the baseline scenario and mitigation scenario restricting the area of application on the most vulnerable soils, September 2006 to August 2009.....165

Table 7.6. Predicted 90th percentile propyzamide concentrations and the frequency of detections greater than 0.1 µg L⁻¹ in the Lugg for the baseline scenario and mitigation scenario restricting the area of application on the most vulnerable soils, September 2006 to August 2009.....166

List of Abbreviations

ADE	Advection Dispersion Equation
BADC	British Atmospheric Data Centre
BGS	British Geological Survey
BFI	Baseflow Index
CEH	Centre for Ecology and Hydrology
CSF	Catchment Sensitive Farming
DEFRA	Department for Environment, Food and Rural Affairs
DrWPA	Drinking Water Protected Area
DWD	Drinking Water Directive
DWI	Drinking Water Inspectorate
EA	Environment Agency
EC	European Commission
EFSA	European Food Safety Authority
EIS	Environmental Information Sheet
EU	European Union
FERA	Food and Environment Research Agency
FOCUS	Forum of the Co-ordination of Pesticide Fate Models and their Use
GIS	Geographical Information System
GUS	Groundwater Ubiquity Score
HER	Hydrologically Effective Rainfall
HGCA	Home Grown Cereals Authority
HOST	Hydrology of Soil Type
HRU	Hydrological Response Unit

LandIS	Land Information System
LOQ	Limit of Quantification
MAC	Maximum Admissible Concentration
MORECS	Meteorological Office Rainfall and Evaporation Calculation System
MSRV	Minimum Standard Rainfall Volume
NATMAP	National Soil Map
NRCS	National Resources Conservation Service
NRFA	National River Flow Archive
NSRI	National Soil Resources Institute
NSE	Nash Sutcliffe Efficiency
OSR	Oilseed Rape
PBIAS	Percentage Bias
PPDB	Pesticide Properties Database
SEISMIC	Spatial Environmental Information System for Modelling the Impact of Chemicals
SNIFFER	Scotland and Northern Ireland Forum for Environmental Research
SPR	Standard Percentage Runoff
WFD	Water Framework Directive

List of Publications, Presentations and Awards

Publications

- Tediosi, A., Whelan, M.J., Rushton, K.R., Thompson, T.R.E., Gandolfi, C. & Pullan, S.P. (2012) Measurements and conceptual modelling of herbicide transport to field drains in a heavy clay soil with implications for catchment –scale water quality management. *Science of the Total Environment*, **438**, 103 – 112. *Published*

Presentations

- Pullan, S.P. CATCHIS: a catchment scale for pesticide risk assessment in drinking water supplies. *Poster* presentation at: XIV Symposium Pesticide Chemistry – Environmental Fate and Ecological Effects, Piacenza, 30 August – 1 September 2011.
- Pullan, S.P. Predicting pesticide transport at the catchment scale using a simple parsimonious process-based model. *Oral* presentation at: British Society for Soil Science Early Career Conference, York, 27 – 28 March 2013.
- Pullan, S.P. Catchment scale modelling of pesticide fate and transport using a simple parsimonious process-based model. *Poster* presentation at: Engineering Geosciences Union Generally Assembly, Vienna, 07 – 12 April 2013.
- Pullan, S.P. Modelling pesticide exposure at the water table using a parsimonious process-based model. *Oral* presentation at: Pesticide Behaviour in Soils, Water and Air, York, 2 – 4 September 2013.

Awards

- *Best Oral Student Presentation* at Pesticide Behaviour in Soils, Water and Air, York, 2 – 4 September 2013.

Chapter 1. Introduction

1.1. Context of the thesis

1.1.1. Pesticides and drinking water resources

Pesticides are widely used in modern conventional agriculture and contribute to increased yield and quality. However, they can be transferred from land to surface and groundwaters (e.g. Mitchell *et al.*, 2005; Gao *et al.*, 2008; Lapworth *et al.*, 2012; Tediosi *et al.*, 2012), where they can pose problems to receiving water ecology and drinking water quality. Diffuse agricultural sources are often cited as the main origin of pesticides, both in surface water (e.g. Bach *et al.*, 2001; Leu *et al.*, 2004a; Brown and van Beinum, 2009; Tediosi *et al.*, 2012) and groundwater (e.g. Carsel *et al.*, 1985; Foster, 1998; Goody *et al.*, 2001; Rodvang and Simkins, 2001; Lapworth *et al.*, 2006). These sources have the potential to pose significant water quality issues, particularly for drinking water resources.

In the European Union (EU) the maximum admissible concentration (MAC) in drinking water for an individual pesticide, including relevant metabolites, reaction, and degradation products, is $0.1 \mu\text{g L}^{-1}$ set down in the Drinking Water Directive (DWD; EC, 1998). In addition, the total concentration for all pesticides should not exceed $0.5 \mu\text{g L}^{-1}$. These limits are not based on risk (i.e. a comparison of exposure and effects in humans) but on the principle that pesticides should not be present in drinking water (Leistra and Boeston, 1989). The value of $0.1 \mu\text{g L}^{-1}$ represents the typical analytical limit of detection for most pesticides when the DWD was first introduced in 1980, and, therefore, represents a surrogate zero (Dolan *et al.*, 2013).

In addition to concerns about drinking water quality, pesticides also have the potential to affect surface water ecology (De Noyelles *et al.*, 1982; Warren *et al.*, 2003). However, the concentrations at which eco-toxicological effects manifest are highly variable and in most cases much higher than $0.1 \mu\text{g L}^{-1}$ (Crommentuijn *et al.*, 2000).

The Water Framework Directive (WFD; EC, 2000) makes special provision for catchments which are used for drinking water supplies, designated as Drinking Water Protected Areas (DrWPAs). DrWPAs for surface and groundwater resources cover a large proportion of England and Wales. In DrWPAs water abstracted for drinking water must meet the quality standards set out for pesticides in the DWD after treatment. In addition to compliance with the DWD, under the WFD the quality of the raw (untreated) water in catchments must not deteriorate (from a 2007/2008 baseline; DWI and EA, 2012) such that further investment for additional treatment is needed (Chave, 2001; Grath *et al.*, 2007; Dolan *et al.*, 2012).

There are 278 active ingredients registered for use in the UK (Dolan *et al.*, 2012), monitoring for these in both surface and groundwater drinking water resources is impractical. In addition the cost to water companies in the UK for pesticide removal from raw water has been estimated to total between £84 and £129 million annually (Pretty *et al.*, 2000). Therefore simulating the fate and transport of pesticides from agricultural land to surface and groundwater bodies is an important tool in the risk assessment and risk management of water resources in order to identify the timing and magnitude of pesticides at the abstraction point.

It is also worth noting that there are various water treatment technologies available for pesticide removal, such as granular active carbon and slow sand filters, with some technologies more efficient at pesticide removal than others (Dillon *et al.*, 2011). With current technological capabilities removal of some pesticides cannot be easily achieved, e.g. metaldehyde and clopyralid (Dolan *et al.*, 2012). Not all raw drinking water sources have treatment technologies capable of removing significant concentrations of pesticides, particularly groundwater sources which have traditionally been seen as having high quality (Knapp, 2005).

Catchments show a large degree of spatial heterogeneity as well as temporal variation in land cover and weather (Blöschl and Sivapalan, 1995) and, as a result, pesticide concentrations are variable not only between catchments, but

from day to day within a catchment (Kreuger, 1998). Modelling can be used to identify catchments where pesticides are more likely to be present above the MAC and highlight areas within a catchment where targeted strategies could be used to reduce pesticide concentrations. In order to assess the potential risks to drinking water resources in the medium to long term modelling can also be used to predict how changes in land use and climate could affect not only the timing and magnitude of pesticide concentrations at the catchment outlet but a potential change in the suite of pesticides detected.

In summary, a management model is required in order to be used predictively to design monitoring strategies, identify surface and groundwater bodies that are more at risk of pesticides being present above $0.1 \mu\text{g L}^{-1}$, explore the effectiveness of catchment management strategies to reduce pesticide concentrations and predict in the medium to long term the effect that a change in climate and land use could have on the suite of pesticide expected to be greater than $0.1 \mu\text{g L}^{-1}$. To accomplish this a pesticide fate model therefore needs to be able to predict daily pesticide concentrations at the catchment scale taking into account land use, soil type, unsaturated zone geology and weather in order to inform the risk assessment and risk management of drinking water resources with respect to the timing and magnitude of pesticide concentrations in both surface and groundwater.

1.1.2. Limitations of current pesticide fate and transport models

There are a number of pesticide fate models that describe pesticide transfers from soil to surface and groundwater that could be used at the catchment scale, defined by Köhne *et al.* (2009) as over 100 ha. The models range from detailed field-scale models, such as MACRO (Larsbo and Jarvis, 2003), through to European scenario models, e.g. FOCUS (2000) and FOCUS (2001), which are intended to screen out compounds which have a high propensity to leach. Detailed models typically have large data requirements and long run times, thus are typically restricted to run at a very small spatial scale. These characteristics could prove problematic when considering large or multiple catchments.

Furthermore, the broad scale European screening models do not represent the spatial complexity required for flexible catchment scale modelling.

There are only a few pesticide fate models that have been used at the catchment scale to predict pesticide exposure in surface water bodies. These include, SWAT (Neitsch *et al.*, 2002), SWATCATCH (Brown *et al.*, 2002), SEPTWA (Beernaerts *et al.*, 2005) and DRIPS (Bach *et al.*, 2001). A limitation of DRIPS, SEPTWA and SWATCATCH is the time-step of predicted output concentrations (yearly, fortnightly and weekly, respectively), as pesticide concentrations are highly temporally dynamic. SWAT has been successfully applied in individual catchments of different sizes to predict daily pesticide concentrations (e.g. Kannan *et al.*, 2006; Holvoet *et al.*, 2008; Luo and Zhang, 2009). However, it is considered to have large input data requirements and numerous parameters which require calibration (Benaman *et al.*, 2005), and therefore, is not considered to be an appropriate model which can be applied to a wide range of individual catchments.

Predictions of pesticide concentrations in groundwater for the purpose of pesticide registration are made at a depth of 1 m from the surface (i.e. to the base of the soil root zone; FOCUS, 2001). This assessment is intended to be conservative, but it is unrealistic for most groundwater resources in the UK and elsewhere, which have a complex range of hydrogeological environments. This can include: superficial deposits overlying aquifers, as well as a range of transport pathways through the unsaturated zone (matrix flow and fracture flow), all of which could affect both the timing and magnitude of pesticides reaching the water table. Currently, there are no broad-scale models known to the author that explicitly account for pesticide fate and transport through the unsaturated zone to the water table, and that consider the range of hydrogeological settings found in the UK.

Typically, pesticide fate and transport models consider transfers to either surface water or groundwater resources. As a consequence, two separate pesticide fate and transport models could be used, one to predict pesticide concentrations in surface water and the other for groundwater. This could result

in different conceptualisations and assumptions about hydrological processes, potentially leading to inconsistencies in predicted pesticide concentrations between surface and groundwater resources.

As a consequence, there is an unoccupied niche for a new pesticide fate and transport model that contains enough process complexity to be applicable in a wide range of catchments and hydrogeological settings within an integrated hydrological framework that is computationally undemanding.

1.2. Aim and objectives of the thesis

The aim of this thesis is to develop a broad scale, process-based, pesticide fate and transport model to determine pesticide exposure at the catchment outlet and at the water table in drinking water resources in order to be used to inform water company risk assessment and risk management.

The thesis has five specific objectives to achieve the aim:

- To outline a rationale for model development by reviewing catchment-scale pesticide fate and transport models available for pesticide exposure assessment in surface water and groundwater bodies.
- To develop a pesticide fate and transport model with an integrated hydrological framework that can predict pesticide exposure at the catchment outlet and at the water table for a wide range of catchment types and hydrogeological settings in order to inform the risk assessment and risk management of drinking water resources.
- To evaluate the ability of the pesticide fate and transport model to reproduce pesticide concentrations at surface water catchment outlets.
- To explore the importance of the unsaturated zone for determining the timing and magnitude of pesticide transfers to the water table.
- To illustrate how the pesticide fate and transport model can be used predictively to explore mitigation scenarios to reduce pesticide concentrations at the catchment outlet.

1.3. Structure of the thesis

This thesis is divided into eight chapters, shown schematically in Figure 1.1. The first chapter provides an overview of the problems pesticides pose to drinking water resources, both surface and groundwater, why catchment-scale models are required by drinking water companies and the limitations of the current catchment scale pesticide fate and transport models with reference to the purposes required.

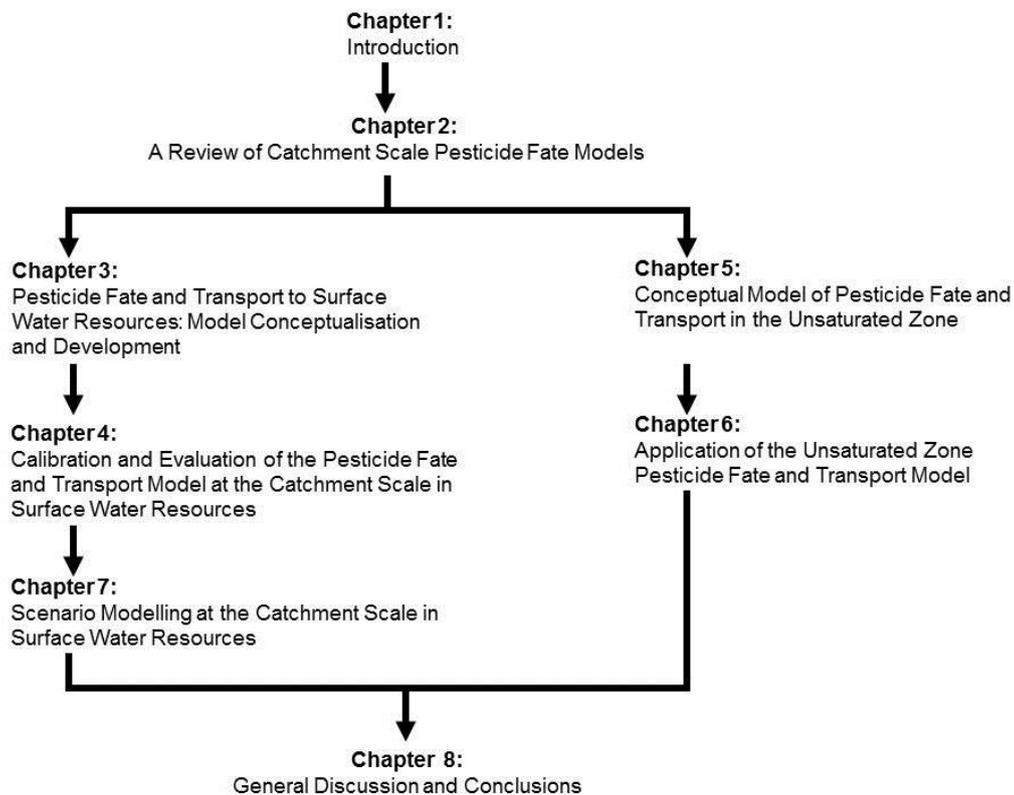


Figure 1.1. Thesis outline by chapter.

Chapter 2 outlines existing catchment-scale pesticide fate models that could be used to predict pesticide exposure at the catchment outlet and transport to the water table and establishes the unoccupied niche that exists for a new pesticide fate and transport model.

Chapter 3 outlines the conceptualisation and mathematical description of the soil water balance model which is used to predict the hydrological pathways from the soil (surface runoff, drain flow, lateral throughflow and percolation). With an innovative representation of the bottom boundary condition at the interface between the soil and the unsaturated zone, idealised into three broad, but physically realistic categories, this allows the model to be used to predict pesticide exposure in surface or groundwater at a broad scale.

Chapter 3 also includes a mathematical description of pesticide fate and transport in the soil. This is used to predict the mass flux of pesticide displaced and available for transport to surface water and/or to the top of the unsaturated zone, calculated using water-flux-dependant partitioning.

The hydrological model and the pesticide fate and transport model described in Chapter 3, is calibrated and evaluated for eight pesticides in five surface water catchments in Chapter 4. This chapter demonstrates that the model is applicable to different catchment types and sizes. This chapter also provides an insight into the analysis of the transport pathways from the soil that contribute to predicted pesticide exposure at the outlet of two contrasting catchments.

Chapter 4 also contains a methodology for the derivation of input parameters to allow broad-scale application of the model in the UK.

Chapter 5 describes a novel conceptualisation and mathematical description of pesticide fate and transport in the unsaturated zone. To be applicable at the broad scale, three hydrogeological settings were developed, accounting for two flow domains (intergranular matrix flow and fracture flow) and the presence and permeability of superficial deposits. In order to explore the role that the unsaturated zone plays on the timing and magnitude of peak pesticide concentrations reaching the water table, the hydrogeological settings (described

in Chapter 5) are applied in Chapter 6 by parameterising the model for three principal aquifers found in the UK (chalk, limestone and sandstone).

Chapter 7 demonstrates the utility of the pesticide fate and transport model (developed in Chapter 3) when used predictively by exploring possible spatial and temporal mitigation scenarios that could be used to reduce pesticide concentrations at the catchment outlet.

Chapter 8 provides a summary of the new pesticide fate and transport model developed and applied in this thesis with respect to achieving the objectives laid out. This chapter also provides a general discussion on the implications that the model results could have for drinking water resource management. Finally, it proposes future model developments and uses.

Chapter 2. A review of Catchment Scale Pesticide Fate Models

2.1. Introduction

The aim of this chapter is to provide a review of the literature on existing pesticide fate and transport models which can be applied at the catchment scale to predict pesticide concentrations at the catchment outlet or at the water table. This chapter is not intended to be a review of pesticide fate and transport models utilised at different scales; articles by Quilbé *et al.* (2006) and Köhne *et al.* (2009) are amongst a number of wider ranging reviews.

A wide range of pesticide fate and transport models exist and model purpose can typically be defined as either research or management (Addiscott and Wagenet, 1985; Jarvis *et al.*, 1997; Quilbé *et al.*, 2006). Research models expand upon current knowledge of process representation that governs pesticide fate and behaviour; usually they are highly mechanistic, physically based, 1-D models (Jarvis *et al.*, 1997; Quilbé *et al.*, 2006). Management models are typically employed as an aid or guide to decision making (Jarvis *et al.*, 1997; Quilbé *et al.*, 2006). Pesticide fate models are also used in regulation, for example in pesticide registration or re-registration, which requires predictions of pesticide concentrations in surface and groundwater (FOCUS, 2000; FOCUS, 2001). It is possible for models to be used for more than one purpose. For example, MACRO (Larsbo and Jarvis, 2003), which is traditionally thought of as a research model, is also used in the pesticide registration process. This is discussed further in Section 2.2.1.

2.2. Pesticide fate and transport catchment scale models

2.2.1. Process representation

Mathematical models can range from “black box models” to “white box models” (Figure 2.1). Black box models, which are often empirically-based, describe the transformation of inputs into outputs with no detailed process representation. An example of a black box model is the Groundwater Ubiquity Score (GUS), an indexing method developed by Gustafson, (1985) to differentiate between pesticides that are “leachers” and “non-leachers”, as a function of an empirical relationship between DT_{50} (degradation half-life) and K_{OC} (soil organic carbon to water partition coefficient). GUS however ignores the inherent soil and aquifer properties which also influence aquifer vulnerability.

White box models, on the other hand, are highly mechanistic with a high degree of process representation. Examples of highly mechanistic pesticide fate models include MACRO (Larsbo and Jarvis, 2003), MIKE-SHE (Refshaard and Storm, 1995) and TRACE/3DLEWASTE (Herbst *et al.*, 2005). As the degree of process representation increases, the scale of application often decreases (Figure 2.1), as running highly mechanistic research models at the catchment scale is often complicated by the requirements for large quantities of input data and calibration of site-specific parameters (Binley *et al.*, 1991; Quilbé *et al.*, 2006).

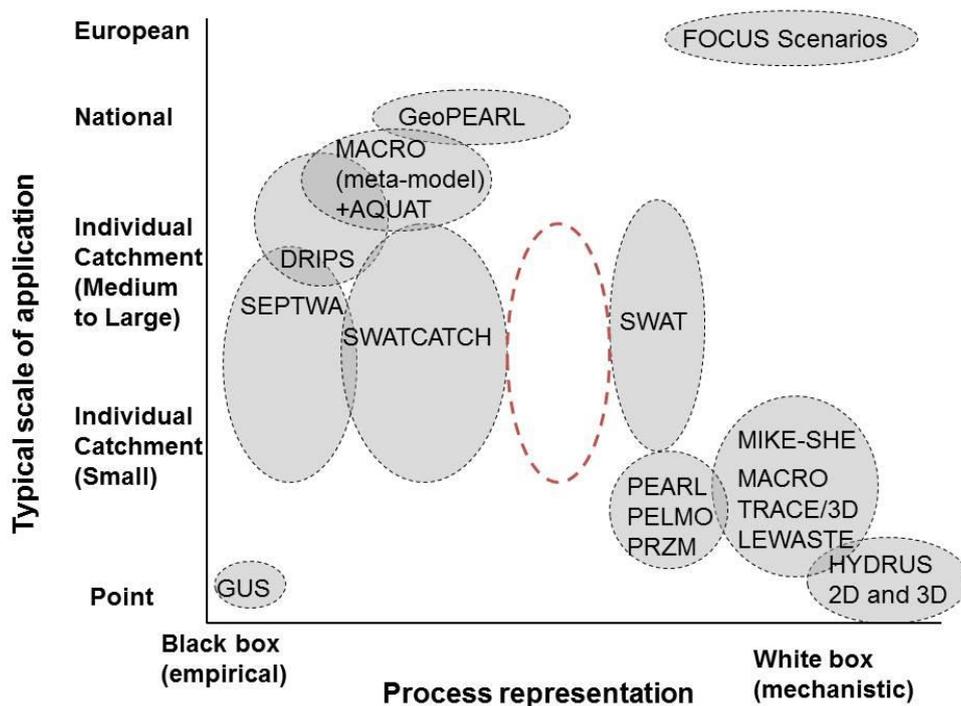


Figure 2.1. Schematic representation of example pesticide fate models with respect to process representation and typical scale of application. The red dotted line represents the unoccupied niche.

Pesticide fate models that are more process based are used at the European scale, for example the FOCUS scenarios (Figure 2.1). FOCUS (Forum of the Co-ordination of Pesticide Fate Models and their Use) established ten standard surface water model scenarios (FOCUS, 2001) and nine standard groundwater scenarios (FOCUS, 2000), for use across Europe, to establish risk of leaching losses as part of registration. The approved models are PEARL (Tiktak *et al.*, 2000), PELMO (Klein, 1991), PRZM (Mullins *et al.*, 1993), and MACRO (Larsbo and Jarvis, 2003). The scenarios are not, however, deigned to predict exposure at the individual catchment scale.

2.2.2. Data requirements

Data requirements are an important consideration as they affect both the ability of the model to be used in new catchments and the amount of calibration required. More mechanistic models tend to have very high data requirements

(Figure 2.2) and are typically only applied at the point, plot or small catchment scales. For example, MIKE-SHE is a fully distributed hydrological model that can simulate pesticide fate and transport from the field scale to the catchment scale and has been applied to surface water catchments (e.g. Fauser *et al.*, 2008) as well as groundwater resources (Christensen *et al.*, 2004). However, the use of MIKE-SHE at the catchment scale is restricted by its detailed input parameter requirements (Renaud *et al.*, 2008). Furthermore, the physical basis of mechanistic hydrological models, such as MIKE-SHE, has been challenged by Beven (1989) when they have been extensively calibrated.

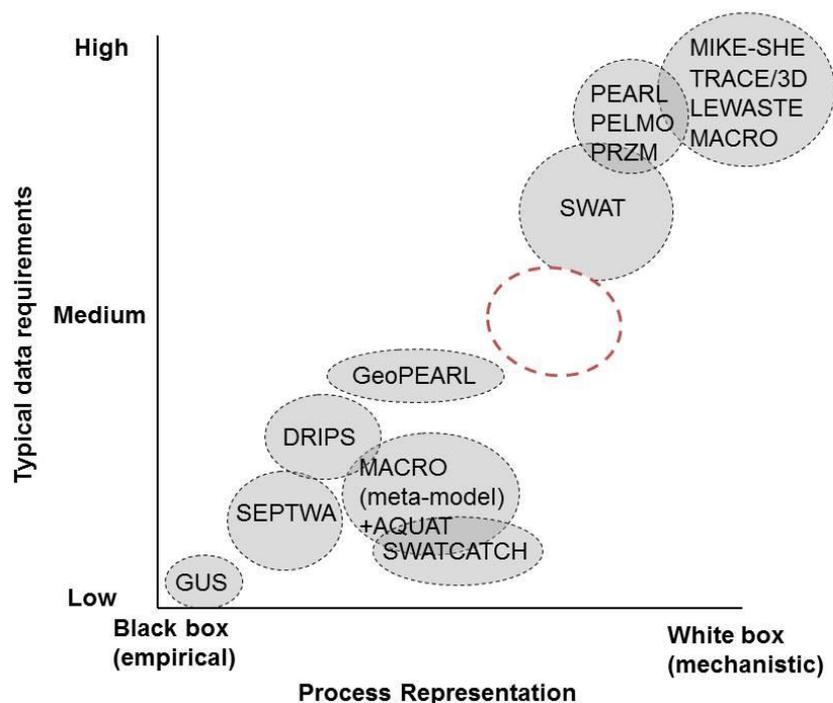


Figure 2.2. Schematic representation of example pesticide fate models with respect to process representation and typical data requirements.

Another example of a highly mechanistic model is MACRO (Larsbo and Jarvis, 2003). MACRO is a one-dimensional dual permeability solute transport model, explicitly accounting for macropore flow in the soil. MACRO is typically employed at the point scale but has also been employed at the catchment scale to make predictions of pesticide concentrations in surface water (e.g. Lindahl *et al.*, 2005). Lindahl *et al.* (2005) noted that MACRO was suited for application in

the Vemmenhog catchment due to the existence of well-defined transport routes and low variability in soil characteristics.

Mechanistic models can be run as meta-models by executing the model for a set of combinations; these outputs can then be used as inputs into another model. PEARL (Tiktak *et al.*, 2000) and MACRO (Larsbo and Jarvis, 2003) have both been utilised to create inputs. GeoPEARL (Tiktak *et al.*, 2002) is a national scale model that consists of 6,405 unique combinations of soil, climate, land use and hydrotype (geometry of the subsoil, Tiktak *et al.*, 2002) run with PEARL (Tiktak *et al.*, 2000) to simulate pesticide fate and SWAP (van Dam, 2000) for the hydrology. The GeoPEARL outputs are linked to a regional groundwater flow model. The outputs are annual average concentrations in groundwater. It is worth noting that there is no specific representation for unsaturated zone geology and unsaturated zone processes in GeoPEARL.

MACRO meta-model outputs were generated for use with a substrate attenuation factor model (AQUAT) to determine the risk of pesticide leaching to groundwater resources (Holman *et al.*, 2004). The meta-model consists of MACRO-predicted annual average concentrations at 1 m depth for 4,704 combinations of soil type, climate, pesticide properties and application patterns. These concentrations are then transformed by the AQUAT model to concentrations at the water table, accounting for unsaturated zone geology.

An advantage of using meta-models is a reduction in data requirements in contrast to running a complex model (Haberlandt, 2010), although data are still required to execute the combinations that have been chosen. Another advantage is the reduced run times, as the more complex model is run *a priori* and only the results are accessed. Disadvantages of using meta-models include missing combinations and associated processes from the initial mechanistic model runs (Haberlandt, 2010).

2.2.3. Examples of pesticide fate and transport models predicting pesticide transport to surface water resources

There are only a few pesticide fate models that have been used at the catchment scale to predict pesticide exposure in surface water bodies. These include: SWAT (Neitsch *et al.*, 2002), SWATCATCH (Brown *et al.*, 2002), SEPTWA (Beernaerts *et al.*, 2005) and DRIPS (Bach *et al.*, 2001). The time step of the model, input data requirements and process representation are important considerations for the suitability of these models for use in drinking water compliance risk assessment at the catchment outlet.

Pesticide fate and transport models that have lower data requirements, typically also have coarser processes representation (Figure 2.3). However, the lower data requirements, in turn mean that they are able to be used in more than one individual catchment, although they may produce outputs at longer time-steps. For example, DRIPS (Drainage Runoff Input of Pesticide in Surface Water; Röpke, *et al.*, 2004) is a regional-scale model which predicts an annual pesticide load for a surface water body from diffuse sources (surface runoff, tiles drains and spray drift) at a 1km by 1km scale in a geographical information system (GIS).

SEPTWA (System for the Evaluation of Pesticide Transport to Waters; Beernaerts *et al.*, 2005), is a catchment scale model that simulates fortnightly average surface water concentrations at the catchment outlet arising from point sources and diffuse sources (runoff, drainage and spray drift) using fixed emission factors. The emissions are calculated as a fixed percentage of the amount applied. The application in a catchment is based on land use database, which consider, for example, area of different crops grown and the density of the railway network. Maximum predicted losses to surface water occur when there is sufficient rainfall in the fortnight. Average fortnightly concentrations are calculated from predicted losses and predicted total flow. The model has been evaluated against measured data in a catchment in Belgium for seven pesticides comparing total annual load, cumulative loads and fortnightly

average concentrations. An advantage of SEPTWA is that it can be adapted easily to new catchments.

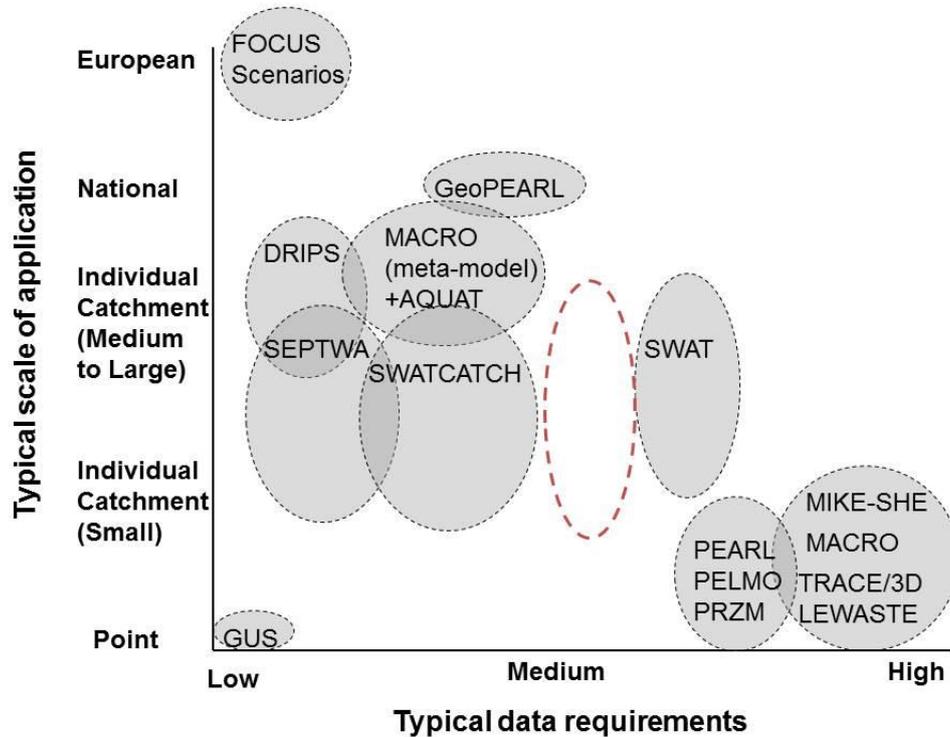


Figure 2.3. Schematic representation of example pesticide fate models with respect to typical data requirements and typical scale of application.

SWATCATCH (Hollis and Brown, 1996; Brown *et al.*, 2002) is a semi-empirical distributed model which makes weekly predictions of pesticides transfers from agricultural diffuse sources accounting for the distribution of land use and soil types in a catchment. The hydrology is based on an empirically-derived link between soil and rapid stream response, underpinned by HOST (Hydrology of Soil Type classification, developed by Boorman *et al.* (1995)). River flow is predicted weekly based on the response of the soil to hydrologically effective rainfall (HER), defined as rainfall that occurs when there is no soil moisture deficit (Brown *et al.*, 2002). The prediction is spatially weighted at the catchment scale to determine total flow. Pesticide transfers are based on hydrological response. The model has been evaluated in 29 catchments for 16 pesticides and was able to simulate peak measured pesticide concentrations within a

factor of 10 (Brown *et al.*, 2002). An advantage of SWATCATCH is that it can be run un-calibrated in any catchment in England and Wales as it is based on national-scale relationships between soil properties in the National Soil Map, precipitation, and pesticide transfers.

A limitation of DRIPS, SEPTWA and SWATCATCH is the time-step of output concentrations (yearly, fortnightly and weekly, respectively). Pesticide concentrations are highly temporally dynamic (Kreuger, 1998) and, therefore, the time-step of outputs means that the models are not fit for the purpose outlined in this thesis for predicting peak pesticide exposure.

SWAT (Neitsch *et al.*, 2002), is a conceptual semi-distributed model, which has been successfully applied in individual catchments of different sizes to predict daily pesticide concentrations (e.g. Kannan *et al.*, 2006; Holvoet *et al.*, 2008; Luo and Zhang, 2009). SWAT divides a catchment into Hydrological Response Units (HRUs), which are intended to represent homogenous areas of topography, soil and land use. SWAT attempts to represent a wide range of environmental processes, e.g. fate process in soil such as volatilization, photolysis, hydrolysis and biological degradation, as well as leaching and horizontal movement of water and pesticides in surface runoff, lateral throughflow and in-stream processes. As a consequence, this has high input data requirements and contains a large amount of parameters that require calibration (e.g. Benaman *et al.*, 2005; Moriasi *et al.*, 2007; Stehr *et al.*, 2008). For this reason, it is not appropriate as a risk assessment tool which can be applied to varying individual catchment types.

2.2.4. Examples of models predicting pesticide fate and transport to groundwater

When predicting pesticide exposure at the water table, several pesticide fate and transport models consider transfers only to 1 m depth from the surface (e.g. FOCUS, 2000). This assessment is intended to be conservative, but it is unrealistic for most groundwater resources in the UK and elsewhere, which have a complex range of hydrogeological environments. As a result, potentially

important processes that could affect timing and magnitude of pesticide transfers to the water table are ignored, such as: the presence and permeability of superficial deposits, depth to the water table (which could potentially allow pesticides to be attenuated via degradation, sorption and dispersion), and transport mechanisms through the unsaturated zone (intergranular matrix flow and fracture flow).

Models that do account for unsaturated zone processes, however, tend to be computationally demanding, requiring a large amount of parameters and take a long time to set-up and run (e.g. MIKE-SHE; Christiansen *et al.*, 2004). As a consequence, these models would not be appropriate for use in a risk assessment tool which is required to be applied to numerous hydrogeological situations. The MACRO meta-model and AQUAT model (Holman *et al.*, 2004) does explicitly represent the unsaturated zone, but lacks important process description, such as fracture flow and the presence and permeability of superficial deposits, which could affect the timing and magnitude of pesticide transfers (Griffiths *et al.*, 2011).

It is also worth noting that typically, pesticide fate and transport models consider transfers to either surface water or groundwater resources. As a consequence, two separate pesticide fate and transport models could be used, one to predict pesticide concentrations in surface water and the other for groundwater. This could result in different conceptualisations and assumptions about hydrological processes, potentially leading to inconsistencies in predicted pesticide concentrations in surface and groundwater resources.

2.3. Conclusions

Despite the fact that a large number of pesticide fate and transport models have already been developed, a niche still exists for a new pesticide fate and transport model that contains enough process complexity to be applicable in a wide range of catchments and hydrogeological settings (explicitly accounting for unsaturated zone processes) within an integrated hydrological framework, but that is computationally undemanding and runs at a daily time step.

Chapter 3. Pesticide Fate and Transport to Surface Water Resources: Model Conceptualisation and Development

3.1. Introduction

This chapter outlines the conceptualisation, and associated mathematical model, to describe pesticide fate and transport to surface water resources, in order to predict peak concentrations arising from diffuse agricultural sources to aid in water company risk assessment. A conceptual model is a theory-based description of idealising assumptions and justifications which are intended to capture the key characteristics of natural environmental behaviour (Brassington and Younger, 2010). These assumptions have for the most part been informed by field and laboratory studies reported in the literature. The aim of the pesticide fate and transport model is to represent soil to water transport, in a simple, but physically realistic way as catchment hydrological response plays a critical role in determining how solutes, including agriculturally applied pesticides, are transported from land to water (Holvoet *et al.*, 2005).

The chapter is divided into six sections:

- Section 3.2 describes the soil water balance model, including the calculation of evapotranspiration and the conceptualisation of the flow pathways considered key for water and pesticide transport.
- Section 3.3 describes the boundary conditions in the model at the interface between the soil and the unsaturated zone.
- Section 3.4 outlines the conceptual model for pesticide fate and transport in the soil.
- Section 3.5 outlines pesticide fate and transport at the catchment scale.
- Section 3.6 provides the conclusions of the chapter.

3.2. Soil water balance model

A soil water balance model can be used to predict the hydrological (and therefore pesticide transport) pathways from the soil. Soil water balance models have many practical applications, such as: determining irrigation water requirements (Smith, 1992), calculating evapotranspiration (Malek and Bingham, 1993; Wilson, 2001), predicting groundwater recharge in humid and arid areas (Ragab *et al.*, 1997; Kendy *et al.*, 2003; Rushton, 2005), estimating consequences of a soil water deficit on yield (Barron *et al.*, 2003; Mandal *et al.*, 2007) and predicting river flows (Arnold *et al.*, 1998; Middelkoop *et al.*, 2001), as well as studies of diffuse source pollution (Whelan *et al.*, 2002).

Simulating the flow of water through a soil often follows a “tipping bucket” approach where a soil store is filled to a threshold (usually field capacity); anything above the threshold is assumed to drain vertically into the underlying layer (Emerman, 1995). Although this is straight forward and requires a relatively small number of parameters, particularly in comparison to other methods of simulating water flow through soils such as the Richards equation (Emerman, 1995; Ranatunga *et al.*, 2008), it often fails to represent hydrograph recessions well due to the fixed threshold.

In contrast, a gravity flow approximation to soil water flow can be used to represent continuous drainage between saturation and a point at which the flow becomes negligible (Jury and Horton, 2004). This method relates vertical drainage to unsaturated hydraulic conductivity, which in turn is related to soil water content. Matric potential contributions to the hydraulic gradient are ignored because when soil water tensions are significant hydraulic conductivity is often low, limiting water movement out of the soil profile. This method has been used successfully by Whelan and Gandolfi (2002) to predict spatial and temporal patterns of denitrification, by Whelan *et al.* (2002) to predict phosphorus transfers from agricultural land to surface water and by Kendy *et al.* (2003) to quantify groundwater recharge.

In the soil water balance model the soil is split into two discrete stores, a topsoil store and a subsoil store. This division is based on the soil horizons described in the LandIS database (available from the National Soil Resources Institute; LandIS, 2013c). The A horizon is classified as topsoil and the B horizon as subsoil. Where present, the E horizon is assumed to be part of the topsoil and the C horizon the subsoil.

The amount of water stored in the soil is calculated as a continuous deficit from saturation. In the topsoil store, the deficit is assumed to decrease, i.e. move towards 0, with the addition of rainfall. The deficit is assumed to increase due to evapotranspiration, drainage to the subsoil store and lateral throughflow (Figure 3.1).

$$SMT_t = SMT_{t-1} + \Delta t \times (ET_a \times f_t + q + qL_{top} - R_{WB}) \quad (3.1)$$

where SMT is the soil moisture deficit from saturation in the topsoil store (mm), Δt is the time increment (days), ET_a is actual evapotranspiration (mm day^{-1}), f_t is the fraction of actual evapotranspiration assumed to be derived from the top soil store (-), q is drainage from the topsoil to the subsoil (mm day^{-1}) and qL_{top} is lateral throughflow from the topsoil (mm day^{-1}), R_{WB} is rainfall entering the soil water balance (mm day^{-1}).

$$R_{WB} = R - IeOF - SeOF \quad (3.2)$$

where R is rainfall (mm day^{-1}), $IeOF$ is infiltration excess overland flow (mm day^{-1}) and $SeOF$ is saturation excess overland flow (mm day^{-1}).

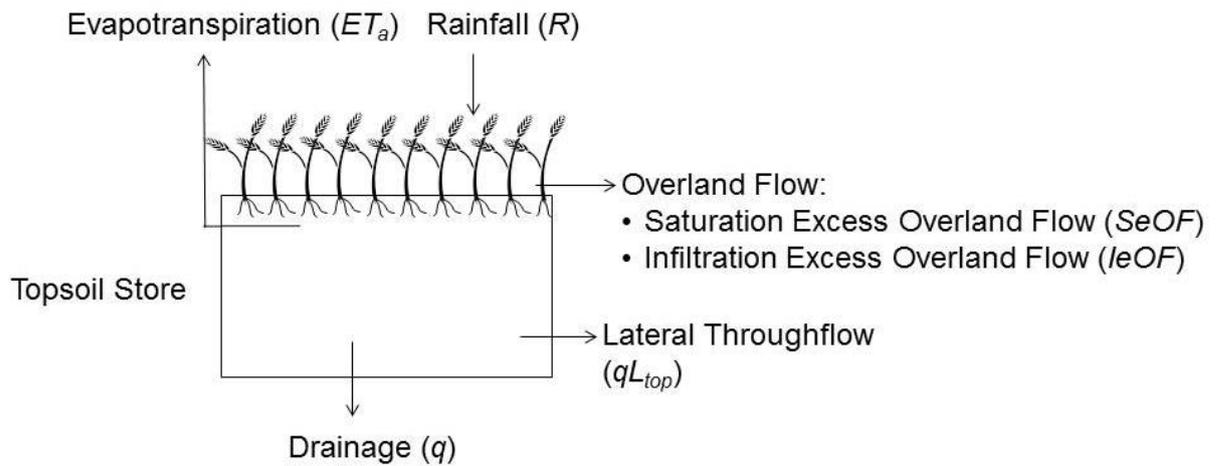


Figure 3.1. Conceptual diagram of key transport pathways from the topsoil store.

In the subsoil store, the saturation deficit is decreased by drainage from the topsoil store and increased by evapotranspiration (if roots are present), percolation to the unsaturated zone, drain flow and lateral throughflow (Figure 3.2). To determine whether the subsoil layer allows percolation the soil is subdivided into one of three classes based on HOST classification (Boorman *et al.*, 1995); this is further explored in Section 3.3.

For the subsoil we may write:

$$SMS_t = SMS_{t-1} + \Delta t \times [(1 - f_t) \times ET_a + qP + qL_{sub} + q_{drain} - q] \quad (3.3)$$

where SMS is soil moisture deficit in the subsoil store (mm), qP is percolation to the unsaturated zone (mm day^{-1}), qL_{sub} is lateral throughflow from the subsoil (mm day^{-1}) and q_{drain} is flow from sub-surface artificial field drains (mm day^{-1}).

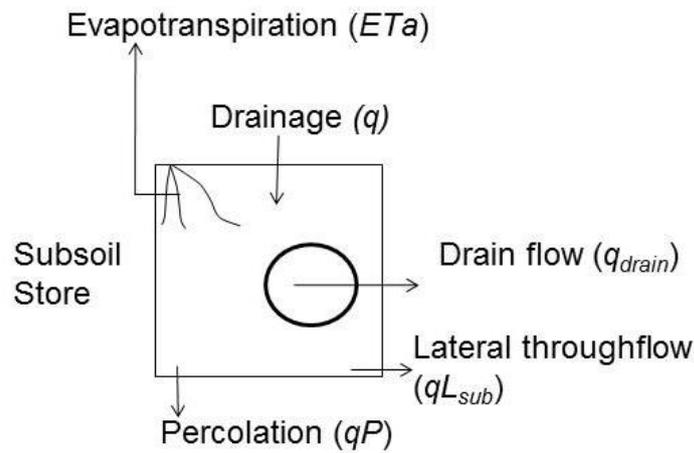


Figure 3.2. Conceptual diagram of the key transport pathways from the subsoil.

Volumetric water content (θ) for each layer can be determined from the soil moisture deficit. For the topsoil:

$$\theta_{top} = \frac{(\theta_{sat} \times Z_{top} - SMT_t)}{Z_{top}} \quad (3.4)$$

where θ_{top} is the volumetric water content of the topsoil ($\text{cm}^3 \text{cm}^{-3}$), θ_{sat} is the volumetric water content at saturation ($\text{cm}^3 \text{cm}^{-3}$) and Z_{top} is the topsoil depth (mm).

For the subsoil:

$$\theta_{sub} = \frac{(\theta_{sat} \times Z_{sub} - SMS_t)}{Z_{sub}} \quad (3.5)$$

where θ_{sub} is the volumetric water content of the subsoil ($\text{cm}^3 \text{cm}^{-3}$) and Z_{sub} is the subsoil depth (mm).

Although the water balance model produces predictions at a daily time-step, Euler's method is used to discretise the daily time step into smaller time-steps (with 10 time steps in each day). Euler's method (sometimes known as the Euler-Cauchy or point-slope method) is a one-step method of integrating ordinary differential equations.

3.2.1. Precipitation

The definition of precipitation includes: rain, snow, hail and sleet. In England and Wales most of the year precipitation as rainfall is dominant. In the model only rainfall processes are accounted for.

Losses of rainfall from interception are ignored in the model because of the difficulties in calculating leaf surface area for a variety of crops at different growth stages. In addition, supplemental irrigation has not been accounted for in the model. However, in some areas in the East of England irrigation is required to maximise crop yield and secure high quality for crops such as fruit and vegetables (Knox *et al.*, 2010).

3.2.2. Evapotranspiration

3.2.2.1. Reference evapotranspiration

Reference evapotranspiration (ET_0) is defined by Allen *et al.* (1998) as the evapotranspiration rate from a well-watered hypothetical reference crop. ET_0 is calculated with the Hargreaves Equation (Hargreaves and Samani, 1985; Equation 3.6) as for many areas the full set of meteorological variables required to calculate ET_0 using the Penman-Monteith equation are not available.

$$ET_0 = 0.0135 \times R_s \times (TC + 17.8) \quad (3.6)$$

where ET_0 is reference evapotranspiration (mm day^{-1}), R_s is solar radiation in units of equivalent water evaporation (mm day^{-1}) and TC is daily average temperature ($^{\circ}\text{C}$). Solar radiation is estimated using temperature difference (Hargreaves and Samani, 1985).

$$R_s = K_T \times (T_{max} - T_{min})^{0.5} \times R_a \quad (3.7)$$

where R_a is extra-terrestrial radiation in units of equivalent water evaporation (mm day^{-1}), K_T is an empirical coefficient (-), T_{max} is the maximum temperature ($^{\circ}\text{C}$) and T_{min} is the minimum temperature ($^{\circ}\text{C}$). Extra-terrestrial radiation can be calculated as Allen *et al.* (1998).

By combining Equations 3.6 and 3.7 the full-form of the Hargreaves equation is given in Equation 3.8.

$$ET_O = 0.135 \times K_T \times (T + 17.8) \times (T_{max} - T_{min})^{0.5} \times R_a \quad (3.8)$$

The full form Hargreaves equation is often further simplified (Shahidian *et al.*, 2012), by replacing $0.135 K_T$ in Equation 3.8 with 0.0023, assuming a fixed K_T of 0.17 (Jensen *et al.*, 1997; Hargreaves and Allen, 2003; Lu *et al.*, 2005; Yoder *et al.*, 2005; Weiß and Menzel, 2008).

$$ET_O = 0.0023 \times (T + 17.8) \times (T_{max} - T_{min})^{0.5} \times R_a \quad (3.9)$$

3.2.2.2. Potential evapotranspiration

Potential crop evapotranspiration (ET_C) can be calculated using ET_O and a crop coefficient (K_C ; -). Unless stated otherwise equations up to Section 3.3.3 are from Allen *et al.* (1998).

$$ET_C = ET_O \times K_C \quad (3.10)$$

where ET_C is the potential crop evapotranspiration (mm day^{-1}).

K_C varies from crop to crop and with development stage. For a detailed explanation of crop K_C values for a range of crops and development stages see Table 12 in Allen *et al.* (1998). K_C values are provided for key stages in the plant growth cycle: initial stage (assumed to be between planting and 10% crop cover; Allen *et al.*, 1998), crop development (10% crop cover to full crop cover), mid-season (full cover to maturity) and late season (maturity to harvest). During the initial stage and the mid-season the K_C remains fixed (Figure 3.3). Linear interpolation in the development growth stage and between the late season growth stage and harvest is required to provide daily estimates of K_C (Figure 3.3). Between harvest and planting there is assumed to be bare soil (Section 3.2.2.5).

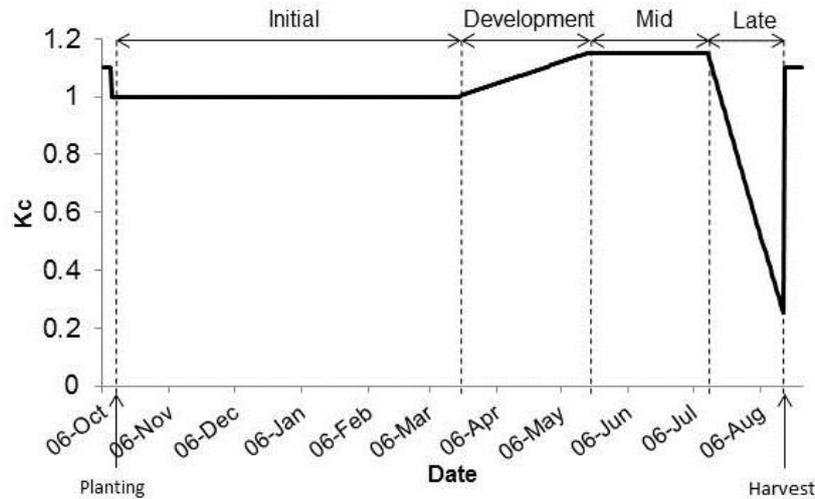


Figure 3.3. Linear interpolation of K_c values for winter wheat in one year growth cycle.

3.2.2.3. Effect of water stress on evapotranspiration

Potential crop evapotranspiration assumes that the crop in question is: disease free, well-watered and subject to ideal growing conditions (Allen *et al.*, 1998). Water stress can reduce crop evapotranspiration from the potential rate. The effect of a reduction in soil water content on ET_c is described in Allen *et al.* (1998) with a water stress coefficient (K_s).

$$ET_a = ET_c * K_s \quad (3.11)$$

where ET_a is the actual crop evapotranspiration (mm day^{-1}) and K_s is the water stress coefficient (-).

The amount of water available for plant roots is divided between Readily Available Water (RAW) and Total Available Water (TAW). The TAW is defined by Allen *et al.* (1998) as the total amount of water in the root zone that is available for the plant. It is calculated in the topsoil and subsoil store, depending on rooting depth. Further information is provided in Section 3.2.2.4.

$$TAW = (\theta_5 - \theta_{1500}) \times Zr \quad (3.12)$$

where TAW is the Total Available Water (mm), θ_5 is the water content at -5 kPa tension ($\text{cm}^3 \text{cm}^{-3}$), θ_{1500} is the water content at permanent wilting point ($\text{cm}^3 \text{cm}^{-3}$) and Zr is the root depth (mm).

RAW is calculated as a fraction of the TAW :

$$RAW = p \times TAW \quad (3.13)$$

where RAW is Readily Evaporable Water (mm), p is the fraction of TAW that can be depleted before the crop suffers water stress (Allen *et al.*, 1998). Values of p vary between crops.

When there is no water stress, (i.e. there is readily available water accessible), the water stress coefficient is equal to 1. Once the RAW threshold is reached ETc becomes limited, and decreases proportionally with soil water content. Once the soil water content reaches permanent wilting point (i.e. when the deficit = TAW), the water stress coefficient is equal to zero and evapotranspiration is assumed to cease.

3.2.2.4. Evapotranspiration from two soil stores

Root growth is calculated assuming that during the initial stage of growth the root depth is constant at 0.1 m for all crops (Figure 3.4). During the development stage until the mid-stage the roots are assumed to grow linearly to maximum root depth. From the mid-stage until harvest (or full senescence) the roots are assumed to remain at maximum root depth.

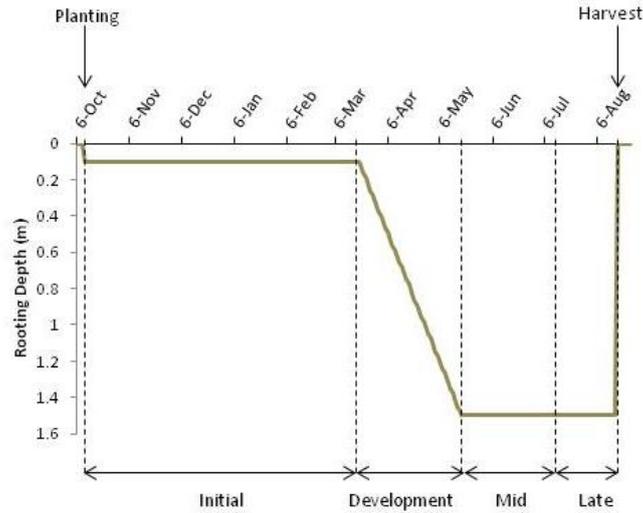


Figure 3.4. Root growth for winter wheat between planting and harvest.

The contribution of the topsoil and subsoil stores to evapotranspiration depends on the fraction of the total root length assumed in each store (Finch, 1998). In young plants the concentration of roots is greatest in the upper soil profile (Ritchie, 1974). As the roots grow into the lower soil profile, the extraction of water is still greatest from the upper soil profile. However, if roots are present in the subsoil there is potential for removal by evapotranspiration.

Assuming that water uptake is proportional to the root density (Huang and Fry 2000) and that the upper soil profile has the greatest root zone density, Hansen *et al.* (1979) proposed a triangular function to describe root water extraction with depth, with the greatest water-uptake taking place at the top. This method has been used in water balance models by Rageb *et al.* (1997) and Finch (1998) and is employed here.

3.2.2.5. Bare soil evaporation

In autumn and winter bare soil is typically dominant in arable environments in the UK. The potential evaporation from bare soil is calculated as.

$$ES = K_e \times ET_0 \quad (3.14)$$

where ES is evaporation from bare soil (mm day^{-1}) and K_e is a bare soil evaporation coefficient (-), set at 1.10 (Rushton, 2003).

The water available for bare soil evaporation is limited by the depth to which evaporation can occur, and as in evapotranspiration, when not enough water is available evaporation stops. The Total Evaporable Water (TEW) available for evaporation is calculated as:

$$TEW = (\theta_5 - 0.5 \times \theta_{1500}) \times Z_e \quad (3.15)$$

where TEW is Total Evaporable Water (mm), Z_e is the depth of the soil surface layer that is liable to drying by evaporation and is set at 100 mm (Allen *et al.*, 1998).

Bare soil is assumed to be able to dry to a water content below the permanent wilting point (i.e. halfway between zero and permanent wilting point, i.e. $0.5 \times \theta_{1500}$). Actual evaporation will be below potential bare soil evaporation once the soil moisture deficit exceeds the Readily Evaporable Water (REW ; mm). The REW is assumed to be 10 mm (Allen *et al.*, 1998).

3.2.3. Drainage from the topsoil store to the subsoil store

Water flow from the topsoil store to the subsoil store is calculated with a gravity flow equation (i.e. assuming a unit hydraulic gradient) after Jury and Horton, 2004).

$$q = K(\theta_t) \quad (3.16)$$

where $K(\theta_t)$ is the unsaturated hydraulic conductivity (mm day^{-1}) and θ_t volumetric water content of the soil at time t ($\text{cm}^3 \text{cm}^{-3}$). The unsaturated hydraulic conductivity is calculated with van Genuchten (1980).

$$K(\theta_t) = K_{sat} \times \theta_*^{0.5} \times \left[1 - \left(1 - \theta_*^{\frac{1}{m}} \right)^m \right]^2 \quad (3.17)$$

where K_{sat} is the saturated hydraulic conductivity, and θ_* is a dimensionless water content (-) and m is a curve parameter (-).

$$\theta_* = \frac{(\theta_{top} - \theta_{1500})}{(\theta_{sat} - \theta_{1500})} \quad (3.18)$$

3.2.4. Surface runoff

Surface runoff, as defined by Beven, (2012), is the fraction of the stream hydrograph from overland flow. If pesticides are present at high concentrations at the soil surface when surface runoff occurs there is potential for them to be transported downslope and into surface waters. Leu *et al.*, (2004b) measured atrazine concentrations from a single grab sample of surface runoff in Switzerland and observed a concentration of $88 \mu\text{g L}^{-1}$. In southern Louisiana, concentrations in surface runoff reached a peak of $410 \mu\text{g L}^{-1}$ for atrazine and $360 \mu\text{g L}^{-1}$ for metolachlor (Southwick *et al.*, 2003).

Overland flow can occur as infiltration excess (IE_{OF}) generated when the rainfall intensity is greater than the infiltration rate of the soil (Beven, 2012). Infiltration excess overland flow can be important in situations of high rainfall intensity and can strongly contribute to river flow (Niehoff *et al.*, 2002). Infiltration excess is more likely to happen in soils with low permeability particularly when there is little cover from vegetation (Burt, 2001). In permeable soils infiltration excess overland flow can be caused by surface compaction as a result of overgrazing or heavy machinery (Burt, 2001).

Infiltration excess overland flow is difficult to estimate as high intensity rainfall events tend to occur only for a short duration and detailed rainfall data at the hourly, or even sub-hourly time-step are required but are not typically available. Instead, it is estimated by assuming that a fraction of rainfall above a certain threshold cannot infiltrate sufficiently quickly and becomes IE_{OF} . This threshold is set at the Minimum Standard Rainfall Volume ($MSRV$; mm), multiplied by an empirical constant (p_2 ; -). Therefore, when

$$R \geq MSRV \times p_2$$

$$IE_{OF} = R \times fractR \tag{3.19}$$

where $fractR$ is the fraction of the rainfall that becomes IE_{OF} (-). The $MSRV$ is a parameter associated with a soil's HOST class (Brown and Hollis, 1996). A low $MSRV$ is associated with soils that have a high standard percentage runoff

(*SPR*), defined as the fraction of rainfall that in the first 24-hour period of a storm events causes a short term increase in stream flow (Brown and Hollis, 1996) are, therefore, expected to only require a small volume of rainfall to induce a stream response. Conversely, a high MSR_V is associated with soils that have a low SPR and are more dominated by baseflow.

Overland flow can also occur as saturation excess, generated by incoming rainfall onto soil that is saturated or close to saturation (Beven, 2012).

Saturation Excess Overland Flow (*SE_{OF}*) occurs in the model when *SMT_t* in the soil water balance reaches zero.

3.2.5. Artificial field drains

Artificial field drains are installed on agricultural land to remove excess water from the soil. In the UK approximately 66% of arable land is drained (De la Cueva, 2006). Installation of field drains is also present in some grassland areas in the UK, particularly in areas of intensive dairy farming (Robinson, 1990). Artificial field drains are a critical pathway for pesticide transport to surface water (Brown and van Beinum, 2009).

The ability of field drains to transport significant loads of pesticides from the soil profile to surface water has been demonstrated by Williams *et al.* (1996) who reported that maximum concentrations over 10 µg L⁻¹ were quite often found for a range of pesticides (e.g. isoproturon, atrazine and mecoprop) in the stream where the drains discharged in a field study in the UK. The authors noted that higher concentrations would be expected in the drain as the stream flow could be diluted from untreated areas. Tediosi *et al.* (2012) measured drain flow concentrations from a heavy clay soil in the UK and reported peak carbetamide concentrations of 694 µg L⁻¹ and peak propyzamide concentrations of 56 µg L⁻¹.

Where artificial field drains are assumed to be in place, drain flow from the subsoil store is calculated using an exponential equation based on TOPMODEL concepts (Beven *et al.*, 1984):

$$q_{drain} = C_d \times \exp(-SMSt/C_m) \quad (3.20)$$

where C_d is the maximum drain flow constant (mm day^{-1}) and C_m is a drain flow parameter that controls the shape of the recession curve (-). C_d and C_m are parameters that both require calibration. The drain flow is calculated from the soil moisture deficit from saturation in the subsoil.

3.2.6. Lateral throughflow

Lateral throughflow can occur when a permeable soil layer overlies a less permeable soil layer (Burt, 2001), or when the soil overlies a lower permeability unsaturated material (Tang *et al.*, 2012; Figure 3.5). Lateral throughflow is assumed to occur naturally in situations where there is an absence of artificial drainage (Carter, 2000b) and significant topographic gradients (Anderson and Burt, 1978).

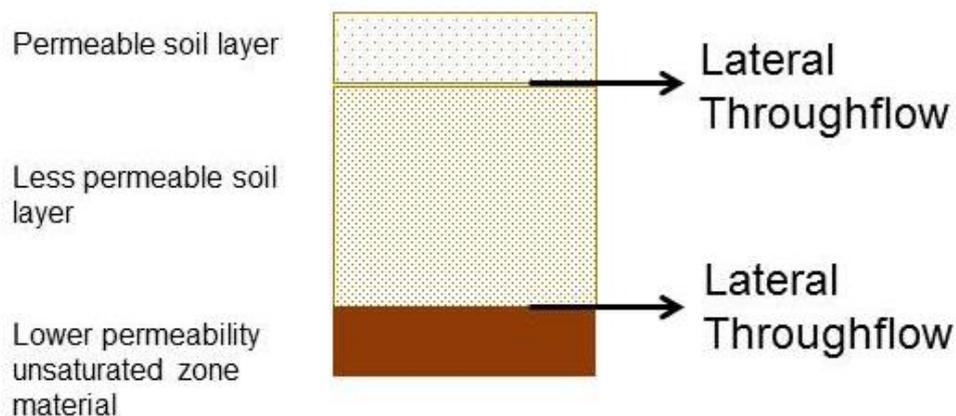


Figure 3.5. Schematic illustration of the generation of lateral throughflow in the soil.

Lateral throughflow has been cited in several papers as a potential transport pathway for pesticides to surface waters (Carter, 2000b; Brown and van Benium, 2009; Tang *et al.*, 2012). However, there is little, if any, field-scale

experimental literature investigating pesticide transport via lateral throughflow. Nevertheless, in a lysimeter study Heppell *et al.* (2004b) demonstrated the loss of isoproturon via lateral throughflow between the A and B horizons at 29 cm (Heppell *et al.*, 2004a). The peak isoproturon concentration in the throughflow was $22 \mu\text{g L}^{-1}$ resulting from an application rate of 0.9 kg ha^{-1} 64 hours before simulated rain. In the first simulated rainfall event (12.9 mm) isoproturon was measured in throughflow after 120 minutes, indicating rapid transport to the A/B boundary.

The generation of lateral throughflow in the topsoil store of the soil water balance model is predicted to occur when the subsoil is temporarily saturated thereby restricting drainage from the topsoil store, or when the drainage from the topsoil store exceeds the saturated hydraulic conductivity of the subsoil store.

In the subsoil store lateral throughflow is calculated as:

$$qL_{sub} = K_{lat} \times \exp(-SMS_t/C_{lat}) \quad (3.21)$$

where qL_{sub} is the lateral flow generated in the subsoil (mm day^{-1}), K_{lat} is the saturated lateral hydraulic conductivity (mm day^{-1}) and C_{lat} is a parameter that controls the shape of the curve; this is a catchment scale fitted parameter (-). This equation is similar to the exponential storage model employed in TOPMODEL (Beven *et al.*, 1984).

In the model there is no explicit consideration of topography, although the formation of soil types will be in response to topography and is therefore indirectly included.

3.2.7. Percolation into the unsaturated zone

Percolation is the process of vertical water transport from the base of the soil zone into the unsaturated zone to recharge groundwater. Recharge to groundwater is an important pathway of pesticide transport for agriculturally applied pesticides (Carsel *et al.*, 1985; Foster, 1998; Lapworth *et al.*, 2006).

The volume of water able to percolate from the soil into the unsaturated zone depends on the permeability of the unsaturated zone material. For example, in some field situations percolation may be restricted by the presence of low permeability material (such as till; Section 5.2.2), although, even when the hydraulic conductivity is low some percolation can usually still occur. For example, in the Lowestoft Till calculated recharge to the water table was estimated between 10 - 20 mm annum⁻¹ (Klinck *et al.*, 1996). Similarly, in the Gipping catchment, in eastern England, Jackson and Rushton (1987) estimated recharge to the water table through the boulder clay to be 24 mm annum⁻¹. The primary transport pathway in these situations will, however, be laterally. For example, in the Waveney catchment in East Anglia (Soley and Heathcote, 1998) postulated that a significant proportion of rainfall was transported to the river via tile drains that had been installed on the heavy clay soils, rather than vertically to produce recharge to the underlying chalk.

Percolation below the subsoil is calculated using similar concepts as those employed in the topsoil (Equation 3.17, Section 3.2.3). In the subsoil store however percolation is restricted by a set of lower boundary conditions at the interface between the subsoil and the unsaturated zone (Evans *et al.*, 1999). For a full description of these boundary conditions see Section 3.3.

The lower boundary condition restricts the hydraulic conductivity based on a soil's HOST class (Table 3.1), by replacing K_{sat} in Equation 3.17 with K_{BC} :

$$K(\theta_t) = K_{BC} \times \theta_*^{0.5} \times \left[1 - \left(1 - \theta_*^{\frac{1}{m}} \right)^m \right]^2 \quad (3.22)$$

where K_{BC} is the maximum hydraulic conductivity of the bottom boundary (mm day⁻¹). The curve parameter (m) was derived from the lowest soil horizon present in SEISMIC (Spatial Environmental Information System for Modelling the Impact of Chemicals; LandIS, 2013b). The θ_* is calculated as Equation 3.18, with θ_{sub} replacing θ_{top} . The outline of pesticide fate and transport in the unsaturated zone is provided in more detail in Chapter 5.

3.2.8. Other pathways to surface water resources

Alternative pathways for diffuse pesticide transport to surface waters, not originating directly from agricultural soil include: urban surface, spray drift and baseflow (Carter, 2000b; Schultz, 2001; Müller *et al.*, 2003; Blanchoud *et al.*, 2004; Skark *et al.*, 2004).

In some catchments, losses from urban surfaces (arising for example from weed control by local authorities along roads and railways or domestic uses) can also potentially contribute to contamination of surface and groundwater (Ramwell *et al.*, 2002; Blanchoud *et al.*, 2004; Ramwell *et al.*, 2004; Lapworth and Goody, 2006). However, the extent to which these contributions are significant relative to agricultural losses is largely unknown. A study by Wittmer *et al.* (2010) concluded that in mixed land use catchments pesticide input from urban areas was at least as important as agricultural areas. It is worth noting however, that the study catchment contained 20% arable agriculture, 15% urban areas and the remaining 65% was pastures and forestry and therefore different results and conclusions could be expected in catchments with different proportions of arable and urban areas.

Baseflow is the proportion of stream flow that originates from groundwater, as well as other delayed sources (Smakhtin, 2001). The baseflow component of flow is the part of the hydrograph that will continue after a rainfall event has ceased (Beven, 2012). In the model developed, percolation of water from the soil reaches a groundwater store and is released as baseflow (Section 3.5.1). The transport of pesticides in the unsaturated zone to the water table is also considered in the model (Section 5.2), however, there is no accounting for further transport of pesticides in the saturated zone, therefore, pesticides entering surface water resources via baseflow are not considered.

3.3. Boundary conditions between the subsoil and the unsaturated zone

In the soil water balance model the interface between the subsoil and the unsaturated zone is idealised into three broad but physically realistic categories (Figure 3.6): (A) unsaturated and free draining, (B) low permeability (with or without field drains) and (C) partially saturated subsoil. These conditions are based around a soil's HOST classification (Table 3.1). This interface determines for each soil the major and minor hydrological pathways considered for water and pesticide transport.

HOST is a widely accepted classification of hydrological settings of soil in the UK which includes a description of the hydrological pathways in different soils and underlying substrate geology. To allow for variation in soil properties and wetness regime eleven conceptual response models were developed (Boorman *et al.*, 1995, pg 27) which were used to create 29 HOST classes. HOST is based on three conceptual models of important conditions at the interface between the soil and the unsaturated zone: soil overlying a permeable geology with the water table >2 m below the surface; soil overlying a permeable geology with a shallow water table and soil (or soil and geology) which contains a low permeability layer within 1 m of the surface (Boorman *et al.*, 1995). Each of the 296 soil associations in the UK (LandIS, 2013a), where a soil association is named after the most frequently occurring soil series (soil types), is assigned to a HOST class. Each HOST class has been assigned to one of the three bottom boundary conditions in Figure 3.6 and Table 3.1. Note there is a fourth boundary condition in Table 3.1, peat soils, which will be considered separately after the first three.

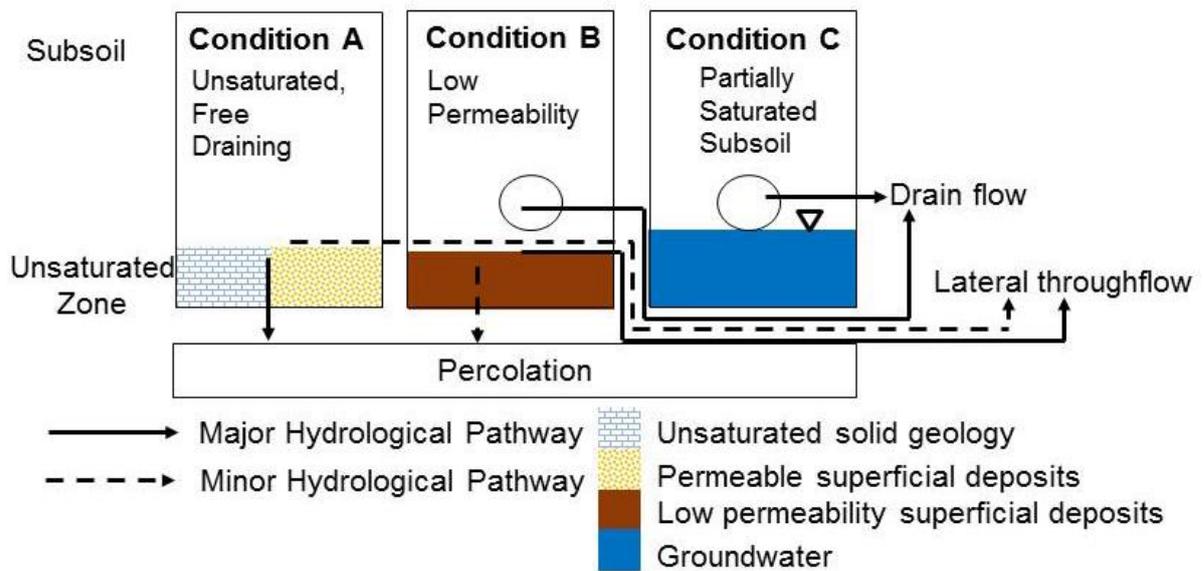


Figure 3.6. Schematic diagram of the three boundary conditions at the interface between the soil and the unsaturated zone considered in the model.

Table 3.1. Boundary conditions at the interface between the subsoil and the unsaturated zone and related HOST classifications. Adapted from Boorman *et al.* (1995) and Evans *et al.* (1999).

	Bottom boundary condition (from Figure 3.9)	Classification using HOST
A	Unsaturated and free draining	1,2,3,4,5,6,7,8,13,14
B	Low permeability (with or without field drains)	16,17,18,19,20,21,22,23,24,25
C	Partially saturated subsoil	9,10
D	Peat	11,12,15,26,27,28,29

3.3.1. Unsaturated and free draining boundary condition

In the unsaturated and free draining bottom boundary condition no restrictions to percolation into the unsaturated zone are assumed. Vertical transport into the unsaturated zone is the major pathway and percolation is calculated as a function of the unsaturated hydraulic conductivity of the subsoil (Section 3.2.7). Lateral throughflow is also possible, although this is a minor pathway (Figure 3.7).

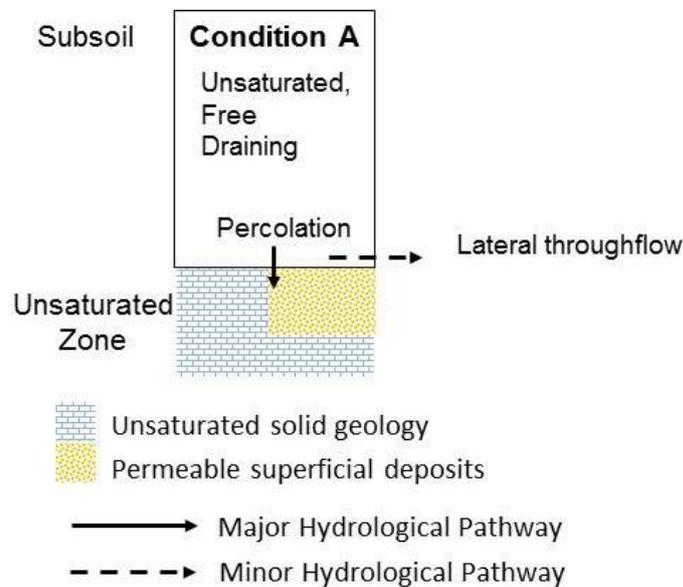


Figure 3.7. Schematic diagram of boundary condition A between the soil and the unsaturated zone.

3.3.2. Low permeability boundary condition

In the low permeability bottom boundary condition the principal pathway for water is laterally (Figure 3.8). When field drains are not likely to be present lateral throughflow is the dominant transport pathway from the subsoil (Carter, 2000b; Section 3.2.6). When field drains are present this is assumed to be the principal transport pathway to surface water (Section 3.2.5).

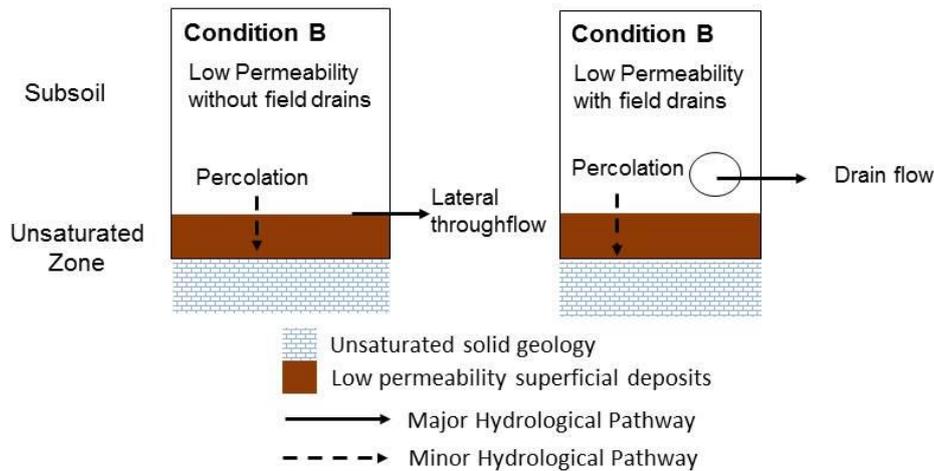


Figure 3.8. Schematic diagram of the interface between the subsoil and the unsaturated zone for the low permeability boundary condition, without drains (left) and with drains (right).

Vertical movement of water percolating into the low permeability material in the unsaturated zone is a minor hydrological pathway and therefore the hydraulic conductivity at the lower boundary has been restricted (Table 3.2). The low permeability boundary condition covers a wide range of HOST classes (Table 3.1), and some soils and unsaturated zone geologies will be more permeable than others. The Baseflow Index (BFI), defined as the proportion of stream flow which is represented by baseflow (Brown and Hollis, 1996), is used to categorise the soil-unsaturated zone boundary into slowly permeable and very slowly permeable (see Table 3.2). The more permeable the unsaturated zone geology, superficial deposits, or soils, the higher the BFI. A BFI > 0.35 is classed as slowly permeable and if BFI < 0.35 they are considered to be very slowly permeable (Table 3.2). The hydraulic conductivity values at the lower boundary assigned to slowly permeable and very slowly permeable soils are after Evans *et al.* (1999).

Table 3.2. Maximum saturated hydraulic conductivity values at the interface between the subsoil and unsaturated zone based on HOST class (after Evans *et al.*, 1999).

Bottom Boundary Condition	Hydraulic conductivity at the lower boundary (K_{BC}; mm day⁻¹)	HOST classes
A Unsaturated and free draining	Saturated hydraulic conductivity of the lowest soil horizon	1,2,3,4,5,6,7,8, 13,14
B Low permeability: slowly permeable (BFI >0.35)	8.6	16, 17,18,19,20
B Low permeability: very slowly permeable (BFI ≤0.35)	0.086	21,22,23,24,25,26,27
C Partially saturated	-	9,10,

3.3.3. Partially saturated subsoil boundary condition

The partially saturated bottom boundary condition (condition C) occurs in soils that have a permanent groundwater table within 2 m of the soil surface and refers to HOST classes 7-12 (page 27, Boorman *et al.*, 1995). However, Boorman *et al.* (1995) states that for HOST classes 7-8 the dominant flow pathway is vertical and have, therefore, been assigned to boundary condition A (unsaturated and free draining). HOST classes 11 and 12 are also not considered in this boundary condition as they relate to peaty soils (Section 3.4.4).

No percolation is assumed in this boundary condition and the pathway for water out of the soil is assumed to be entirely via field drains (Figure 3.9). Calculating drain flow when the subsoil is partially saturated (or completely saturated) is complex as the position of the water table will control whether the field drains are active and flowing. The position of the water table will vary due to vertical flow from the soil zone, lateral groundwater flow, and water exchange with

adjacent surface water bodies (Krause and Bronstert, 2007; Pirastru and Niedda, 2013). It is not possible to represent this in the model as each soil type is considered independently of its position within the catchment and its connectivity to other hydrological pathways that influence the position of the water table. Therefore, a pragmatic approach to modelling drain flow under these boundary conditions is employed, which assumes that the water table is always below the level of the installed field drain and that the subsoil store ends at the depth the drain is installed (Figure 3.9). The water deficit from saturation, used in the drain flow equation (Equation 3.20), therefore only considers the water within the subsoil store which is assumed to increase as a consequence of vertical drainage from the topsoil store above.

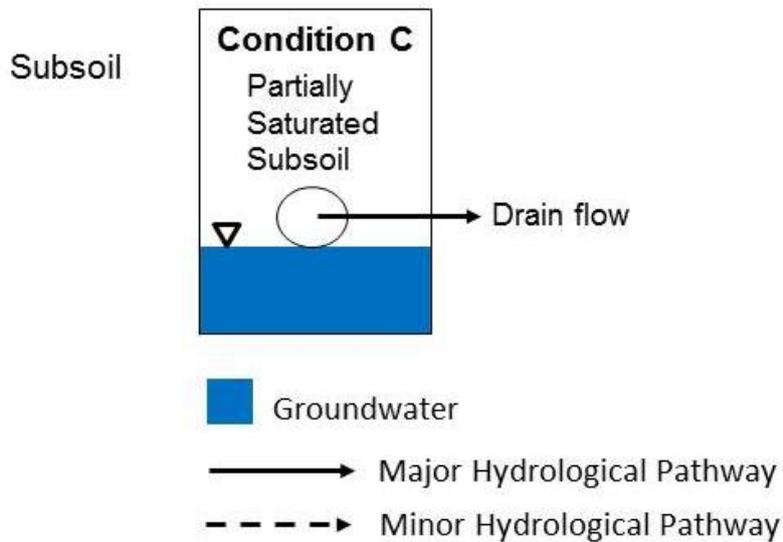


Figure 3.9. Schematic diagram of the interface between the subsoil and the unsaturated zone for the partially saturated subsoil boundary condition, with drains.

3.3.4. Peat soils

Peat soils can be an important soil in many catchments. In a study of runoff in blanket peat catchments in the northern Pennines in the United Kingdom by Holden and Burt (2003), most of the storm flow is produced from saturation excess overland flow.

To capture the hydrology of peat soils requires a small alteration of the assumptions previously made. Instead of assuming two soil stores (a topsoil and a subsoil), as previously, there is now only one. The hydrological pathways considered in the model for peat soils are saturation excess overland flow and lateral throughflow. If a soil is HOST class 11 then it is assumed that artificial drainage will be installed (Boorman *et al.*, 1995).

3.4. Description and conceptual model of pesticide fate and transport processes in the soil

Pesticide fate and transport is split into two stages in the soil:

- Pre-rainfall processes (Section 3.4.1 to 3.4.4) – i.e. pesticide fate and transport in the soil between application and a rainfall event and between rainfall events.
- Pesticide fate and transport during a rainfall event (Section 3.4.5 and 3.4.6).

At the heart of the pesticide fate model is a mass balance of the pesticide in the soil, which can be written as:

$$M_{soil(t)} = M_{soil(t-1)} + \Delta t \times [(k \times M_{soil(t)}) - J] \quad (3.23)$$

where $M_{soil(t)}$ is the mass of pesticide in the soil at time t ($\mu\text{g m}^{-2}$), k is first-order dissipation rate constant (day^{-1}) and J is the mass flux of pesticides out of the soil from the soil water phase ($\mu\text{g m}^{-2} \text{day}^{-1}$). This is solved via Euler's method of integration.

3.4.1. Pesticide application to the soil

On application the pesticide is assumed to immediately penetrate into the soil (Brown and Hollis, 1995). Once in the soil pesticides are subject to: first-order rate degradation, linear sorption and advective transport (Figure 3.10). The pesticide is assumed to be applied entirely to the soil surface as a uniform dose (e.g. via spraying). No account is taken of interception by the crop canopy, losses of mass due to application method (e.g. spray drift from machinery), interception losses from plants or volatilisation from the soil surface.

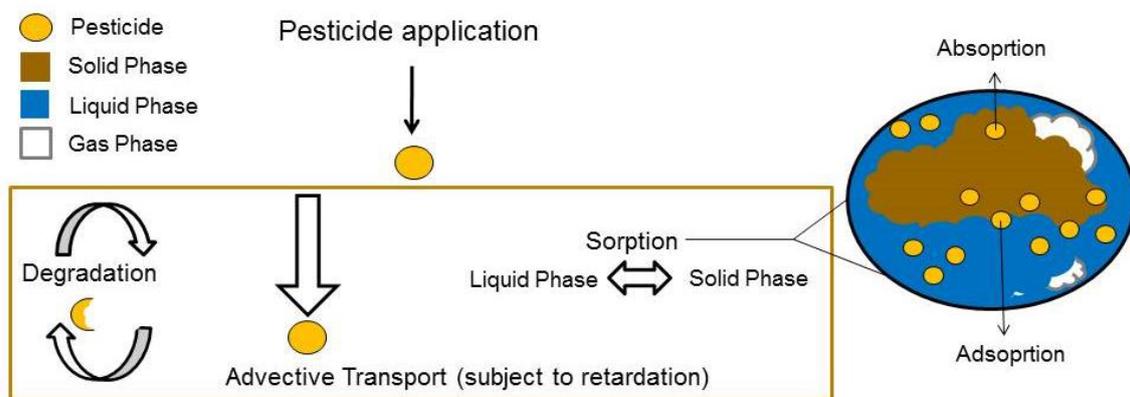


Figure 3.10. Schematic diagram for pesticide fate processes in the soil between application and a rainfall event.

Interception of pesticide by the crop canopy increases with growth stage (Jensen and Splind, 2003; van Beinum and Beulke, 2010). In the UK, agricultural practices are dominated by winter arable crops (Heathwaite *et al.*, 2005) and pesticide application, particularly for herbicides (which are the most frequently detected pesticides in DrWPAs, apart from metaldehyde; Pesticide Forum, 2011), is typically between October and January (see example product labels in Appendix E). Therefore, pesticide application typically occurs when leaf emergence slows and stops (HGCA, 2008) and interception losses by the crop canopy can be considered to be low. Losses from the soil due to plant root uptake have also been ignored as this is assumed to be a relatively small loss pathway for most pesticides (Chilton *et al.*, 1998).

The mass of pesticide lost due to spray drift depends on wind speed, sprayer type, sprayer forward speed, spray nozzle size and boom height (Ganzelmeier *et al.*, 1995; Carter, 2000b; Hewitt *et al.*, 2002). At the catchment scale this information is unknown and consequently spray drift as a loss pathway for pesticides is not accounted for in the model. However, it is recognised that, locally at least, spray drift can be an important exposure pathway (Crossland *et al.*, 1982; Ganzelmeier *et al.*, 1995; Shultz, 2001; Brown and van Beinum, 2009).

Volatilisation from the soil surface can represent a significant loss mechanism for compounds such as lindane (Rüdel, 1997; Bedos *et al.*, 2002), although most pesticides are effectively involatile. In the soil volatilisation, in terms of the fraction lost, is generally not a major route of loss for water-soluble pesticides (Burkhard and Guth, 1981; Bloomfield *et al.*, 2006b). Ten of twelve models in a study of 1-dimensional pesticide leaching models by Vanclooster *et al.* (2000) did not include volatilisation.

The process of pesticide deposition from rainfall and dry deposition is not included within the model. Dubus *et al.* (2000) comprehensively reviewed papers and published reports investigating the presence of pesticides in rainfall in Europe and showed that pesticide concentrations in rainfall were mostly below $0.1 \mu\text{g L}^{-1}$.

3.4.2. Degradation in the soil

Once in the soil, pesticides are subject to sorption and degradation which reduces their availability for transport to surface and ground water systems (Carter, 2000a; Walker *et al.*, 2001; Wauchope *et al.*, 2002; Bloomfield *et al.*, 2006b). Assuming first order kinetics, the dissipation rate constant is calculated as:

$$k = \frac{\ln 2}{DT_{50}} \quad (3.24)$$

It is assumed most pesticide degradation takes place in the soil water phase, as pesticides sorbed to the soil solid phase are assumed to be less accessible to micro-organisms (Guo *et al.*, 2000), a bulk DT_{50} is assumed in the model. This takes no account of partitioning between phases and relies solely on an empirically-derived rate constant. Degradation by micro-organisms (bio-degradation) is implicitly assumed to be the dominant process. Hence losses will be high particularly where microbial activity is high (Walker *et al.*, 2001; Bloomfield *et al.*, 2006b). Parent to metabolite transformation and subsequent fate and transport of metabolites is not currently included in the model.

3.4.3. Sorption in the soil

On application to the soil pesticides are assumed to undergo instantaneous partitioning between the soil water phase and the soil solid phase using a linear sorption isotherm.

$$M_{soilwater} = E \times f_d \quad (3.25)$$

where $M_{soilwater}$ is the mass of pesticide in the soil water phase ($\mu\text{g m}^{-2}$), E is the emission (on application) to the soil ($\mu\text{g m}^{-2}$), and f_d is the fraction of the chemical in the dissolved phase (-).

$$f_d = \frac{1}{1 + K_d \times \rho_b} \quad (3.26)$$

where K_d is the partition coefficient (L kg^{-1}) and ρ_b is the soil bulk density (g cm^{-3}).

$$K_d = K_{oc} \times f_{oc} \quad (3.27)$$

where f_{oc} is the mass fraction of organic carbon in the soil (-).

Sorption is the partitioning between the liquid and solid phases. The term sorption usually refers to both absorption (incorporation of a pesticide into the matrix of organic matter) and adsorption (the adhesion of pesticides to organic or mineral surfaces) as distinguishing between the two can be difficult (Hornsby *et al.*, 1996; Hillel, 1998; Warren *et al.*, 2003). The partitioning of a pesticide

between the gas phase and liquid phase is ignored because most pesticides used today have very low Henry's Law Coefficients (i.e. they do not readily partition into the gas phase).

3.4.4. Advective transport in the soil after application

The pesticide is assumed to diffuse uniformly through the 'interactive' water filled pore space. This is defined as the difference between the water content of the soil and 50 % of the water content at 1,500 kPa tension (i.e. permanent wilting point). The 'interactive' water filled pore space is assumed to be the fraction of the total water filled pore space that the pesticide will interact with (Brown and Hollis, 1996).

Pesticides in the soil water phase are assumed to be subject to advective transport in the soil matrix after application (Kördel *et al.*, 2008) within the 'interactive pore space', adapted from Brown and Hollis (1996). However, unlike Brown and Hollis (1996) the fixed hydraulic conductivity at 5 kPa tension is replaced by the unsaturated hydraulic conductivity based on the volumetric water content, calculated with van Genuchten (Equation 3.17). The depth to which pesticides can penetrate is restricted by retardation due to sorption to the surrounding soil matrix during transport.

$$Z_{(t)} = Z_{t-1} + \Delta t * \left(\frac{K(\theta_t)}{RF_{(t)}} \right) \quad (3.28)$$

where $Z_{(t)}$ is depth penetrated (mm) and $RF_{(t)}$ is a retardation factor (-) adapted from Brown and Hollis (1996):

$$RF_{(t)} = 1 + \left(\frac{(K_{oc} \times f_{oc}) \times \rho_b}{\theta_{int}} \right) \quad (3.29)$$

where θ_{int} is the interactive soil water content ($\text{cm}^3 \text{cm}^{-3}$).

The concentration of pesticide in the 'interactive' water-filled space is calculated from the mass of pesticide in the soil water phase and the volume of the 'interactive' water.

$$C_{int} = \frac{M_{soilwater}}{(\theta_{int} \times Z)} \quad (3.30)$$

where C_{int} is the concentration of pesticide in the interactive soil water phase ($\mu\text{g L}^{-1}$). Note that the water content in the soil depth containing pesticide ($Z_{(t)}$) is assumed to be the same as the overall water content in the topsoil store, which is calculated using the soil water balance (Section 3.2).

3.4.5. Pesticide displacement at the time of a rainfall event

The timing and intensity of rainfall events after application is a critical factor in determining pesticide mobility from the soil; for example, flow arising from rainfall following application typically produces events with the highest observed pesticide concentrations (Capel *et al.*, 2001; Leu *et al.*, 2004a). Two threshold conditions must be met in the model for pesticides to be transported from the soil: daily rainfall must be greater than a threshold, and a hydrological pathway (surface runoff, drain flow, lateral thorough flow or percolation) must be active.

When a rainfall event greater than the threshold occurs a fraction of the pesticide within the 'interactive' water-filled pore space is assumed to be displaced and transported via an active hydrological pathway to surface or groundwater (Figure 3.11). This fraction available for displacement is described as the 'mobile' water-filled pore space (i.e. the largest water filled pores). This is defined in terms of the difference between the volumetric water content at the time of the rainfall event (Equation 3.17 in Section 3.2.3) and the volumetric water content at 200 kPa tension (Brown and Hollis, 1996). Pesticides are assumed to be evenly distributed throughout the interactive soil water phase to depth $Z_{(t)}$.

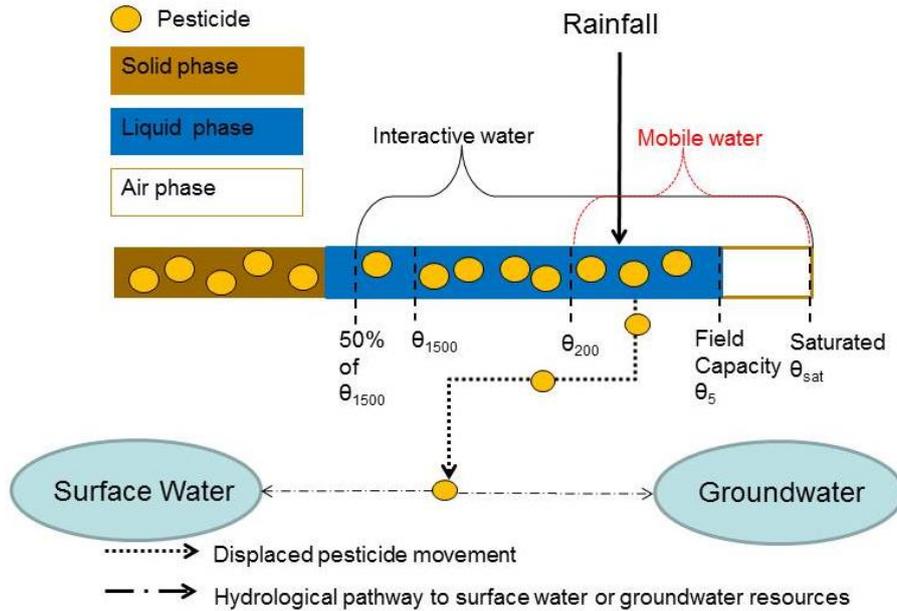


Figure 3.11. Schematic diagram of the key processes generating pesticide transport in the soil zone.

The volume of mobile water displaced is assumed to be a function of the ratio of the unsaturated hydraulic conductivity to the saturated hydraulic conductivity; such that a larger volume of water will be displaced the closer the soil is to saturation.

$$V_{mob} = \theta_{mob} \times Z_{(t)} \times \left(\frac{K(\theta_t)}{K_{sat}} \right) \quad (3.31)$$

where V_{mob} is the volume of displaced water from the most mobile pores ($\text{l m}^{-2} \text{ day}^{-1}$) and θ_{mob} is the mobile water content defined as difference between the water content of the soil and the water content at 200 kPa tension.

The mass flux generated by the displacement of V_{mob} is calculated as:

$$J = C_{int} \times V_{mob} \quad (3.32)$$

which is assumed to be transported to surface water and/or to the water table based on water flux dependant partitioning.

3.4.6. Pesticide transport from the soil at the time of a rainfall event

Pesticide transport from soil is intrinsically linked to hydrological response. The model builds on the important influence which soil properties have on the translation of rainfall into runoff and, hence, the transfer of pesticides out of the soil profile. The principal hydrological pathways from the soil profile, identified as entry routes for pesticides to water bodies, are: field drains, surface runoff, lateral throughflow and percolation into the unsaturated zone (Foster, 1998; Heppell *et al.*, 2004a; Holvoet *et al.*, 2007; Brown and van Beinum, 2009). The importance of these pathways will vary according to several key drivers including: climate, soil type, antecedent soil water content, topography, geology, land management, application date and rate, and pesticide physico-chemical properties (Brown *et al.*, 1995; Blanchard and Lerch, 2000; Carter, 2000a; Leu *et al.*, 2004a; Bloomfield *et al.*, 2006b). These drivers are often inter-related and can vary spatially and temporally (Capel *et al.*, 2001; Leu *et al.*, 2004b).

The explicit pathway of pesticide transport through the soil zone during a rainfall event (i.e. via macropores or through the bulk matrix) is not explicitly represented because it is a complex process and hence difficult to represent using a few readily available parameters at a daily time-step (a requirement of the model developed in this thesis). There is, however, an implicit assumption of the pesticide mass flux bypassing the soil matrix when a rainfall event occurs which is greater than a certain magnitude. Pesticide transport via macropores, where present in the soil, can promote preferential flow to deeper layers or connect to field drains potentially rapidly transporting pesticides to surface water (Harris *et al.*, 1994; Jones *et al.*, 2000; Peterson *et al.*, 2002; Brown and van Beinum, 2009; Tediosi *et al.*, 2012; Tediosi *et al.*, 2013).

Several field studies (e.g. Johnson *et al.*, 1995; Uusitalo *et al.*, 2001; Shipitalo *et al.*, 2004; Tediosi *et al.*, 2012) have suggested that a large proportion of water in field drains originates from the topsoil. In drained clay soils a good connectivity can exist between the soil surface and subsurface field drains due to a network of macropores (Harris and Catt, 1999; Heppell *et al.*, 2000),

thereby providing a route for rapid pesticide transport from the soil surface layers to field drains (Harris and Catt, 1999; Shipitalo *et al.*, 2004; Tediosi *et al.*, 2012). In a study on an alluvial aquifer in Switzerland, Mermoud and Meiwirth, (2004) found that the first significant rainfall event would quickly transport pesticides through the soil and unsaturated zone to groundwater. The transportation of pesticides through the unsaturated zone is covered in detail in Section 5.2.

Any displaced pesticide is assumed to be transported, during the current time-step, directly to the surface water catchment outlet and/or to the top of the unsaturated zone for transportation to the water table (Figure 3.11) depending on the water flux boundary conditions at the interface between the soil and the unsaturated zone (Section 3.3). It should be noted that the pathways taken by water and solutes out of the soil profile are not explicit in the model. It is therefore assumed implicitly that pesticide will be transported by an active hydrological pathway: field drains, lateral throughflow, surface runoff or percolation to the top of the unsaturated zone (further explanation of the hydrological pathways mentioned above is provided in Sections 3.2.3 – 3.2.7).

During transportation to the catchment outlet or to the top of the water table it is assumed there will be relatively little transformation or sorption. Of course, in reality, pesticide travelling down macropores and in overland flow could be exchanged with the soil matrix and may be subject to degradation en route (as described in more physically-explicit models such as MACRO: Larsbo and Jarvis, 2003). However, the fact that a relatively simple description of displacement, similar to the model described here, can represent observed pesticide concentrations in field drains (Tediosi *et al.*, 2012) suggests that the limiting step in the leaching processes is the process description of displacement itself (i.e. sorption and degradation along transport pathways are limited), at least where field drains dominate the hydrological response.

Pesticides can be transported in either the dissolved phase or sorbed to eroded soil particles or soil colloids (Liess *et al.*, 1999; Carter, 2000a; Holvoet *et al.*, 2007). In the model only pesticides in solution are considered. However, for

pesticides classified as strongly sorbing, $K_{OC} > 1,000 \text{ L kg}^{-1}$ transport of eroding soil particles is potentially a significant mechanism (Wu *et al.*, 2004), who found that for pesticides with a very high K_{OC} , almost 50 % of the pesticides in the water samples were particle bound. Transport pathways for pesticide sorbed to soil particles include surface runoff (Syversen and Bechmann, 2004) and field drains (Williams *et al.*, 1996).

In the model any displaced pesticide is assumed to be transported directly to the surface water catchment outlet and/or to the top of the unsaturated zone for transportation to the water table (Figure 3.11) depending on the water flux boundary conditions. The pesticide mass flux to surface water (J_{sw} ; $\mu\text{g m}^{-2} \text{ day}^{-1}$) is calculated as:

$$J_{sw} = J \times \frac{q_{quick}}{q_{tot}} \quad (3.33)$$

where q_{quick} is the water flux from the hydrologically active pathways that will reach surface water resources (this is the sum of surface runoff, lateral throughflow and drain flow; mm day^{-1}) and q_{tot} is the total flux of water displaced from the soil (this includes the q_{quick} and the water percolating to the top of the unsaturated zone; mm day^{-1}).

The pesticide mass flux entering the top of the unsaturated zone (J_{uz} ; $\mu\text{g m}^{-2} \text{ day}^{-1}$) is calculated as:

$$J_{uz} = J \times \frac{qP}{qtot} \quad (3.34)$$

Between subsequent rainfall events there is assumed to be no transport of pesticides out of the soil profile and the remaining mass of pesticide is assumed to undergo further sorption, degradation and internal redistribution as described in Sections 3.3.2, 3.3.3 and 3.3.4.

3.5. Pesticide fate and transport at the catchment scale

The catchment is treated as “semi-lumped” and divided into soil type and land use combinations. Within the model each pesticide is assigned to one or more land uses and the mass flux at the catchment outlet is weighted by the mass flux contribution for each soil type and land use combination within the catchment. This approach allows for variation in land use and pesticide use combinations in a catchment.

The pesticide reaching the catchment outlet will be subject to dilution from water originating from soil type and land use combinations where pesticides have not been applied, as well as dilution from baseflow. The concentration at the catchment outlet is calculated as:

$$C_{outlet} = \frac{(J_{outlet(t)} \times A)}{Q_t} \quad (3.35)$$

where C_{outlet} is the predicted concentration of a pesticide at the surface water catchment outlet ($\mu\text{g L}^{-1}$), $J_{outlet(t)}$ is the weighted average mass flux of pesticide from each soil type and crop combination ($\mu\text{g m}^{-2} \text{day}^{-1}$), A is the total catchment area (m^2) and Q is the total flow (l day^{-1}).

$$J_{outlet(t)} = \sum_{i=1}^N J_{i(t)} \times W_i \quad (3.36)$$

where $J_{i(t)}$ is the pesticide flux at time t from land use and soil combination i ($\mu\text{g m}^{-2} \text{day}^{-1}$), W_i is the fraction of the total catchment area which is under land use and soil combination i and N is the total number of land use and soil combinations in the catchment regardless of whether they receive the pesticide under consideration or whether there is any leaching.

The total flow in the river is calculated from the baseflow from a groundwater store (Section 3.5.1) and the weighted contribution each soil type and crop combination makes to surface runoff, discharge from field drains and lateral throughflow (collectively termed here as quick flow):

$$Q = Q_{quick} + Q_{baseflow} \quad (3.37)$$

where $Q_{baseflow}$ is the baseflow from the groundwater (l day⁻¹).

$$Q_{quick} = A \times \sum_{i=1}^N q_{quick,i} \times W_i \quad (3.38)$$

where Q_{quick} is the quick flow from each land use and crop combination (l day⁻¹).

$$q_{quick,i} = qSF_i + q_{drain,i} + qL_{top,i} + qL_{sub,i} \quad (3.39)$$

where qSF is surface runoff (i.e. the sum of infiltration excess overland flow and saturation excess overland flow; mm day⁻¹).

In-stream processes such as: sorption to sediment, degradation, volatilisation and plant uptake can affect the fate of pesticides in rivers (Petit *et al.*, 1995; Warren *et al.*, 2003; Holvoet *et al.*, 2007). However, the effect these processes have on concentrations at the catchment outlet is not considered in the model.

3.5.1. Baseflow

Baseflow is calculated assuming the percolation from the subsoil store, weighted by soil type and crop combination in the catchment, augments a groundwater store which is depleted by a store-dependant baseflow:

$$GW_t = GW_{t-1} + \Delta t \times (qP - qBF) \quad (3.40)$$

where GW_t is the water in the groundwater store (mm) and qBF is the baseflow leaving the groundwater store (mm day⁻¹) which is described using an exponential model in Equation 3.41.

$$qBF = C_g \times e^{(GW_t/BF)} \quad (3.41)$$

where C_g is a groundwater constant (mm day⁻¹), and BF is a baseflow constant that controls the shape of the recession (-). C_g and BF are both fitted catchment parameters.

The groundwater store is assumed to have the same catchment boundary as the surface water catchment.

$$Q_{baseflow} = A \times qBF \quad (3.42)$$

3.6. Edge-of-field application of the pesticide fate and transport model

To assess the performance of the pesticide fate and transport model in representing the key processes that influence pesticide transfer from agricultural fields to surface water resources the model developed in this chapter has been applied to a small headwater sub-catchment in the upper Cherwell. In this catchment there is detailed input information such as active ingredients applied, rate of application and date of application, as well as drain flow and pesticide concentration monitoring data at the edge-of-field. For a more detailed explanation of the experimental methodology and data collection see Tediosi *et al.* (2012, 2013).

3.6.1. Introduction to the upper Cherwell catchment

The upper Cherwell catchment is a small head water sub-catchment (area 15.5 ha) of the upper reaches of the river Cherwell. The sub-catchment is comprised of an artificially drained arable field (8.6 ha) and an undrained interfluvium (6.9 ha). The arable field is primarily underlain by Denchworth series soil, a heavy clay which typically requires under-draining. On the interfluvium the soils are lighter and made up of soils of the Banbury Association which overlie the Northampton Sands. The flows at the drain outlet also include a baseflow component from the Northampton Sands, with the recharge area to the aquifer principally calculated as the 6.9 ha of the interfluvium (Tediosi *et al.*, 2013). The arable field was cropped with oilseed rape in 2009/10 and two pesticides were applied, propyzamide on 7 November 2009 at a rate of 800 g ha⁻¹ and

carbetamide on the 15 February 2010 at a rate of 2,100 g ha⁻¹ (Tediosi *et al.*, 2012).

3.6.2. Set-up of the pesticide fate and transport model

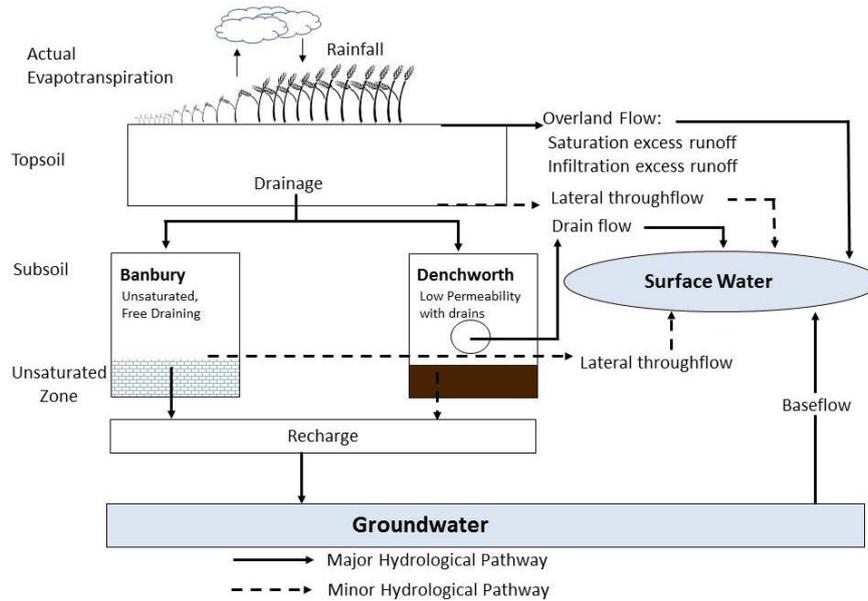


Figure 3.12. Conceptual diagram the upper Cherwell sub-catchment and the key hydrological pathways to surface water and groundwater resources.

In the upper Cherwell sub-catchment only the arable field receives pesticides. The groundwater flow generated from the grass field is assumed to have no pesticide associated with it and will dilute the pesticide concentration at the ditch outlet.

Reference evapotranspiration was calculated with the Hargreaves equation (Tediosi *et al.*, 2012), hourly rainfall was measured on site. The pesticide fate and transport model has been executed at an hourly time step. The initial soil water content for the topsoil store in the Denchworth arable field was set at the average observed value for the 6th October, 0.4 cm³/cm³. The initial water content was set to field capacity for the sub-soil store in the Denchworth soil type and also in the topsoil store and sub-soil store in the grass field (Banbury soil type). For more a detailed explanation on the selection of input data (i.e. soil

type, land use and crop data) see Section 4.3. The main chemical-specific parameters required were DT_{50} and K_{OC} , 56 days and 840 L kg⁻¹ for propyzamide and 8 days and 89 L kg⁻¹ for carbetamide.

The pesticide fate model is split into a calibration period (06/10/2009 – 27/12/2009) and a validation period (11/02/2010 – 03/03/2010). The parameters that required calibration were the drain flow parameters (C_m and C_d) and the baseflow parameters (C_g and BF). This was done with a one-at-a-time step-wise approach, see Section 4.5.

3.6.3. Upper Cherwell results and discussion

The overall performance of the pesticide fate and transport model in predicting drain flow in the upper Cherwell is good (Table 3.3 and Figure 3.13b). The timing and magnitude of the soil water balance for drain flow in the calibration period is good with only a slight over-prediction of the first two peak events, (Figure 3.13b). In the validation period the model does not reproduce the measured drain flow as well, particularly on the 25th February (Figure 3.14b) where a large drain flow event can be seen in the measured data. There is also a high percent bias where the model is underestimating drain flow. This could be due to an under-estimation in the rainfall at the rain gauge (proposed by Tediosi *et al.*, 2013 to have occurred in this period) or as a result of snowmelt in the catchment (January 2009 saw snow cover much of the UK) influencing the drain flow volume (Tediosi *et al.*, 2013).

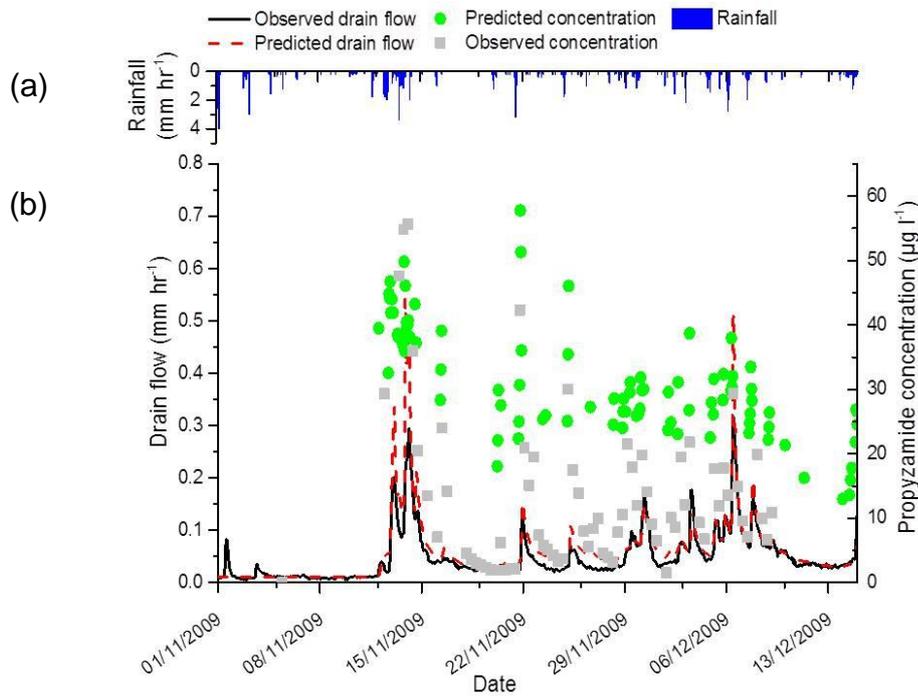


Figure 3.13. Rainfall in the upper Cherwell (a) and observed and predicted drain flow with observed and predicted propyzamide concentration in drain flow in the upper Cherwell during the calibration period (b).

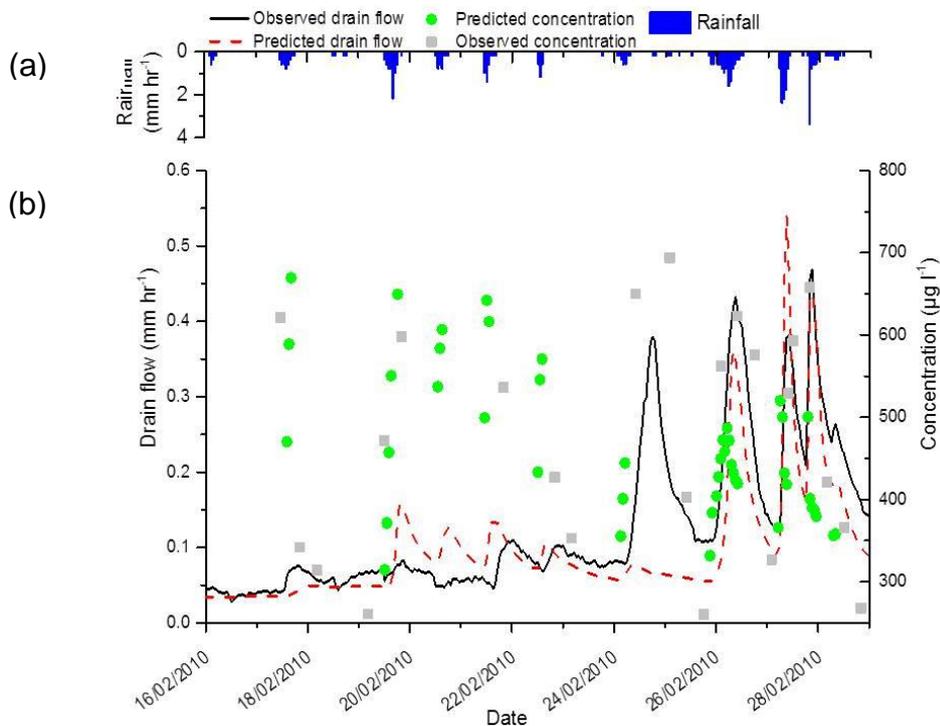


Figure 3.14. Rainfall in the upper Cherwell (a) and observed and predicted drain flow with observed and predicted carbetamide concentration in drain flow in the upper Cherwell during the validation period (b).

MACRO (Larsbo and Jarvis, 2003) a one-dimensional dual permeability solute transport model, explicitly accounting for macropore flow in the soil, was applied to the upper Cherwell data by Tediosi *et al.* (2012, 2013). The results produced by the MACRO model, and results from running the MACRO model with a separate model developed by Tediosi *et al.*, (2013) to account for contribution from the Northampton Sands, are presented in Table 3.3. The pesticide fate and transport model developed in this chapter performs better than the MACRO only model, particularly in the validation period and is similar to the modified MACRO model when predicting drain flow in the upper Cherwell (Table 3.3).

Table 3.3. Model performance statistics for predicted drain flow in the upper Cherwell catchment in the calibration period and validation period for the pesticide fate and transport model, MACRO model and MACRO + contribution from Northampton sands.

	Pesticide fate and transport model		MACRO	MACRO + Northampton Sands
	NSE	PBIAS (%)	NSE	NSE
Calibration period	0.66	12.6	0.45	0.77
Validation period	0.61	-20.5	0.02	0.56

In the upper Cherwell the prediction of timing and magnitude of peak propyzamide concentrations (Figure 3.13b) and peak carbetamide concentrations (Figure 3.14b) in comparison with the measured data is fairly reasonable. However, the recessions of concentrations for both pesticides are not captured. This is because without a rainfall event there is no mass of pesticide assumed to be displaced from the soil in the model.

Exploring the predictions of peak concentrations further for propyzamide the model tends to over-predict the peak concentrations in comparison with the measured data towards the end of November and into December (Figure 3.13b). For carbetamide the model tends to under-predict the peak concentrations from the 26th February (Figure 3.14b). This could be as a result of the K_{OC} and DT_{50} values chosen. The rate of degradation varies with site specific conditions such as; soil type, pH, nutrient status, organic matter content, soil temperature and soil moisture content (Walker *et al.*, 2001; Spitz and Moreno, 2006; Kah *et al.*, 2007).

With respect to carbetamide the cold temperatures leading up to the pesticide application on the 15th February could have caused the degradation rate to be slower than predicted (the model assumed a DT_{50} of 8 days). Sorption can also be affected by soil properties such as the quantity of organic matter and clay, water content, temperature and pH (Helling *et al.*, 1971; Spark and Swift, 2002; Boivin *et al.*, 2005; Kah and Brown, 2007). The more strongly a pesticide is sorbed to the solid soil phase the lower the likelihood of leaching (Hornsby *et al.*, 1996; Carter, 2000a). However, chemicals that are sorbed are often assumed to be less accessible to micro-organisms, particularly if sorbed into un-accessible areas, and therefore degradation could be limited (Guo *et al.*, 2000; Arias-Estévez *et al.*, 2008).

The soil water balance model, applied in the upper Cherwell catchment, predicts drain flow well. We can therefore be confident that the model is capturing the key hydrological process in this catchment. Artificially drained soils, particularly in agricultural catchments, are commonplace and play an important role even in catchments which are not heavily drained (Section 4.6).

3.7. Conclusions

This chapter has outlined the development of a broad-scale, process-based, conceptual model for pesticide fate and transport in the soil within an integrated hydrological framework describing the key hydrological pathways to surface water and to top of the unsaturated zone. The model is divided into two components: a soil water balance model to predict the hydrological pathways to surface waters and a pesticide fate model. Boundary conditions at the base of the subsoil and the top of the unsaturated zone are especially important. Soils are assigned to one of three broad, but physically realistic, boundary conditions (unsaturated and free draining, low permeability with and without drains, and partially saturated subsoil) to determine whether the water flux and pesticide mass flux are transported to surface water or to the top of the unsaturated zone.

The pesticide fate model has a pre-rainfall event component, in which first-order degradation, linear sorption and advective transport (subject to retardation) are assumed. When a rainfall event takes place, pesticide in the most mobile pore water is displaced out into a (non-explicit) hydrologically active pathway. This pathway can lead to surface water and/or to the top of the unsaturated zone, depending on antecedent conditions, soil properties and hydrogeological settings.

The model has been applied to a small headwater sub-catchment in the upper Cherwell the model simulates peak pesticide concentrations that are a good match with measured data, suggesting that pesticide transport pathways are being well simulated. The model also performs well in comparison with the mechanistic MACRO model.

Chapter 4. Calibration and Evaluation of the Pesticide Fate and Transport Model at the Catchment Scale

4.1. Introduction

The aim of this chapter is to present the calibration and validation of the hydrological model (soil water balance) and evaluation of the pesticide fate model, both described in Chapter 3. The models have been applied to eight pesticides in five surface water case-study catchments in order to demonstrate that a broad-scale, process-based approach can generate acceptable reproductions of both hydrological response and pesticide concentrations at the catchment outlet.

This chapter is organised as follows:

- Section 4.2 outlines the description of five case study catchments.
- Section 4.3 provides a description of input data.
- Section 4.4 details the methodology of the calibration, validation and evaluation procedures used.
- Section 4.5 presents results for the performance of the hydrological model in the five case-study catchments, over 3 years, and provides a discussion with respect to model performance across all the catchments. In addition, the results for model performance against measured concentrations for eight pesticides in five catchments are also presented.
- Section 4.6 details the contribution of different pesticide transport pathways to the catchment outlet in two contrasting catchments, for two pesticides and three land uses.
- Section 4.7 provides conclusions to the chapter.

4.2. Case-study catchments

The model was applied to five case-study surface water catchments in England and Wales: the Lugg, the Teme, the Waveney, the Wensum and the Yare (Figure 4.1). These catchments include a range of size, climate, runoff, land use, soil type, and geology (Appendix B). In addition, regular pesticide monitoring as part of Catchment Sensitive Farming (CSF) has taken place in these catchments (CSF Evidence Team, 2011).

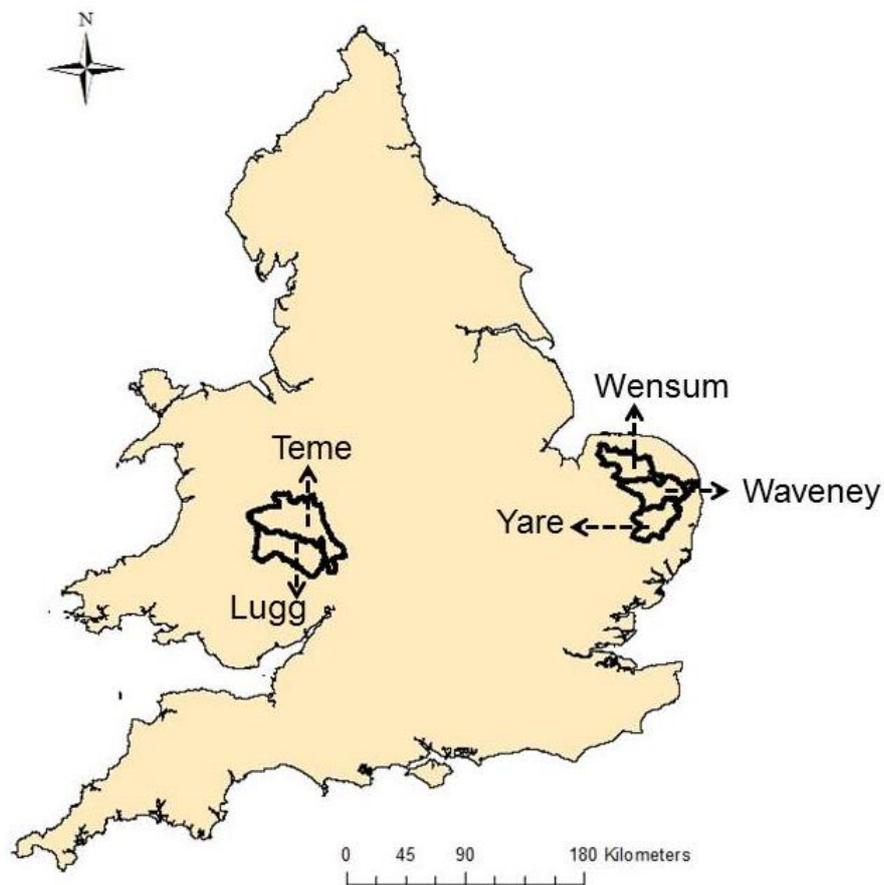


Figure 4.1. Location of case-study catchments.

4.2.1. River Lugg at Lugwardine

The river Lugg catchment (area 885 km² at Lugwardine gauging station) is situated in the West Midlands (Figure 4.1). Mean annual rainfall is approximately 812 mm year⁻¹ (1961 – 1990) and mean annual flow is approximately 390 mm year⁻¹ (1966 – 2011; CEH, 2012a). The Environment Agency monitoring point for pesticides is at Mordiford Bridge (Figure 4.2), the catchment area at this point is larger than at the gauging station (1,077 km²). The summary statistics for both the catchments are presented in Table 4.1.

The main consequence of the pesticide monitoring catchment being larger than the gauging station catchment is that a slightly greater proportion of soil in the catchment is assumed to require artificial drains. In addition, a slightly greater area of the catchment is assumed to be under arable agriculture (Table 4.1), reflecting more arable land in the lower reaches.

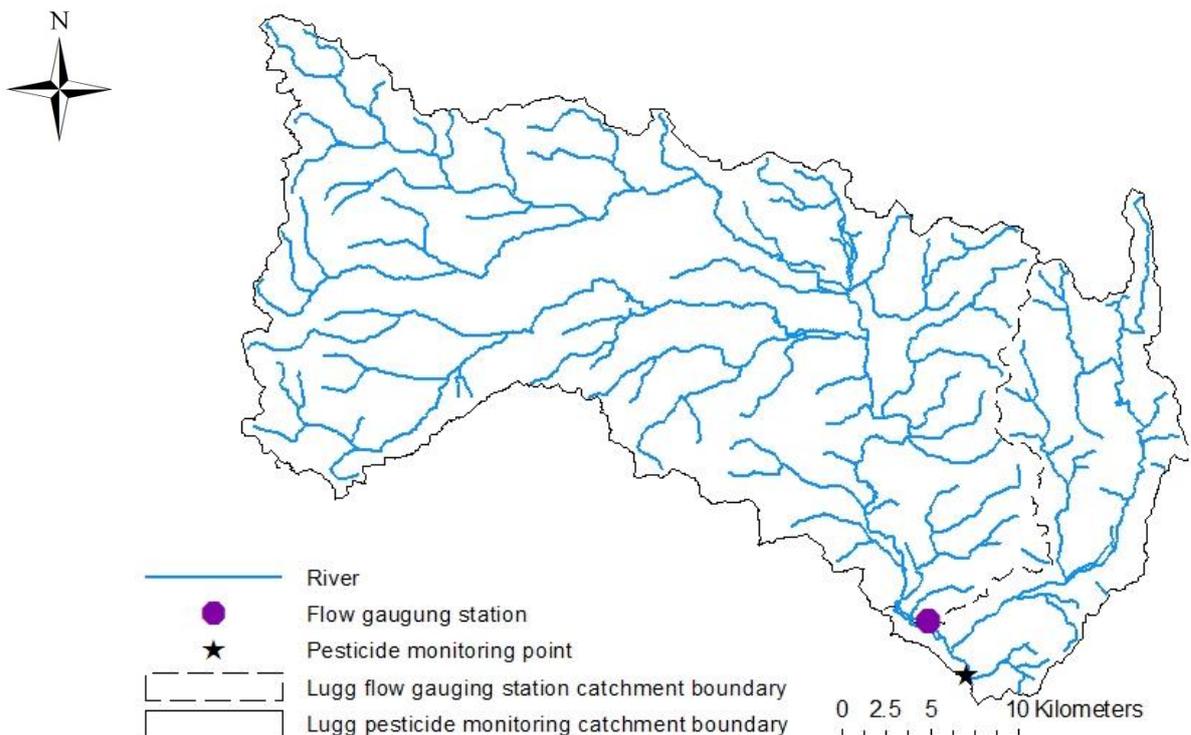


Figure 4.2. Map of the Lugg catchment for the gauging station (circle) and the pesticide monitoring point (star).

Table 4.1. Summary statistics for the Lugg catchment at Lugwardine gauging station and the pesticide monitoring point at Mordiford Bridge.

	Flow gauging catchment	Pesticide monitoring catchment
Catchment area (km²)	885	1,077
Soil (%)*		
Boundary condition A	45 %	39 %
Boundary condition B (field drains)	29 %	38 %
Boundary condition B (no field drains)	18 %	16 %
Boundary condition C	8 %	7 %
Land use (%)#		
Arable	43 %	50 %
Grassland	47 %	41 %
Urban	1 %	1 %
Other	9 %	8%

* The National Soil Map is used to identify the soil type, and therefore HOST class, in each catchment. See Section 3.3 for classification of HOST classes to boundary conditions between the subsoil and unsaturated zone.

See Section 4.3.4 for the creation of these broad land use categories from CORINE Land Cover 2000 (CLC 2000).

4.2.2. River Teme at Knightsford Bridge

The river Teme catchment (area 1,484 km² at Knightsford Bridge) is a tributary to the River Severn and is situated in the West Midlands and Wales (Figure 4.1). Mean annual rainfall is approximately 818 mm year⁻¹ (1961 – 1990) and mean annual flow is approximately 380 mm year⁻¹ (1970-2010) (CEH, 2012b). The Environment Agency monitoring point for pesticides is at Powick (Figure 4.3). The catchment area at this point is, again, larger than at the gauging station (1,653 km²). The summary statistics for both the catchments are

presented in Table 4.2. In the pesticide monitoring catchment the extra area added increases both the proportion of the soils in the catchment assumed to require artificial field drains and the area of the catchment under arable agriculture (Table 4.2). This, again, reflects that the lower reaches of the catchment contains more arable land in comparison with the upper reaches.

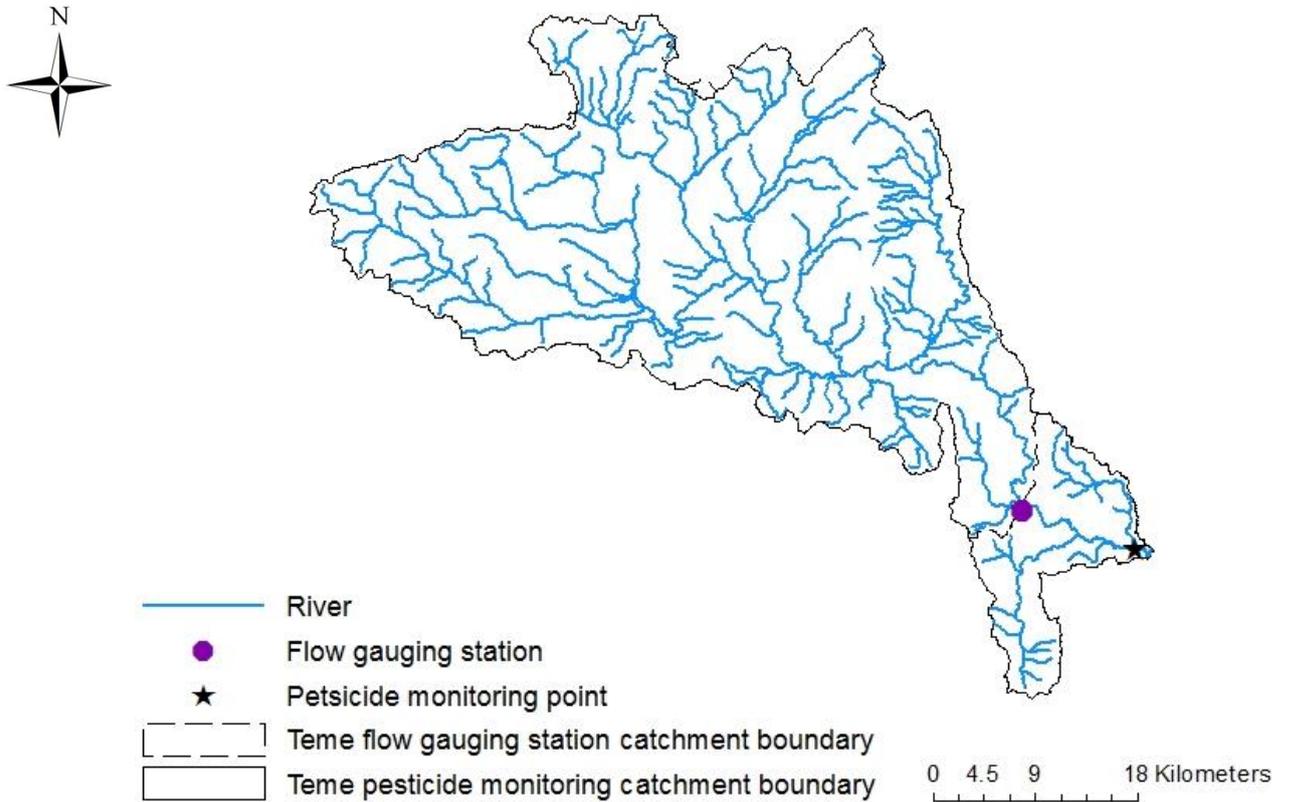


Figure 4.3. Map of the Teme catchment for the gauging station and the pesticide monitoring point.

Table 4.2. Summary statistics for the Teme catchment at Knightsford Bridge gauging station and the pesticide monitoring point at Powick.

	Flow gauging catchment	Pesticide monitoring catchment
Catchment area (km²)	1,484	1,653
Soil (%)		
Boundary condition A	43 %	40 %
Boundary condition B (field drains)	35 %	39 %
Boundary condition B (no field drains)	20 %	19 %
Boundary condition C	3 %	3 %
Land use (%)		
Arable	43 %	46 %
Grassland	47 %	45 %
Urban	1 %	1 %
Other	9 %	8 %

4.2.3. River Waveney at Needham Mill

The river Waveney catchment at Needham Mill (area 376 km²) is situated in the East Anglia (Figure 4.1). Mean annual rainfall is approximately 594 mm year⁻¹ (1961 – 1990) and mean annual flow is 170 mm year⁻¹ (1963-2010) (CEH, 2012c). The Environment Agency monitoring point for pesticides is at Ellingham Mill (Figure 4.4). The catchment area at this point is larger than at the gauging station (670 km²). The summary statistics for both catchments are presented in Table 4.3. In the pesticide monitoring catchment the extra area added increases the proportion of grassland in the catchment (Table 4.3). In the Waveney catchment there are widespread superficial till deposits present (Appendix B) which will influence recharge (Ander *et al.*, 2006).

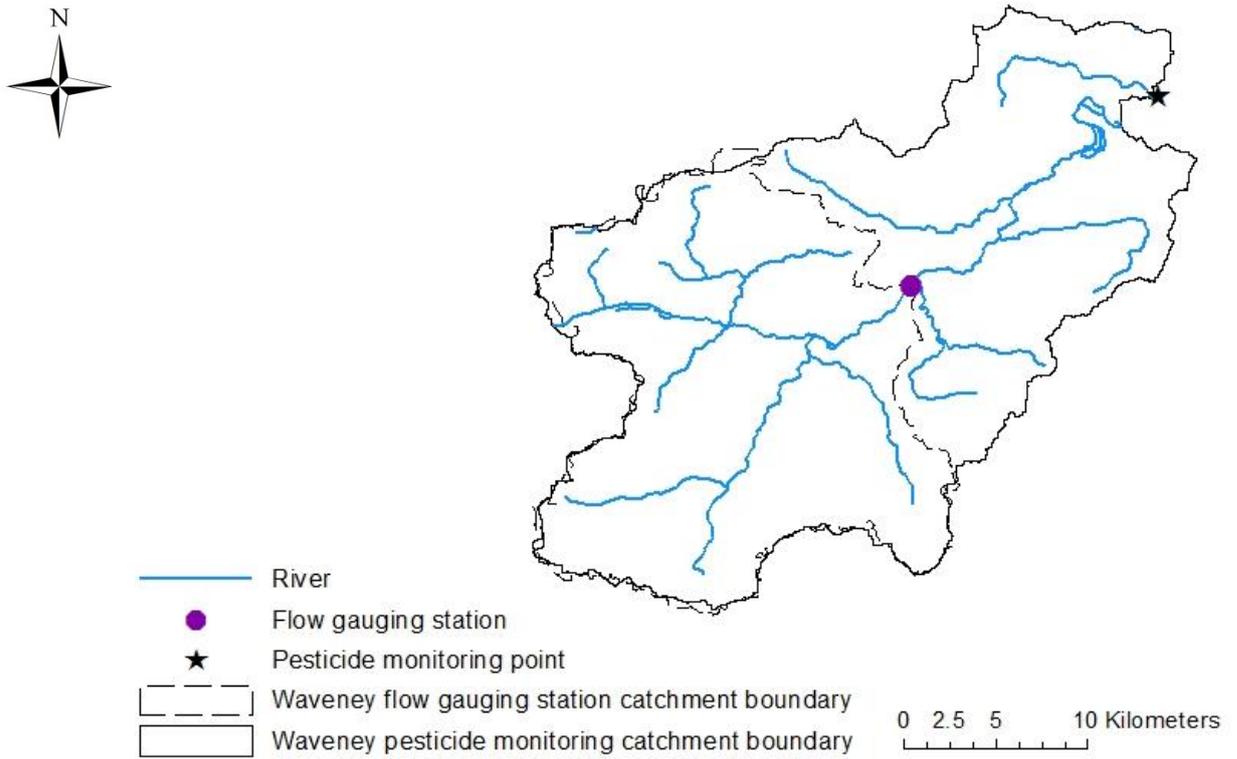


Figure 4.4. Map of the Waveney catchment for the gauging station and the pesticide monitoring point.

Table 4.3. Summary statistics for the Waveney catchment at Needham Mill gauging station and the pesticide monitoring point at Ellingham Mill.

	Flow gauging catchment	Pesticide monitoring catchment
Catchment area (km²)	376	670
Soil (%)		
Boundary condition A	10 %	10 %
Boundary condition B (field drains)	90 %	90 %
Boundary condition B (no field drains)	n/a	n/a
Boundary condition C	n/a	n/a
Land use (%)		
Arable	93 %	91 %
Grassland	4 %	6 %
Urban	2 %	2 %
Other	1%	0.5 %

4.2.4. River Wensum at Costessey Mill

The river Wensum catchment (area 560 km² at Costessey Mill) is situated in North Norfolk (Figure 4.1). Mean annual rainfall is approximately 672 mm year⁻¹ (1960 – 1990) and mean annual flow is approximately 170 mm year⁻¹ (1960 – 2010) (CEH, 2012d). The Environment Agency monitoring point for pesticides is at Sweet Briar Road Bridge (Figure 4.5). The catchment area at this point is larger than at the gauging station (699 km²). The summary statistics for both the catchments are presented in Table 4.4. In the pesticide monitoring catchment the extra area added increases slightly the proportion of grassland in the catchment and the fraction of urban area present (Table 4.4). The Wensum is predominantly underlain by chalk but overlain by superficial till deposits (Appendix B).

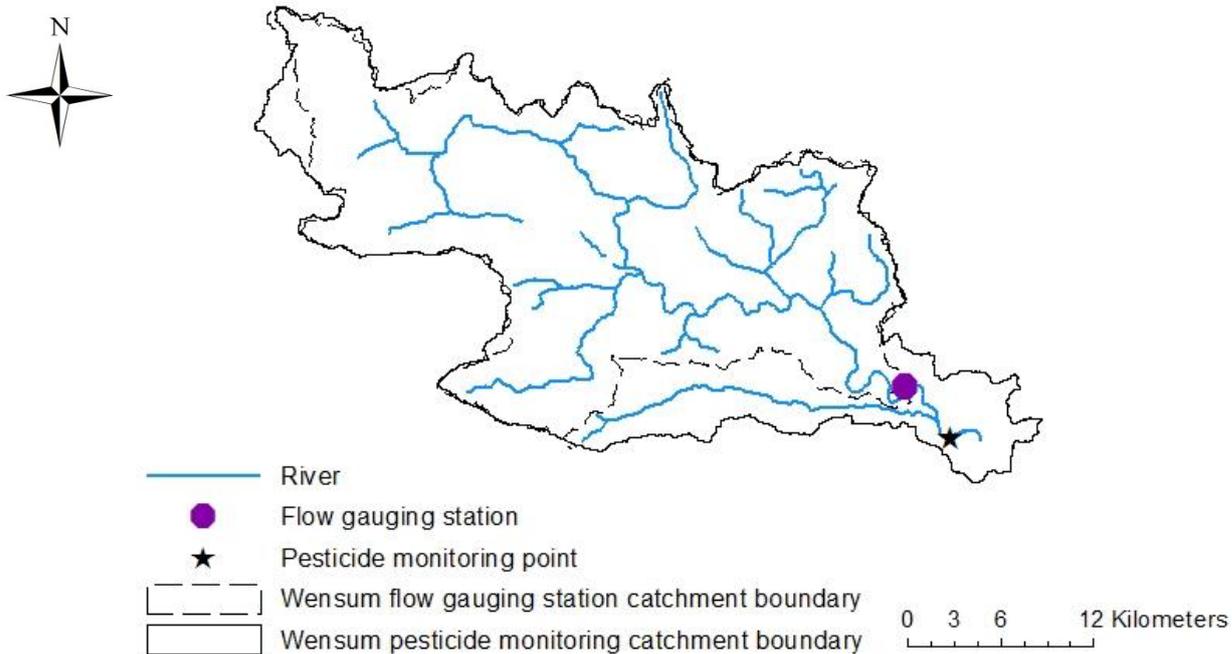


Figure 4.5. Map of the Wensum catchment for the gauging station and the pesticide monitoring point.

Table 4.4. Summary statistics for the Wensum catchment at Costessey Mill gauging station and the pesticide monitoring point at Sweet Briar Road Bridge.

	Flow gauging catchment	Pesticide monitoring catchment
Catchment area (km²)	560	672
Soil (%)		
Boundary condition A	37 %	40 %
Boundary condition B (field drains)	54 %	52 %
Boundary condition B (no field drains)	n/a	n/a
Boundary condition C	9 %	8 %
Land use (%)		
Arable	88 %	83 %
Grassland	4 %	5 %
Urban	3 %	8 %
Other	5 %	4 %

4.2.5. River Yare at Colney

The river Yare catchment (area 229 km² at Colney) is situated in Norfolk (Figure 4.1). Mean annual rainfall is approximately 635 mm year⁻¹ (1960 – 1990) and mean annual flow is approximately 190 mm year⁻¹ (1959 – 2010) (CEH, 2012e). The Environment Agency monitoring point for pesticides is at Trowse Mill (Figure 4.6). The catchment area at this point is larger than at the gauging station (479 km²). The summary statistics for both catchments are presented in Table 4.5. In the pesticide monitoring catchment the extra area added decreases the proportion of arable agriculture in the catchment and doubles the fraction of grassland (Table 4.5). The catchments is predominantly underlain by

Chalk overlain by superficial till deposits and glaciofluvial sand and gravel superficial deposits (Appendix B).

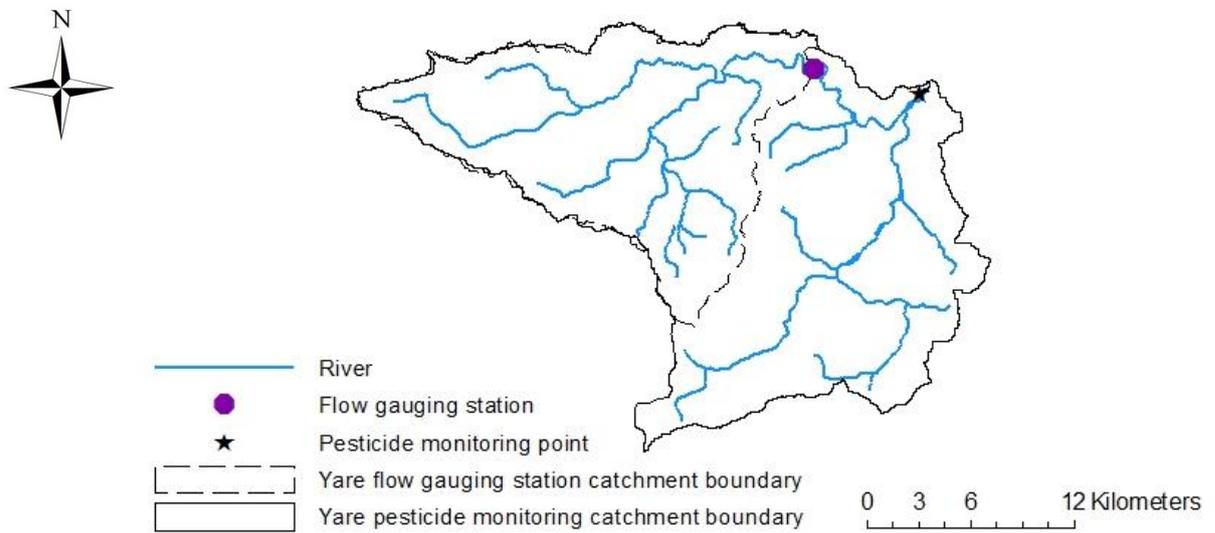


Figure 4.6. Map of the Yare catchment for the gauging station and the pesticide monitoring point.

Table 4.5. Summary statistics for the Yare catchment at Colney gauging station and the pesticide monitoring point at Trowse Mill.

	Flow gauging catchment	Pesticide monitoring catchment
Catchment area (km²)	229	479
Soil (%)		
Boundary condition A	9 %	8 %
Boundary condition B (field drains)	87 %	88 %
Boundary condition B (no field drains)	n/a	n/a
Boundary condition C	3 %	4 %
Land use (%)		
Arable	94 %	90 %
Grassland	2 %	4 %
Urban	4 %	4 %
Other	1 %	1 %

4.2.6. Measured Data

In each catchment daily river flow was available from 1989 – 2010 (provided by the National River Flow Archive; NRFA) and pesticide concentrations, taken as grab samples, collected approximately once every two weeks from 2006 – 2009 (provided by the Environment Agency; EA). Where measured flow data were missing the model predictions were not considered in the analysis. From the monitoring data only eight pesticides were frequently detected over $0.1 \mu\text{g L}^{-1}$ and these were selected for modelling: 2,4-D, carbetamide, chlorotoluron, clopyralid, isoproturon, MCPA, mecoprop and propyzamide.

4.3. Selection of input data

In order to be applicable in a wide range of catchment types in the UK the model has been designed to run with readily available data; this can be point data or national scale data, depending on cost, spatial and temporal scale and availability. The data for application in the case-study catchments is derived from national scale soil and land cover data sets, national survey of pesticide loading and point scale weather data. The source of the input data is outlined in the following sections along with any assumptions made for use at a broad-scale.

4.3.1. Rainfall and temperature input data

Rainfall is the primary input into the soil water balance. Rainfall within a catchment can be highly heterogeneous; varying in depth and intensity. However, a rain gauge measurement represents only a single point, which may not be representative of the spatially average input to the catchment. One weather station was chosen from the British Atmospheric Data Centre (BADC) to represent each catchment based on: data availability in the model run period (1989 – 2010) and data quality (i.e. without large amounts of missing data, for example, whole months of data missing). Temperature data are required for the calculation of evapotranspiration. As with rainfall, a representative weather station was chosen for each catchment from BADC.

Missing measured data can occur as a result of: malfunctioning equipment, instrumentation change, human error, data processing error and station maintenance (Harvey *et al.*, 2010). For gaps in measured rainfall and temperature data values from neighbouring stations (which were not used typically due to lack of data during the model run period) were analysed for suitability as replacements. To assess the suitability of the replacement weather station a regression model was constructed to describe the relationship between the replacement station (x) and the main chosen station (y). If R^2 was greater than 0.7 and m (from the regression equation $y = mx + c$) was between 0.7 and 1.3, then the replacement station was considered suitable (Allen *et al.*,

1998), in all other situations the substitute was rejected. Regression statistics between main stations and replacement stations for rainfall and temperature for each catchment are given in Appendix C. The main weather stations and the replacement weather stations for rainfall and temperature in each catchment are shown in Table 4.6.

Table 4.6. Chosen weather stations measuring rainfall and temperature in each catchment.

	Lugg	Teme	Waveney	Wensum	Yare
Main rainfall weather station (station ID)	Lyonshall (666)	Pennerley (634)	Uplands Farm (4856)	North Creake (4712)	Browick Hall (4758)
Replacement rainfall weather station	Newchurch (10608)		Pulham St. Mary (4870)	Heydon (4807)	Hethersett Tower (30465)
Main temperature weather station (station ID)	Lyonshall (666)	Pennerley (634)	Charsfield (442)	Santon Downham (413)	Santon Downham (413)
Replacement temperature weather station	Shobdon Airfield (669)		Brooms Barn (435)	Brooms Barn (435)	Brooms Barn (435)

4.3.2 Evapotranspiration input data

Reference evapotranspiration is calculated with the Hargreaves equation (Equation 3.9 in Section 3.2.2.1) using daily minimum and maximum temperature (from the weather station in Table 4.6) and a theoretical distribution of extra-terrestrial radiation. The value of the parameter K_T in the Hargreaves

equation is often assumed to be 0.17. However, this value has been reported to vary. For example, in Senegal a K_T of 0.16 was used (Hargreaves *et al.*, 1985), and in a study of 56 locations in the United States Samani and Pessarakli (1986) found that values of K_T ranged from 0.119 in Concord New Hampshire to 0.212 in Los Angeles, with a mean K_T of 0.154 for all the locations considered. In addition, in a study in Spain by Martínez-Cob and Tejero-Juste (2004) a K_T of 0.14 was concluded to be best value for non-windy locations in semi-arid areas.

4.3.2.1 Independent evaluation of Hargreaves K_T

The applicability of using $K_T = 0.17$ for calculating ET_0 in each catchment was assessed by comparing the annual reference evapotranspiration values calculated with the Hargreaves equation to MORECS (Meteorological Office Rainfall and Evaporation Calculation System; Hough and Jones, 1997) predictions. MORECS provides national estimates of evapotranspiration using a modified version of the Penman-Monteith equation at a 40 km by 40 km grid scale (Hough and Jones, 1997). Each catchment weather station was assigned a MORECS square (Table 4.7). Comparison of annual average evapotranspiration (1990 – 2009) between the Hargreaves equation, assuming a K_T of 0.17 and 0.15, and MORECS (from the Hydrological Review of the Year, published by the NRFA; CEH, 2013) is shown for each catchment weather station in Table 4.7. Note the Hydrological Review provides a range of annual evapotranspiration values. For the Lugg, the Waveney, the Wensum and the Yare $K_T = 0.15$ was most appropriate compared to MORECS data. For the Teme $K_T = 0.17$ was superior.

Table 4.7. Comparison of average annual ET_O (1990-2009) from the Hargreaves equation ($K_T=0.17$ and $K_T=0.15$) with MORECS ET_O (calculated from a modified Penman-Monteith equation for grass cover) for the case-study catchments.

Weather station (MORECS square and catchment)	Average annual evapotranspiration (mm annum ⁻¹)		
	Hargreaves*		MORECS
	$K_T = 0.17$	$K_T = 0.15$	
Lyonshall (135; Lugg)	675	596	559 – 598
Pennerley (124; Teme)	605	534	591 – 628
Charsfield (141; Waveney)	713	625	613 – 649
Santon Downham (130; Wensum and Yare)	758	668	638 – 671

* Assuming a well-watered grass with a $K_c = 1$ in the Hargreaves equation.

4.3.3. Soils

The soils present within a catchment are determined from the National Soil Map for England and Wales (available from the NSRI) which provides spatial information at the soil association scale. Mapping is at a scale of 1:250,000. The main soil series (soil type) in a soil association is used to name each soil association.

The soil series properties required by the model are outlined in Table 4.8 and are available from SEISMIC which contains measured soil parameter data for each characteristic soil layer. The soil properties are available for four broad land uses: arable, long-term 'permanent' grassland, short-term rotational 'ley' grassland, and 'other' (i.e. land that is used for recreation or is semi-natural). Soil properties for the arable land use group have been used unless arable land

is not found on that soil type in the catchment. In this instance the most suitable land use group is used instead.

Table 4.8. Topsoil and subsoil input data requirements for the model.

Soil parameters for topsoil and subsoil	Symbol
Water content at saturation (0 kPa; $\text{cm}^3 \text{cm}^{-3}$)	θ_{sat}
-5 kPa, -10 kPa, -200 kPa and -1,500 kPa tension ; $\text{cm}^3 \text{cm}^{-3}$)	$\theta_5, \theta_{10}, \theta_{200}, \theta_{1500},$
Bulk density (g cm^{-3})	P_b
Sub-vertical saturated hydraulic conductivity (mm day^{-1})	K_{sat}
Lateral saturated hydraulic conductivity (mm day^{-1})	K_{lat}
van Genuchten n parameter (-)	n
Organic carbon content (%)	OC
Depth of topsoil and subsoil layer (mm)	$Z_{\text{top}}, Z_{\text{sub}}$
Drain installation depth (mm)	Z_{drain}
Maximum hydraulic conductivity of the last soil horizon (mm day^{-1})	K_{BC}
For each soil type	
Hydrology of Soil Type Classification (-)	HOST
Minimum Standard Rainfall Volume (mm)	MSRV

Each soil type has been assigned a HOST class (Boorman *et al.*, 1995). The HOST classes are used to determine the transport pathway from the soil zone at the interface between the subsoil and the unsaturated zone (Section 3.3). The presence of field drains in the low permeability boundary conditions (Section 3.3.2) is based on the *Soils and Their Use Series* (e.g. Hodge, 1984) produced by the Soil Survey of England and Wales. The model is run for all soil type and land use combinations in a catchment.

4.3.4. Land use

The land use in each catchment was determined using the CORINE Land Cover 2000 (CLC 2000). CORINE considers 44 land cover classes. However, so as not to over-complicate the model inputs these classes were grouped to form broader categories: arable, grassland, urban and other; (Appendix D). The “other” land use categories includes, for example: forests, moorland and estuaries.

Within the arable land cover category, land use was assumed to be winter cereals (represented with winter wheat in the soil water balance model) and winter oilseed rape (OSR). Winter wheat was used as a representative crop as pesticide use across winter-sown cereal crops (for the pesticides listed in Section 4.2.6) is similar, with pesticide active ingredients, application dates and application rates often identical (Whitehead, 2008 and Appendix E). Winter OSR was chosen as two of the pesticide frequently detected in DrWPAs are applied to winter OSR (propyzamide and carbetamide; Pesticide Forum, 2011). The arable land in a catchment in the model is divided between winter cereal and winter OSR and is based on the DEFRA June survey statistics (e.g. DEFRA, 2005), which provides detailed information on the hectares of crops grown at a county level (DEFRA, 2010).

In the soil water balance, grass is used to represent the grass land use as well as the urban and other land use categories. In urban areas vegetated surfaces, such as gardens and parks, can cover significant areas (Grimmond and Oke, 1999) although it is recognised that impermeable surface will dominate hydrological response.

4.3.5. Vegetation parameters

Vegetation-specific parameters (Table 4.9) are required in the soil water balance model to calculate actual evapotranspiration (Section 3.2.2). Crop development parameters (for example, planting date and crop growth stage durations) and evapotranspiration parameters (such as K_c crop coefficients for various stages) are needed for each land use (grass, winter wheat and winter OSR; Table 4.9) and are taken from the crop calendar database developed by Holman *et al.* (2005). The parameters for grass are assumed to be constant all year round, i.e. a constant root depth with planting on the first day of the model run and no harvest. Note that the maximum rooting depth for winter wheat was restricted to the depth of the soil.

Table 4.9. Crop parameters and crop dates for grass, winter wheat and winter oilseed rape.

	Grass	Winter wheat	Winter OSR
Rooting depth at emergence (m)	n/a	0.025	0.025
Maximum rooting depth (m)	1	1.5	1.2
K_c initial (-)	1	1	1
K_c middle (-)	1	1.10	1.05
K_c end (-)	1	0.2	0.3
Depletion factor (p)	0.62	0.65	0.7
Planting date	n/a	15 th September	31 st August
Emergence (days)	n/a	10	11
10 % cover (days)	n/a	30	21
100% cover (days)	n/a	189	211
Senescence (days)	n/a	95	76
Harvest date	n/a	30 th August	30 th July

4.3.6. Pesticide properties

The model requires pesticide properties (K_{OC} and DT_{50} ; Table 4.10) which were taken from the Pesticide Properties Data Base (University of Hertfordshire, 2013), safety data sheets, pesticide manufacturers and the European review of active substances (e.g. European Food Safety Authority, 2010). Both K_{OC} and DT_{50} values exhibit a large degree of variability (Table 4.10) which can lead to issues of subjectivity about which values to choose (Boesten and Gottesbüren, 2000; Dubus *et al.*, 2003). Therefore, the model was run using a best case (a high K_{OC} and a low DT_{50}) combination and a worst case (a low K_{OC} and a high DT_{50}) combination to capture the edges of the parameter envelope.

Table 4.10. Pesticide properties, analytical limit of quantification reported by the EA and main uses in the UK of the pesticides in the model.

Pesticide active ingredient	Organic carbon to water partition coefficient K_{OC} (L kg⁻¹)	Soil DT_{50} (days)	Limit of Quantification* (LOQ; µg L⁻¹)	Main Uses in the UK
2,4-D	5-212	2-59	0.04	Grassland, cereals, non-agricultural
Carbetamide	45-180	15-60	0.04	Oilseed rape
Chlorotoluron	108-384	26-40	0.04	Cereals
Clopyralid	2-30	14-56	0.04	Oilseed rape
Isoproturon	67-235	13-40	0.04	Cereals
Mecoprop	10-40	7-21	0.04	Cereals, grassland
MCPA	10-57	6-43	0.04	Cereals, grassland
Propyzamide	128-990	16-54	0.01	Oilseed rape

* The limit of quantification (LOQ) values for each pesticide was provided by the EA.

4.3.7. Pesticide usage

For each pesticide the main use was determined from pesticide usage statistics from the pesticide usage surveys published by FERA (Food and Environment Research Agency), which provides national results for pesticide treated area and tonnes applied for 19 crop groups between 1990 and 2012 (FERA, 2013; Table 4.10). This is also available as a bi-annual report (e.g. Garthwaite *et al.*, 2010). To determine the treated area for winter wheat and winter OSR a national average was determined for 2008 (Table 4.11) calculated based on total crop area for each crop, from agriculture in the United Kingdom (DEFRA, 2009) and total crop treated area for each crop, from the pesticide usage survey (Garthwaite *et al.*, 2010). To estimate the treated area for grass the same method was used but the pesticide usage survey for grassland and fodder crops in Great Britain in 2005 (Garthwaite *et al.*, 2006) and agriculture in the United Kingdom 2005 (DEFRA, 2006) were used instead.

The application rate is assumed to be the maximum label rate for a single application. It is worth noting that during the monitoring period, 2006-2009, isoproturon was subject to restrictions on the maximum application rate (1.5 kg ha⁻¹), with a ban coming into force on the 30 June 2009.

Application windows were estimated for each pesticide (Table 4.12) based on information provided on the product labels and the UK Pesticide Guide 2006 (Whitehead, 2006), which relates application timing to the Zadoks growth stages. For example, mecoprop should ideally be applied between the first leaf stage in autumn (Growth Stage 10) and first node detectable in spring (Growth Stage 31). Relating the growth stage for winter wheat to a particular date was estimated from the Wheat Growth Guide (HGCA, 2008). Some pesticides, such as propyzamide, have a last date of use provided by the manufacturer on the product label. For the estimation of the timing window for each crop and pesticide combination see Appendix E.

In the absence of information to the contrary, it is assumed that across each catchment the same proportion of pesticide is applied each week, i.e. for propyzamide the application window is 17 weeks long and the same mass of pesticide is applied each week. In the model the application day is a Monday, unless rainfall is more than a threshold value, in which case the application moves forward to the next day.

Table 4.11. Estimated percentage of treated area in the UK and maximum application rate.

	Grass		Winter Wheat		Oilseed rape	
	Treated area (%)*	Maximum application rate [#]	Treated area (%) ⁺	Maximum application rate [#]	Treated area (%) ⁺	Maximum application rate [#]
2,4-D	0.5%	1.65 kg ha ⁻¹	0.3%	1.25 kg ha ⁻¹	n/a	n/a
Carbetamide	n/a	n/a	n/a	n/a	10%	3.5 kg ha ⁻¹
Chlorotoluron	n/a	n/a	5%	3.5 kg ha ⁻¹	n/a	n/a
Clopyralid	n/a	n/a	n/a	n/a	6%	0.2 kg ha ⁻¹
Isoproturon	n/a	n/a	41%	1.5 kg ha ⁻¹	n/a	n/a
Mecoprop	0.6 %	1.3 kg ha ⁻¹	21 %	1.3 kg ha ⁻¹	n/a	n/a
MCPA	1.7 %	1.6 kg ha ⁻¹	1.5 %	1.6 kg ha ⁻¹	n/a	n/a
Propyzamide	n/a	n/a	n/a	n/a	34%	0.8 kg ha ⁻¹

* Treated area estimated with pesticide usage statistics from 2005 (Garthwaite *et al.*, 2006) and crop statistics from Agricultural in the United Kingdom 2005 (DEFRA ,2006).

[#] Maximum application rate from product label.

⁺ Treated area estimated from pesticide use statistics from 2008 (Garthwaite *et al.*, 2010) and crop statistics from Agriculture in the United Kingdom 2008 (DEFRA, 2009).

Table 4.12. Estimated application windows for the pesticide land use combinations considered in the model.

Pesticide	Land use	Application dates
2,4-D	Grass	15 th March – 15 th April
2,4-D	Cereal	31 st March – 5 th April
Carbetamide	Oilseed rape	15 th October – 28 th February
Chlorotoluron	Cereal	1 st October – 25 th March
Clopyralid	Oilseed rape	20 th February – 29 th April
Isoproturon	Cereal	1 st October – 20 th April
MCPA	Grass	1 st March – 31 th July
MCPA	Cereal	25 th March – 30 th April
Mecoprop	Grass	1 st March – 31 st May
Mecoprop	Cereal	15 th October – 15 th April
Propyzamide	Oilseed rape	1 st October – 31 st January

4.4. Model Execution

4.4.1 Description of model implementation

The model has been developed and is executed in VBA for Excel. The hydrological model running for 21 years in the Lugg catchment, which contains 26 soils and four land uses, takes 1 minute to run on a computer using and 2 GHz processor and 3.00 GB of RAM. The pesticide fate and transport model takes 30 minutes to run for eight pesticides in the Lugg catchment.

The model is required to be applicable at a broad-scale, have short model run times and contain a small number of parameters requiring calibration in order to predict pesticide exposure in multiple surface water catchments for a variety of actives and to have the utility to explore future scenarios in order to aid water company risk assessment. The run times and number of parameters requiring calibration in the pesticide fate and transport model developed in Chapter 3

were compared with MACRO (Larsbo and Jarvis, 2003) and SWAT (Neitsch *et al.*, 2002), two models that have been used to simulate transfers to surface water resources at the catchment scale at a daily time-step.

MACRO 5.2 has 34 parameters, this values does not include parameters which require calibration in different soil horizons. Not all of these require calibration, for example Tediosi *et al.* (2013) carried out a limited calibration on eight parameters: initial soil water content, drain spacing, Koc, boundary water content, boundary water tension, boundary hydraulic conductivity, effective diffusion path length. The last four are soil parameters that required calibration in the four horizons considered in the study. Armstrong *et al.* (2000) calibrated four MACRO parameters: saturated hydraulic conductivity, macroporosity, macropore tortuosity and saturated conductivity of the matrix, again these values required calibration in each soil horizon.

For the SWAT model Arnold *et al.* (2012) analysed 64 watershed studies that had used SWAT and reported 74 calibration parameters, this includes calibration parameters for hydrology and pesticides as well as sediment, nitrogen, phosphorus and bacteria. There are 42 calibration parameters that cover processes such as surface runoff, baseflow, snow, pesticides, subsurface tile drains and plant growth.

With respect to model run times Dubus and Surdyk (2006) reported that for MACRO it took 4-8 machines three months to complete 4,700 model runs (this was 49 combinations of sorption and DT50 in 8 soils for 6 climates and 2 application scenarios). McQueen *et al.* (2007) restricted the number of MACRO model runs to two pesticides applied to 337 soils, due to the long running times.

In contrast, the pesticide fate and transport model developed in this thesis only has seven parameters to calibrate, and they are catchment specific and not soil specific which gives the model the versatility to run for multiple soils and land uses within a catchment over a long time-period. In the Lugg catchment, for example 26 soils and four land uses are modelled with eight pesticides (each

with a varying application window) over 21 years. The ability of simple-models with well-defined parameters to work well, or better, than complex models has also been noted by Quinn *et al.* (2004) and Jakeman *et al.* (2006). The increasing complexity and quantity of parameters often makes physically-based models less suited to exploring the implications of future changes to the system (Binley *et al.*, 1991).

4.4.2 Calibration, validation and sensitivity analysis of the hydrograph

Calibration involves adjusting model parameters to optimise the fit between predictions and observed data. Once a model has been calibrated a validation process takes place to assess the ability of the calibrated model to reproduce observations outside of the calibration period.

There are seven parameters in the soil water balance model that require calibration: the drain flow parameters (C_m and C_d), the baseflow parameters (C_g and BF), the infiltration excess overland flow parameters ($p2$ and $fractR$) and the subsoil lateral throughflow parameter (C_{lat}). These are catchment-specific parameters, i.e. the same value is applied across each catchment.

To assess the goodness-of-fit, model flow results are plotted against observed flow data and model performance statistics were calculated. In hydrological modelling there are a wide range of performance statistics available to test goodness of fit; for a comprehensive review see Krause *et al.* (2005) and Moriasi *et al.* (2007). The most widely used statistic is the Nash Sutcliffe Efficiency (NSE; Nash and Sutcliffe, 1970), sometimes referred to as the Coefficient of Efficiency (Legates and McCabe, 1999). Values of NSE range from $-\infty$ to 1; where 1 represents a perfect fit between modelled and observed data. An NSE of less than zero indicates that the mean observed value is a better prediction of individual data points than the model, signifying poor model performance.

$$NSE = 1 - \frac{\sum_t (Q_{s,t} - Q_{o,t})^2}{\sum_t (Q_{o,t} - \bar{Q}_o)^2} \quad (4.1)$$

where $Q_{s,t}$ is the simulated flow on day t (mm day^{-1}), $Q_{o,t}$ is the observed daily flow on day t (mm day^{-1}) and \bar{Q}_o is the mean observed flow (mm day^{-1}).

Percent bias (PBIAS) was also used to test goodness-of-fit as this demonstrates whether the model is overestimating (a positive value) or underestimating (negative value) with respect to observed values. Criteria for using NSE and PBIAS to assess overall model performances are shown in Table 4.13 (adapted from Henriksen *et al.*, 2003).

$$PBIAS (\%) = \frac{\sum_t (Q_{s,t} - Q_{o,t})}{\sum_t Q_{o,t}} \times 100 \quad (4.2)$$

Calibration was performed using the trial and error method, with parameter values adjusted one-at-a-time. The model simulation is split into a two year warm-up period, a calibration period and a validation period. In the Lugg, the Teme, the Wensum and the Yare catchments the warm-up period are from 1989 – 1991, the calibration period is from 1992 – 2001 and the validation period from 2002 – 2010. In the Waveney catchment the model warm-up period is 1991 – 1993, the calibration period 1994 – 2002, and the validation period from 2003 – 2010. This is because of availability of temperature data. Observed and predicted hydrographs are presented in the results (Section 4.5.1) for each catchment for 2006 – 2009 during the validation period (which covers the same period of the measured pesticide concentration data), in order to highlight and discuss model performance. The full calibration and validation hydrographs are in Appendix F.

Table 4.13. Overall model performance based on two goodness-of-fit statistics, Nash Sutcliffe Efficiency and Percent Bias. Adapted from Henriksen *et al.* (2003).

Goodness of fit statistic	Model performance				
	Excellent	Very good	Good	Poor	Very poor
NSE	≥ 0.85	≥ 0.65 to < 0.85	≥ 0.50 to < 0.65	≥ 0.2 to < 0.5	< 0.2
 PBIAS (%) 	≤ 5	> 5 to ≤ 10	> 10 to ≤ 20	> 20 to ≤ 40	> 40

In the calibration period the parameter set was chosen so as to maximise the NSE, whilst getting as close to zero on PBIAS. The final calibrated values for each catchment are shown in Table 4.14. The difference between catchments of several of the calibrated parameters, such as the IE_{OF} values p_2 and $fractR$, was narrow (Table 4.14). This could potentially allow the universal parameters to be created and the model to be applied un-calibrated to new catchments. The calibrated parameters remain unchanged for the validation period.

Table 4.14. Calibrated parameter values for each study catchment.

Parameter	Lugg	Teme	Waveney	Wensum	Yare
C_m (mm day ⁻¹)	20	20	10	10	8
C_d (mm)	10	10	0.9	8	1
C_{lat} (mm)	4	2	4	0.2	2
p_2 (-)	2	3	2.2	3	2.2
$fractR$ (-)	0.01	0.01	0.008	0.01	0.01
BF (mm)	50	35	25	50	42
C_g (mm day ⁻¹)	0.01	0.01	0.01	0.01	0.01

A sensitivity analysis of the catchment calibration parameters from (Table 4.14) for the total flow has been performed in the Yare catchment (Figure 4.7). The total flow at the catchment outlet is most sensitive to the calibration parameters that control the release of baseflow from the groundwater store, C_g and BF .

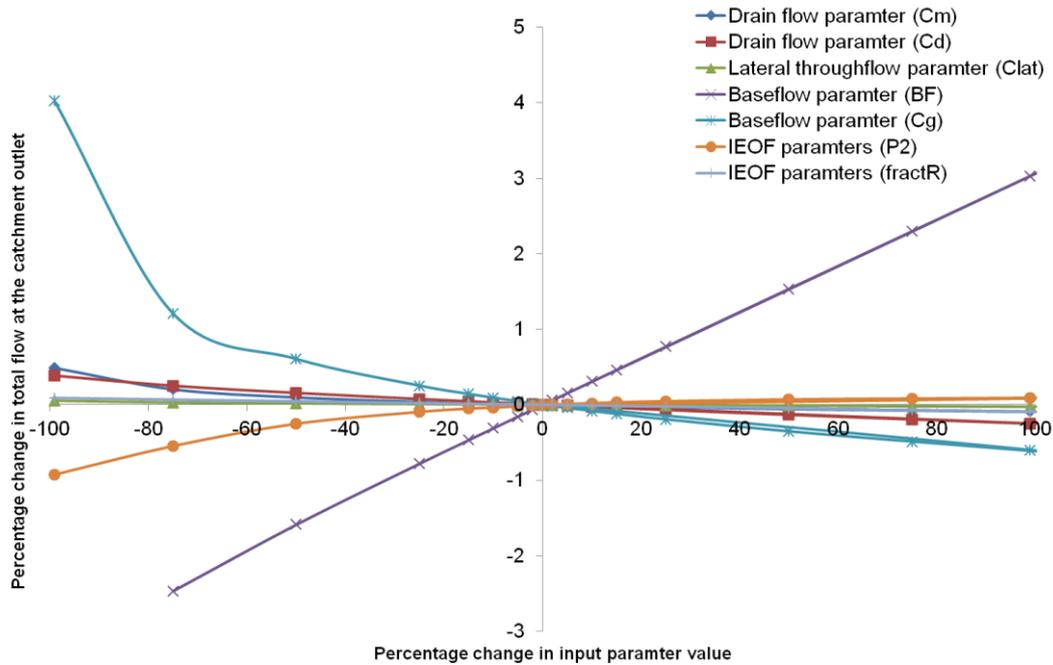


Figure 4.7. Sensitivity analysis of the catchment calibration parameters for total flow between 1991 – 2010 in the Yare catchment.

4.4.3. Evaluation of model performance on predicting pesticide exposure

In the pesticide transport model there are two threshold parameters that require calibration; the volume of daily rainfall required to mobilise pesticides (R_{mob}) and the volume of water required in the active hydrological pathway to transport pesticides (Q_{mob}). This prevents pesticides being transported when there is no hydrologically active pathway. However, no calibration of the pesticide transport model was performed because measured data is only available at a fortnightly time-step, sometimes longer, whilst the model predicts daily concentrations. Concentration patterns of pesticides in surface water resources are highly

dynamic (Kruger, 1998; Holvoet *et al.*, 2007) which means that there is a high probability of an infrequent sampling regimes missing peak events, potentially leading to samples providing an unrepresentative estimation of exposure. The measured data are, therefore, inappropriate for model calibration (Dubus *et al.*, 2002) and the thresholds were fixed at proxy values of zero of 0.5 mm day^{-1} of rainfall and 0.05 mm day^{-1} (R_{mob} and Q_{mob} respectively).

It is important that the model is able to capture peak pesticide concentrations at the catchment outlet for a range of pesticides. Cumulative distributions functions were used to compare the measured and the modelled frequencies (Loague and Green, 1990). Model performance was assessed based an ability to predict the 90th percentile measured concentration and the frequency of detections greater than $0.1 \mu\text{g L}^{-1}$, MAC for individual pesticides in drinking water. Broadly speaking, it is assumed that the model has performed well if the measured data is within the envelope of predicted best case (a high K_{OC} and low DT_{50}) and worst case (a low K_{OC} and high DT_{50}) concentrations. Measured and worst-case modelled time-series of concentrations are also presented.

4.5. Results and discussion

4.5.1. Hydrograph results

Performance of the soil water balance model to reproduce the hydrograph in the calibration and validation period is good in four of the case-study catchments (Table 4.15 and Table 4.16). The Wensum is the only catchment which performs poorly in both the calibration and validation period.

Table 4.15. Model performance statistics for the prediction of flow at the catchment outlet in five case-study catchments.

Catchment	Calibration		Validation	
	NSE	PBIAS	NSE	PBIAS
Lugg	0.71	3.6	0.72	9.3
Teme	0.71	19.6	0.72	9.1
Waveney	0.54	-14.8	0.59	-11.3
Wensum	0.25	29.6	0.19	1.7
Yare	0.53	12.8	0.45	2.1

Table 4.16. Overall model performance for five case-study catchments, based on Nash Sutcliffe Efficiency and Percent Bias.

Catchment	Calibration	Validation
Lugg	Very Good	Very Good
Teme	Good	Very Good
Waveney	Good	Good
Wensum	Poor	Poor
Yare	Good	Poor

*Adapted from Henriksen *et al.* (2003) Section 4.4.1.

4.5.1.1. West Midlands catchments (Lugg and Teme)

In both the Lugg and the Teme catchments the model reproduces both the timing and magnitude of peak flows reasonably well, particularly in the autumn and winter (Figure 4.8a,b). In the Lugg validation period there is a slight over estimation of some peak events by the model (Figure 4.8a); however, from 2002 the gauging station in the Lugg was subject to a rating limit of 3.13 mm day⁻¹. In the Teme catchment the model tends to under-predict peak measured flow, particularly in the summer (Table 4.8b). In both catchments there is a tendency to over-predict baseflow, particularly during the summer (Figure 4.8a,b).

The cumulative flow in the Lugg catchment, Figure 4.9a, also shows a good degree of agreement between observed and predicted in the calibration period (days 1-3648). The validation period the predicted flow is slightly greater than the observed. The cumulative flow of observed against predicted, Figure 4.9b, shows that predicted cumulative flow in the Teme is greater than the observed in both the calibration and the validation period. This over-prediction between observed and predicted is also reflected in the PBIAS values, particularly for the calibration period (Table 4.15).

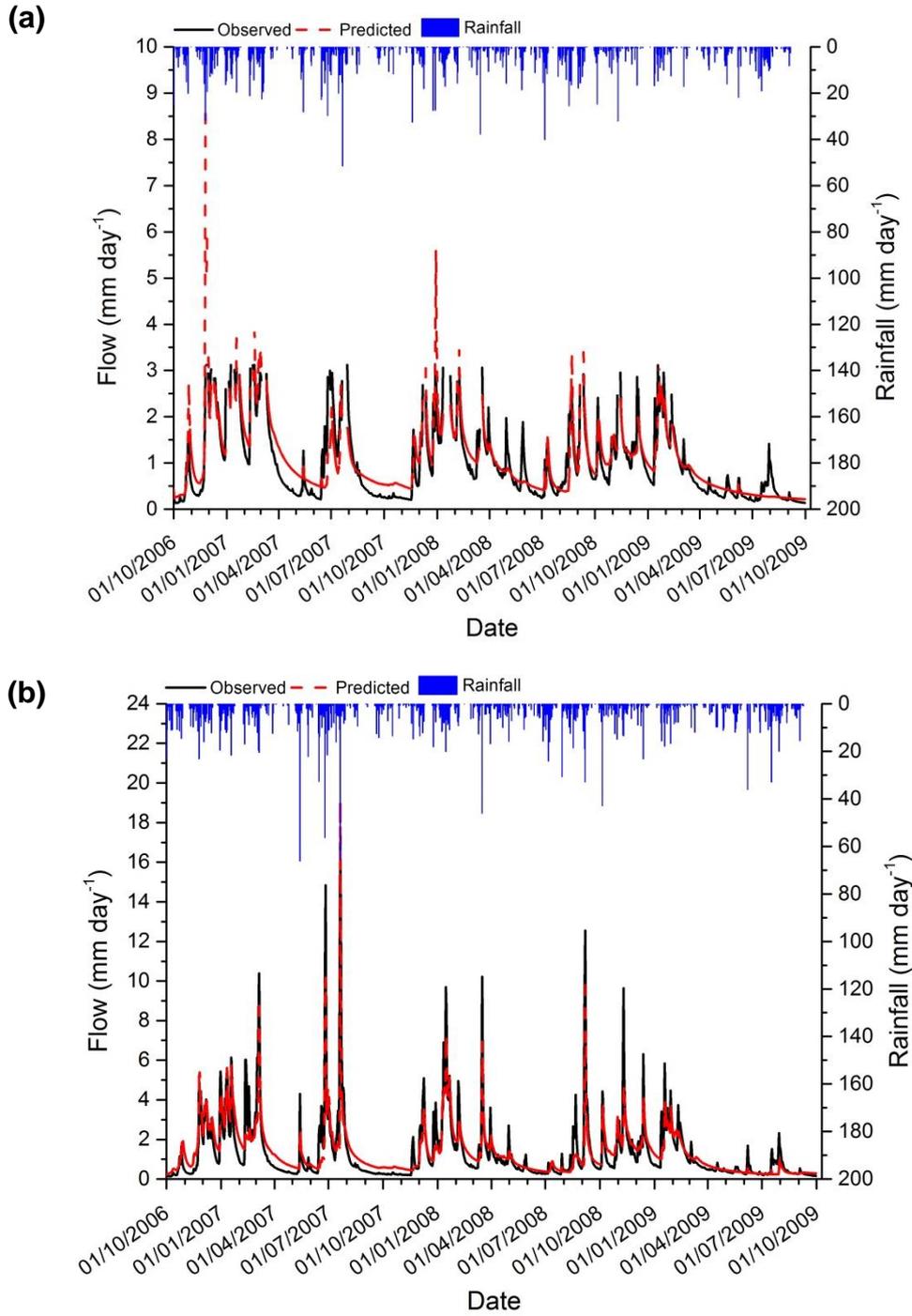


Figure 4.8. Measured rainfall and measured and predicted flow from October 2006 to September 2009 in (a) the river Lugg at Lugwardine and (b) the river Teme at Knightsford Bridge.

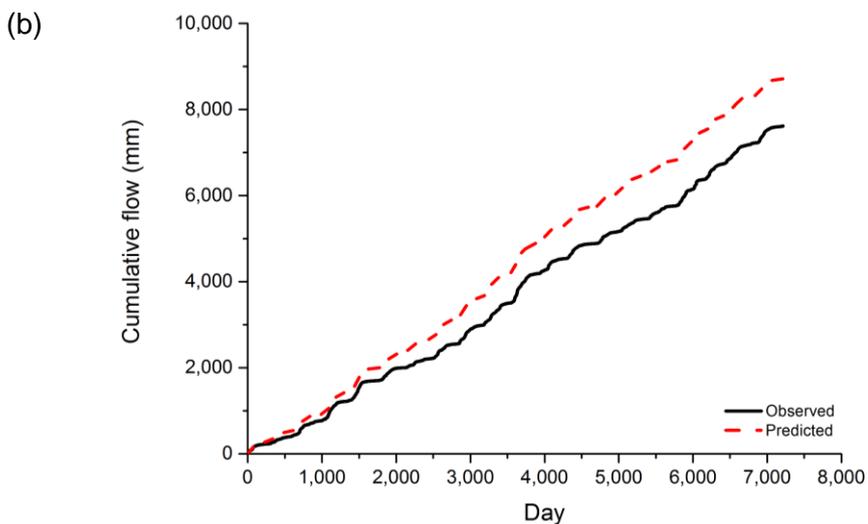
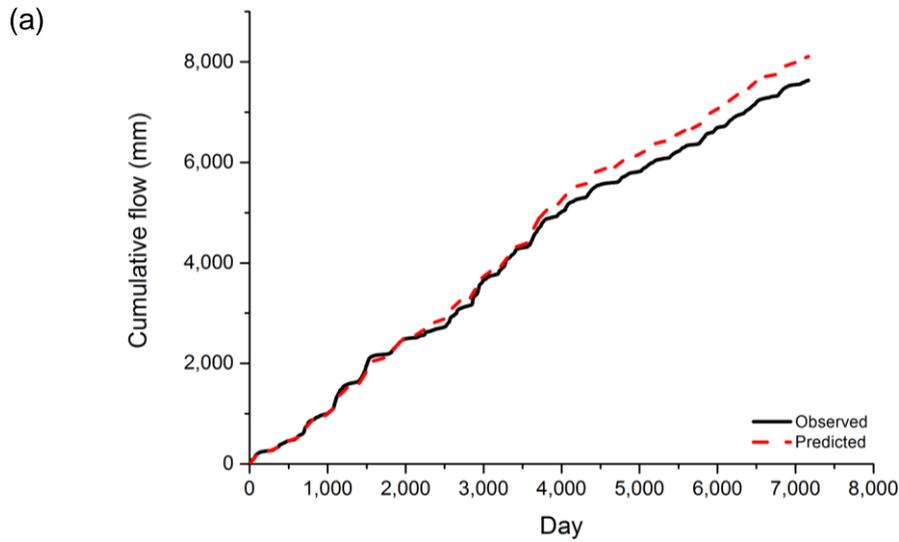


Figure 4.9. Observed and predicted cumulative flow in (a) the river Lugg and Lugwardine and (b) the river Teme at Knightsford Bridge.

4.5.1.2. East Anglian catchments (*Waveney, Wensum, Yare*)

Measured and modelled flow data for the Waveney, Wensum and Yare catchments are shown in Figure 4.9. In the Waveney the model noticeably under-predicts flow in both the calibration and validation periods (Table 4.15). The under prediction is most obvious from May to September (Figure 4.10a) when the model fails to reproduce the magnitude of the peak flows and in some situations fails to respond at all. In the autumn and winter the model performs better, predicting well both the timing and the magnitude of peak flows. Note

that due to missing flow data in 2006 the results in Figure 4.10a are presented starting from January 2007. In the Waveney the comparison between measured and predicted cumulative flow shows that the model is under-predicting, Figure 4.11a.

In the Wensum overall catchment model performance is relatively poor (Table 4.16). With a few exceptions, the model over-predicts the magnitude of peak flow events and struggles with the timing of some events, which are sometime missed completely (Figure 4.10b). Although the basic shape of the hydrograph recession is reasonable, in the validation period the baseflow prediction recesses too far in comparison with the measured data (particularly noticeable between August and December 2008). Poor model performance for the Wensum may, in part, be due to a failure to account for artificial influences such as water abstraction or effluent return flows. In addition, mill structures have been built along two-thirds of the Wensum which act to artificially regulate the flow via sluices. The consequence of this is that they act to impound the river and as a result the river behaves more like a series of lakes (EA, 2010b). The cumulative flow results comparing measured and predicted (Figure 4.11b) demonstrate that the model is over-predicting.

In the Yare catchment model performance is good in the calibration period, but poor in the validation (Table 4.16). In terms of magnitude, the model tends to over-predict peak flow events in the Yare catchment during the autumn and winter period (Figure 4.10c). This over-prediction could potentially affect the NSE as it is sensitive to extreme outliers due to the use of squared differences (Legates and McCabe, 1999, Krause *et al.*, 2005; McCuen *et al.*, 2006). The model reproduces the timing of peak flow in the Yare quite well and only misses a few peaks, principally in the summer periods (highlighted best in June and July 2007; Figure 4.10c). In this period, the UK experienced substantial summer flooding, and was the wettest June to August in England and Wales, since 1912, (Marsh and Hannaford, 2007). Comparing measured and predicted cumulative flow in the Yare catchment (Figure 4.11c) the model over-predicts but overall compares quiet well.

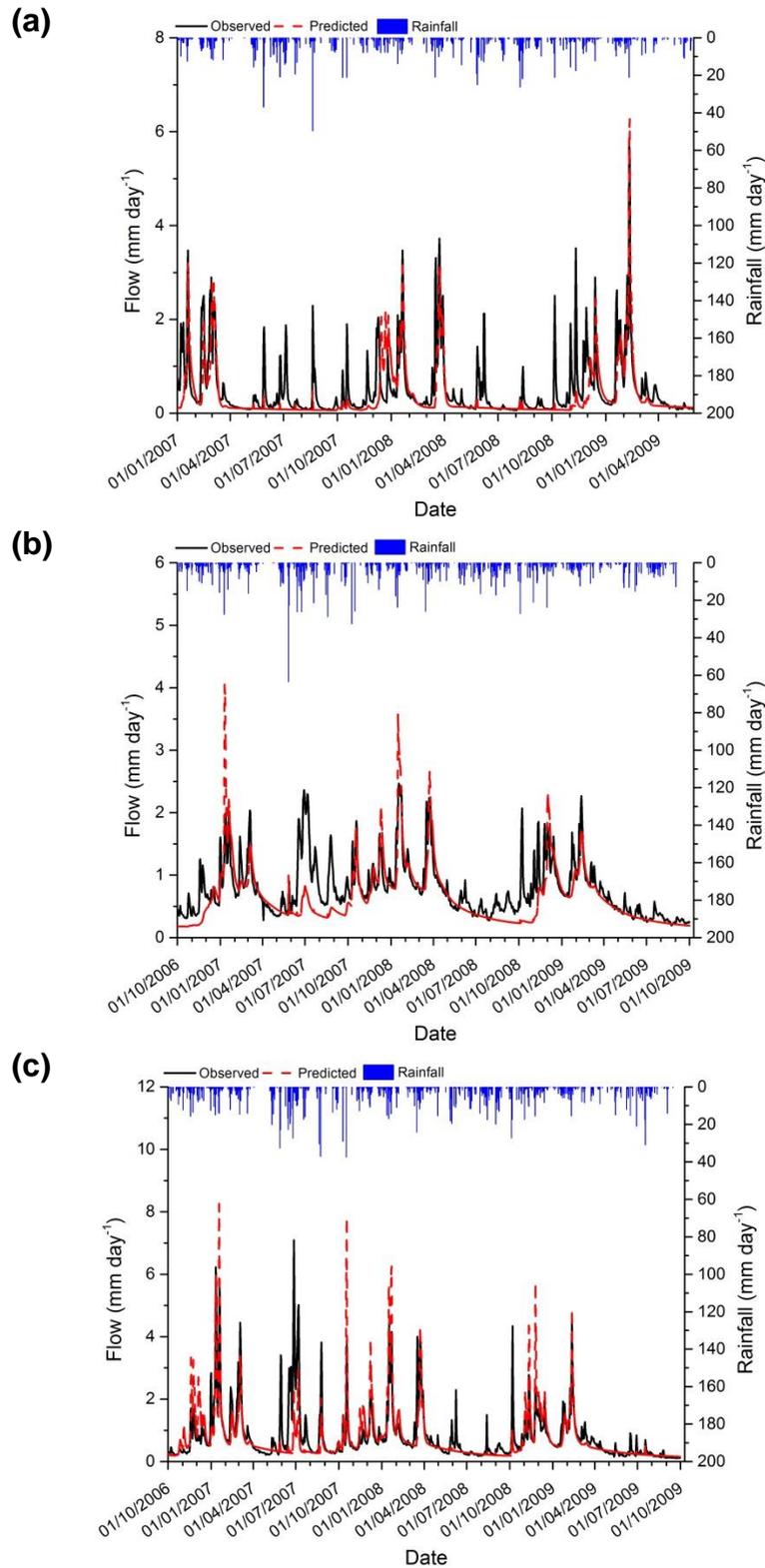


Figure 4.10. Measured rainfall and measured and predicted flow from October 2006 to September 2009 in (a) the river Waveney at Needham Mill (b) the river Wensum at Cottessey Mill and (c) the river Yare at Colney.

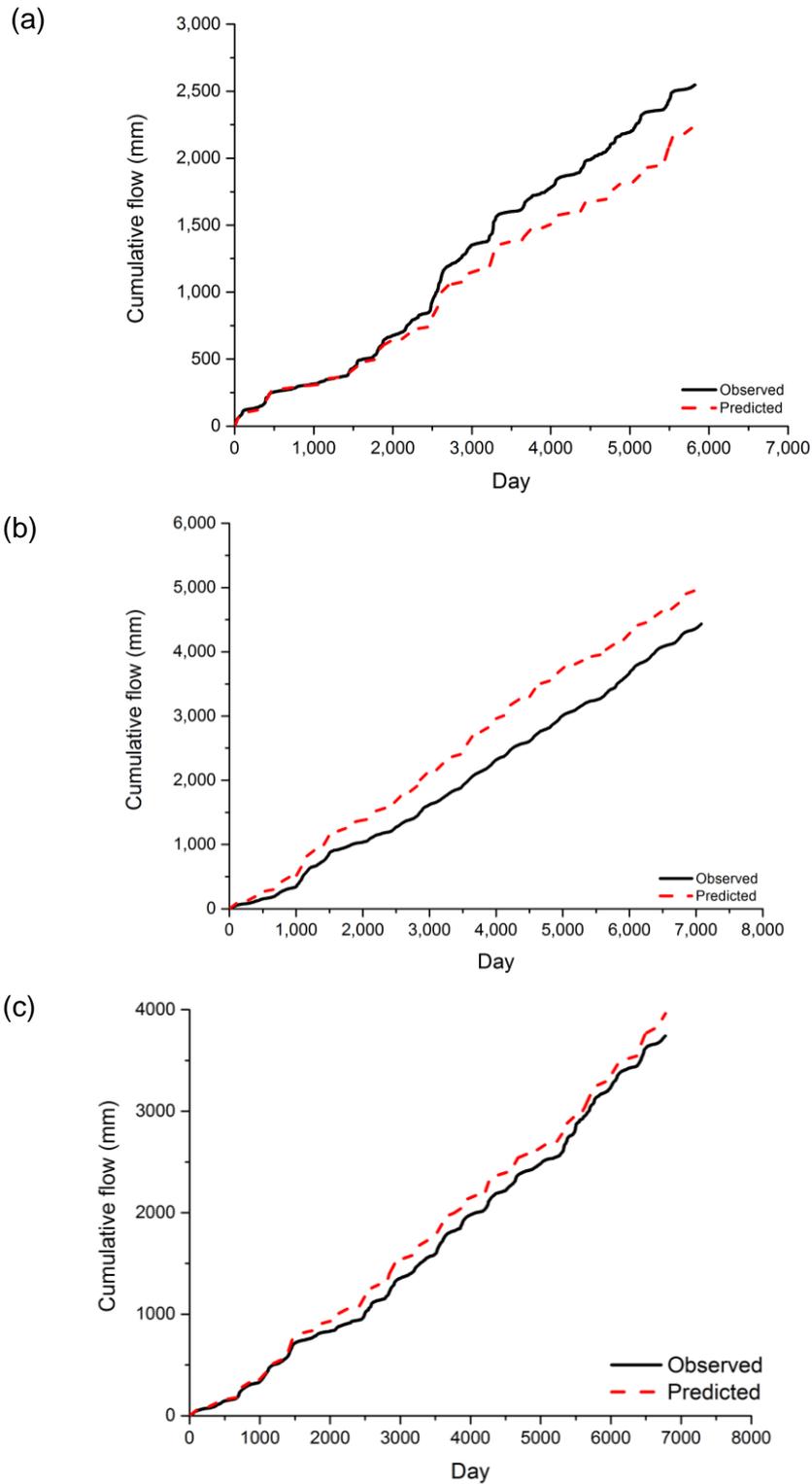


Figure 4.11. Observed and predicted cumulative flow in (a) the river Waveney at Needham Mill (b) the river Wensum at Cottessey Mill and (c) the river Yare at Colney.

4.5.1.3. Discussion of hydrograph results

Discrepancy between model outputs and observations for the time series and cumulative flow can be explained by various factors. Inaccuracies and uncertainty in rainfall data and reference evapotranspiration estimations could affect the hydrograph predictions and cumulative flow predictions in all of the catchments. Rain gauge measurements only represent a single point which may not be representative of the average input to the catchment. In addition, rain gauges can be adversely affected by wind, rainfall intensity, siting of the gauge and snowfall (Rodda, 1967; Larson and Peck, 1974; Chang and Flannery, 2001). Manual measurements can also be affected by user bias, although automated systems such as the tipping bucket rain gauge have been shown to under-estimate storm rainfall (Duchon and Biddle, 2010). Reference evapotranspiration could be affected by variations in cloud cover and wind speed, which may be reflected in temperature (Hargreaves and Allen, 2003), or by the choice of K_T value used.

Under-estimation of peak flow during the summer could be a result of an inadequate prediction of infiltration excess overland flow in the model (Section 3.2.4). An alternative method for calculating infiltration excess overland flow is the National Resources Conservation Service (NRCS) [previously USDA Soil Conservation Service (SCS)] curve number method, which can be applied by defining a single parameter that combines land use and soil type, to estimate runoff. Limitations with this method include that it does not account for temporal and spatial variability of infiltration (Ponce and Hawkins, 1996), and in the simplest form does not explicitly account for the antecedent moisture of the soil (Bevan, 2012).

One of the main assumptions in the model is that the groundwater store is assumed to have the same catchment boundary as the surface water catchment. However, the divide between groundwater catchments is not static and can move as a response to abstraction, season or climate (Black *et al.*, 2012). It is therefore possible recharge could be entering a separate

groundwater catchment and potentially augmenting stream flow in another catchment.

It is also assumed that all the water percolating below the soil zone will travel vertically and reach the groundwater store in the catchment being considered. However, there may be circumstances that cause the water to be move laterally, such as an area of low permeability material or a perched water table, and potentially contribute to stream flow events rather than augmenting baseflow. In addition, in the model only one groundwater store has been accounted for with a set of calibration parameters. Results of a sensitivity analysis conducted in the Yare catchment (see Appendix F) suggest that predicted flow is most sensitive to the baseflow parameters BF and C_g .

4.5.1.4. Conclusions of hydrograph results

The ability of the model to reproduce the hydrograph at the catchment outlet suggests that the key hydrological pathways from soil to surface water bodies may be represented adequately. This is critical as the hydrological pathways predicted in the soil water balance model underpin pesticide mass transfer. It is worth noting that it is still possible for models to give good predictions of hydrological response with poor representation of processes dynamics (Beven 2006).

In relation to pesticide transport, the important sections of the hydrograph that need to be represented with a good degree of accuracy are the peak flow events from October to February, which relate to the key pesticide application periods for winter sown crops. The predictions of timing and magnitude of peak autumn and winter flow at the catchment outlet is reproduced reasonably well. Model performance is better in the two larger catchments in the west Midlands; the Lugg and the Teme, than in the Waveney, the Wensum and the Yare catchments in East Anglia.

4.5.2. Modelled pesticide concentrations

Cumulative frequency distributions for measured and modelled concentrations (for a worst case and a best case K_{OC} and DT_{50}) are calculated for each pesticide catchment combination. An example for carbetamide is presented for all case-study catchments (Figure 4.12). For the full pesticide catchment cumulative frequency combinations see Appendix G. The results are presented below and discussed in more detail comparing measured and modelled 90th percentile concentration and measured and modelled frequency of detections greater than $0.1 \mu\text{g L}^{-1}$.

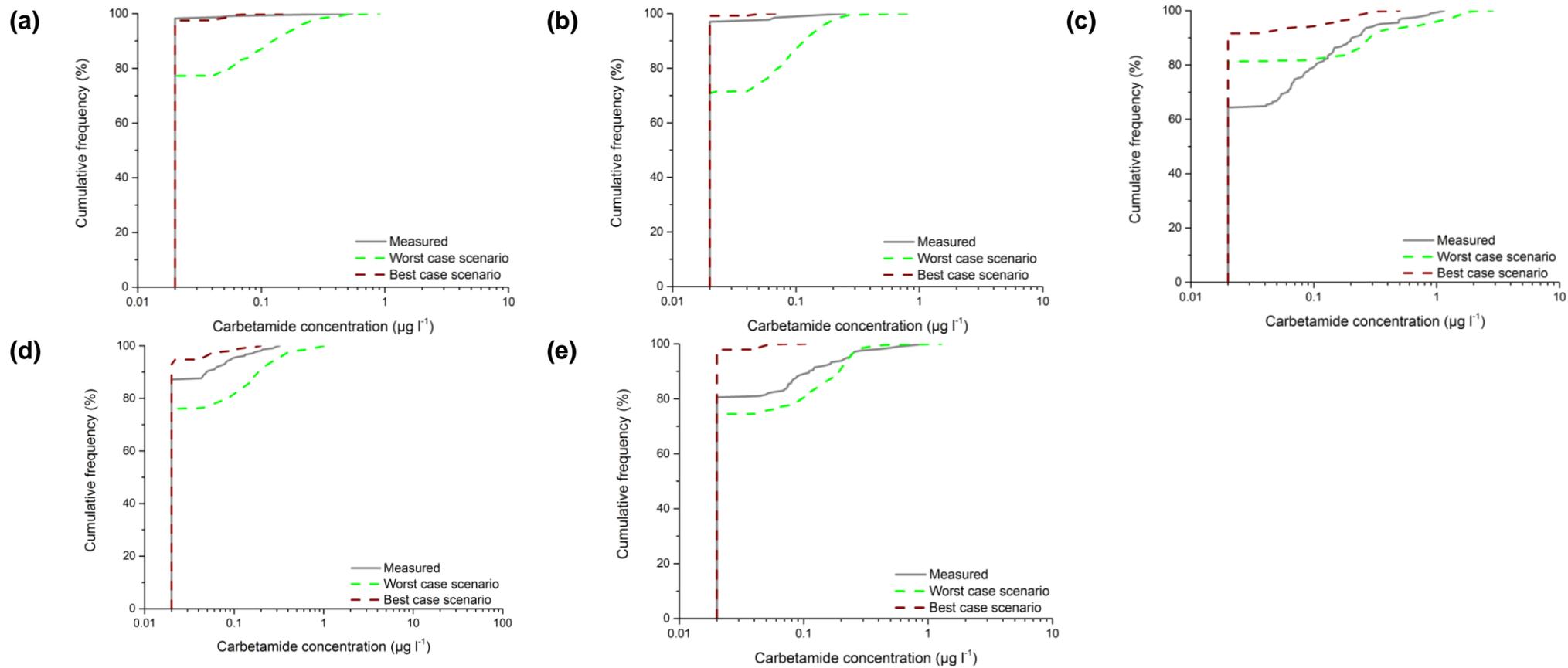


Figure 4.12. Example cumulative frequency distributions for measured carbetamide concentrations with predicted best case and worst case concentrations at the catchment outlet in the (a) Lugg, (b) Teme, (c), Waveney, (d) Wensum, (e) Yare.

4.5.2.1. Model performance with respect to prediction of 90th percentile concentration

The 90th percentile predicted concentrations were within the uncertainty range (envelope of the best case and worst case combinations of K_{OC} and DT_{50}) for 25 out of the 40 pesticide catchment combinations (Table 4.17). Of the remaining 15 pesticide catchment combinations six were within a factor of two, five were within a factor of four and the final four were not considered as the measured values were below LOQ. Model simulations within a factor of 10 can generally be considered acceptable, particularly if being used for policy or regulation (Brown *et al.*, 2002).

Model performance in the Lugg and the Teme catchment was better than for the Waveney, the Wensum and the Yare for the pesticide catchment combinations (Table 4.18). The model performed better for 2,4-D, carbetamide and propyzamide than for the other pesticide active ingredients investigated, although it is worth noting the wide envelope of predictability for propyzamide (Table 4.10).

Table 4.17. Measured and modelled 90th percentile concentration for each pesticide catchment combination.

Predicted values show the range of best case and worst case K_{OC} and DT_{50} combinations.

	Lugg		Teme		Waveney		Wensum		Yare	
	Measured ($\mu\text{g L}^{-1}$)	Modelled [#] ($\mu\text{g L}^{-1}$)	Measured ($\mu\text{g L}^{-1}$)	Modelled [#] ($\mu\text{g L}^{-1}$)	Measured ($\mu\text{g L}^{-1}$)	Modelled [#] ($\mu\text{g L}^{-1}$)	Measured ($\mu\text{g L}^{-1}$)	Modelled [#] ($\mu\text{g L}^{-1}$)	Measured ($\mu\text{g L}^{-1}$)	Modelled [#] ($\mu\text{g L}^{-1}$)
2,4-D	0.02*	0.02*	0.02*	0.02*	0.02*	0.02*	0.02*	0.02*	0.02*	0.02*
Carbetamide	0.02*	0.02* – 0.12	0.02*	0.02* – 0.11	0.2	0.02* – 0.28	0.05	0.02* – 0.18	0.11	0.02*-0.19
Chlorotoluron	0.08	0.06 – 0.23	0.08	0.06 – 0.24	0.02*	0.1 – 0.34	0.02*	0.09 – 0.35	0.02*	0.1 – 0.37
Clopyralid	0.02*	0.02*	0.02*	0.02*	0.08	0.02*	0.02*	0.02*	0.05	0.02*
Isoproturon	0.1	0.26 – 1.65	0.14	0.22 – 1.67	0.41	0.14 – 2.17	0.28	0.32 – 2.35	0.28	0.38 – 2.51
MCPA	0.02*	0.02* - 0.08	0.02*	0.02* - 0.1	0.1	0.02*	0.02*	0.02*	0.07	0.02*
Mecoprop	0.02*	0.13 – 0.59	0.05	0.11 – 0.60	0.18	0.14 – 0.8	0.06	0.15 – 0.71	0.13	0.17 – 0.84
Propyzamide	0.04	0.005* – 0.15	0.02	0.005* - 0.15	0.14	0.005* - 0.34	0.07	0.005* - 0.24	0.1	0.005* - 0.23

Key: Green blocks are measured values between the best case and worst case with respect to the 90th percentile concentration, blue blocks are over-predictions by the model and orange blocks are under predictions by the model.

* Any measured data or model output less than Limit of Quantification (LOQ) is set to ½ LOQ.

Range of predicted best case to worst case combinations.

4.5.2.2. Model performance with respect to prediction of frequency of concentrations greater than 0.1 µg L⁻¹

The frequency of concentration greater than 0.1 µg L⁻¹ were within the uncertainty range (envelope of the best case and worst case combinations of K_{OC} and DT_{50}) for 17 out of the 40 pesticide catchment combinations (Table 4.18). In general, the model tended to under-predict the frequency of concentration in comparison with the measured data, particularly in the Waveney, the Wensum and the Yare catchments.

The relative order of measured frequencies predicted by the model to be greater than 0.1 µg L⁻¹ in comparison with the measured data is shown using Spearman's rank correlation (Table 4.19). In three of the catchments (the Lugg, the Teme and the Wensum) the model predicts well the rank order of pesticides greater than 0.1 µg L⁻¹ (at the $p < 0.05$ significance level). This demonstrates that the model, in some catchments, is able to predict the order of importance of pesticides greater than 0.1 µg L⁻¹.

Table 4.18. Measured and modelled frequency of detections greater than 0.1 µg L⁻¹ for each pesticide catchment combination. Predicted values shown the range of best case and worst case K_{OC} and DT₅₀ combinations.

	Lugg		Teme		Waveney		Wensum		Yare	
	Measured	Predicted [#]								
2,4-D	0 %	0 – 3 %	0 %	0 – 3 %	1 %	0 – 0.4 %	1 %	0 – 0.4 %	3 %	0 – 0.2 %
Carbetamide	0.4 %	0.2 – 13 %	0.7 %	0 – 14 %	21 %	6 – 18 %	5 %	2 – 19 %	11 %	0 – 20 %
Chlorotoluron	9 %	6 – 20 %	7 %	3 – 25 %	1 %	10 – 13 %	3 %	9 – 21 %	0.5 %	10 – 22 %
Clopyralid	0 %	0 – 0.3 %	0.7 %	0 – 0.1 %	9 %	0 – 0.4 %	0.8 %	0 – 0.5 %	4 %	0 – 0.3 %
Isoproturon	10 %	18 – 29 %	15 %	21 – 35 %	46 %	11 – 13 %	27 %	18 – 24 %	35 %	20 – 26 %
MCPA	3 %	0.1 – 9 %	4 %	0.2 – 11%	10 %	0.7 – 2 %	6 %	0.2 – 4 %	8 %	0.1 – 4 %
Mecoprop	3 %	13 – 25 %	7 %	13 – 21 %	15 %	11 – 13 %	7 %	16 – 22 %	12 %	18 – 23 %
Propyzamide	3 %	0 – 15 %	2 %	0 – 19 %	15 %	0.2 – 18 %	7 %	0 – 20 %	10 %	0 – 20 %

Key: Green blocks are measured values between the best case and worst case with respect to frequency of concentrations greater than 0.1 µg L⁻¹, blue blocks are over-predictions by the model and orange blocks are under predictions by the model.

[#] Range of predicted best case to worst case scenarios.

Table 4.19. Model performance with respect to relative rank order of measured frequencies greater than 0.1 µg L⁻¹ and modelled predictions, using Spearman's rank correlation.

	Spearman's Rank
Lugg	0.80*
Teme	0.87*
Waveney	0.60
Wensum	0.76*
Yare	0.61

* $P < 0.05$

4.5.2.3. Discussion of pesticide concentration results

Discrepancy between model outputs and observations can be explained by various factors. Over-predictions of modelled concentrations in comparison with measured concentrations could be as a result of an over-estimation in treated area. Using chlorotoluron as an example, the assumption in the model is that across all the catchments 5 % of winter wheat receives chlorotoluron at a maximum dose rate of 3.5 kg ha⁻¹. In the Waveney, the Wensum and the Yare, the percentage of the total catchment treated with chlorotoluron is much higher than in the Lugg or the Teme (Table 4.20), because the proportion of the catchment that is assumed to be arable (and therefore under winter wheat) is also higher.

Table 4.20. Percentage of the total catchment assumed to be treated with chlorotoluron in the model.

	Chlorotoluron Cereal
Lugg	2.3 %
Teme	2.1 %
Waveney	4.1 %
Wensum	3.8 %
Yare	4.1 %

Over-prediction could also be as a result of the uncertainty associated with the measured data not reflecting what is happening in the river due to the sampling regime used. The temporal scale of the sampling regime (typically once every two weeks) could be missing peak concentrations in the river. The largest peak concentrations are typically observed in the first substantial rainfall event after application (e.g. Capel *et al.*, 2001; Leu *et al.*, 2004a; Tediosi *et al.*, 2013), however if the grab sample was not taken on that day, this would not be reflected in the measured data.

Under-predictions of the modelled concentrations in comparison with measured concentrations could be as a result of not accounting for pesticide use on other crops. For example, clopyralid is used on sugarbeet (FERA, 2013) as well as oilseed rape. Not accounting for use on sugarbeet could have led to the model under-estimation seen in Waveney, Wensum and Yare (Tables 4.17 and 4.18) as almost half the country's sugarbeet is grown in the East Anglian region (EA, 2013a).

Another explanation behind the model under-prediction could be the assumption of an even spread of application in the model with the same proportion of pesticide being applied each week. In reality, pesticide application will depend on availability of machinery, pest growth stage, weather conditions (too windy or too rainy thereby restricting spraying), as well as applying the product to treat the pest or disease to achieve the greatest efficacy (Salmon-Monviola *et al.*, 2011) which could result in a more condensed application window than assumed.

Under-prediction by the model could also be due to not accounting for point sources. For example, 2,4-D is used to treat Giant Hogweed (*Heracleum mantegazzianum*) that typically occurs on river banks (EA, 2010a). Treatment so close to the river could lead to pseudo point sources. Other point sources could also arise from activities such as cleaning spraying equipment or spillages during filling (Rose *et al.*, 2001).

One broad reason for the differences in model performance between the Lugg and Teme compared with the Waveney, the Wensum and the Yare could be the fact that the Lugg and the Teme catchments are generally wetter, with a greater amount of hydrologically effective rainfall. This is important as the mass flux displaced from the

soil is calculated based on the ratio of the unsaturated hydraulic conductivity to the saturated hydraulic conductivity (Figure 4.13). The predicted soil moisture deficits in soil types in the Lugg and the Teme (e.g. Brickfield) tend to be lower than in the Waveney, the Wensum and the Yare (Beccles) and so the unsaturated hydraulic conductivity is closer to the saturated hydraulic conductivity (Figure 4.13) and as a result a greater proportion of pesticide is displaced.

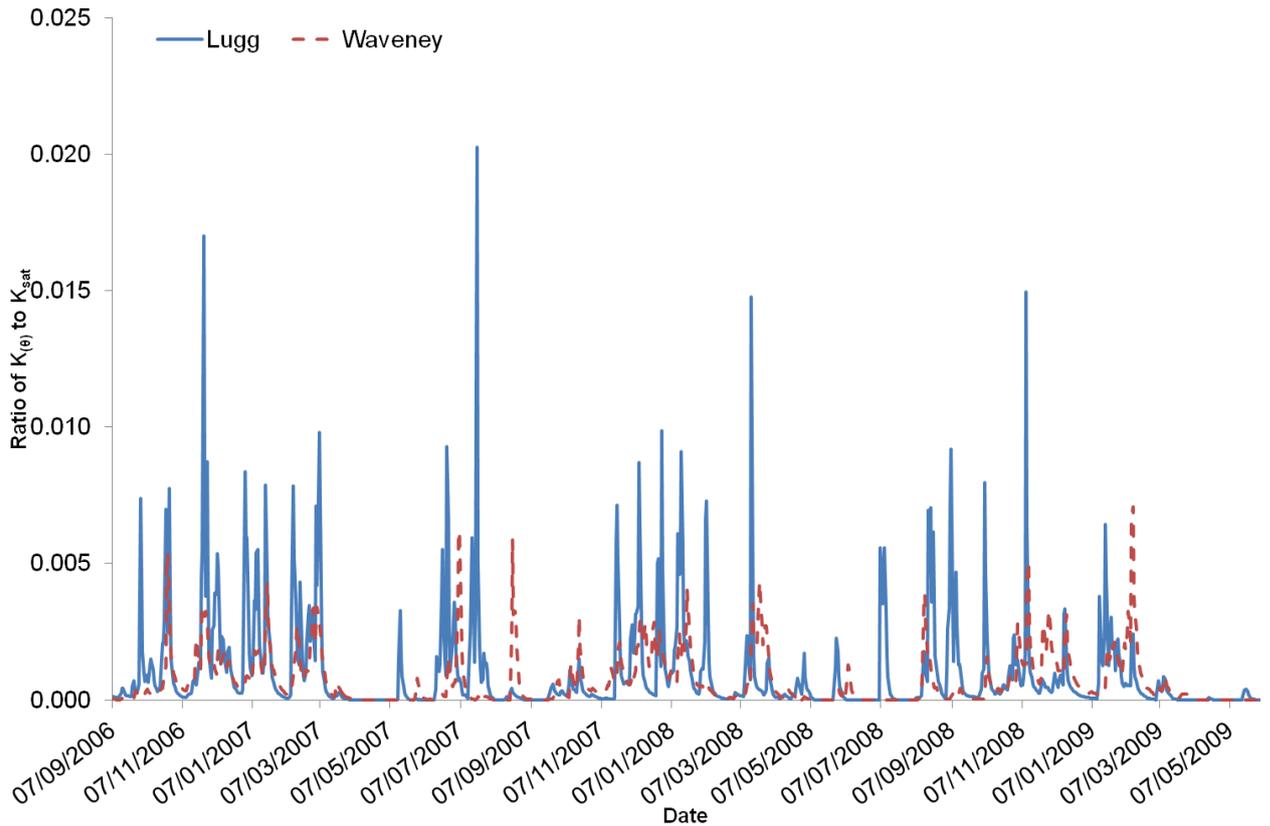


Figure 4.13. Ratio of unsaturated hydraulic conductivity (K_{θ}) to the saturated hydraulic conductivity (K_{sat}) for a representative soil in the Lugg (Brickfield) and Waveney (Beccles) during the pesticide model run period (2006 – 2009).

4.6. Time series results of pesticide concentrations at the catchment outlet and contribution of hydrological pathways

The time-series of measured and predicted propyzamide concentrations from the pesticide fate and transport model, assuming worst case K_{oc} and DT_{50} , is presented between September 2006 and September 2007 with the predicted hydrograph in all five catchments (Lugg, Teme, Waveney, Wensum and Yare) in Figure 4.14.

In all five catchments the model predicts the presence of propyzamide at the catchment outlet earlier than the measured data and also tends to over-predict when compared to measured data (Figure 4.14). One of the reasons behind this early prediction is the application window assumed in the pesticide fate and transport model. For propyzamide the first application is assumed to take place in the model at the beginning of October, whereas in reality pesticide application is influenced by factors such wind speed, likelihood of rainfall, ground conditions and crop growth stage (HSE, 2009). The assumptions made in the model with respect to rate of application and the percentage of crop treated area will influence the magnitude of the predicted pesticide concentration.

Another factor that will influence the measured data is the frequency of the grab samples, which for some pesticide catchment combinations is longer than fortnightly. Concentration patterns of pesticides in surface water resources are highly dynamic (Kruger, 1998; Holvoet *et al.*, 2007) which means that there is a high probability that an infrequent sampling regime could miss peak events, potentially leading to samples providing an unrepresentative estimation of exposure. It is also worth noting that the sampling method can also have an effect on the measured pesticide concentrations, for example Rabiet *et al.* (2010) showed that pesticide concentrations were under-estimated by grab samples.

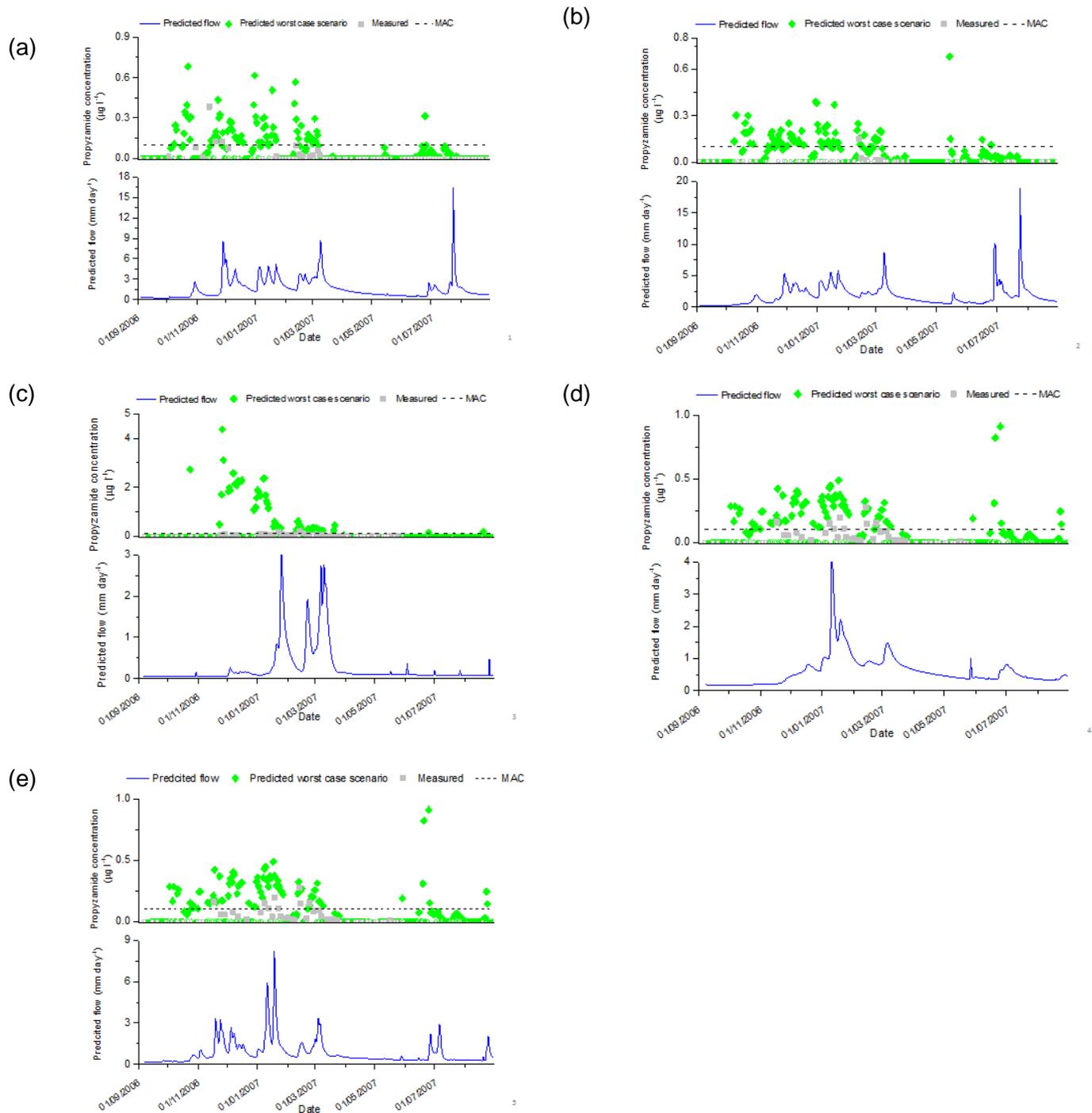


Figure 4.14. Comparison of predicted and measured propyzamide concentrations and predicted flow between September 2006 and September 2007 in the (a) Lugg (b) Teme (c) Waveney (d) Wensum and (e) Yare catchments. Note different scale in different catchments.

The propyzamide concentrations are predicted above the LOQ in May and June in all five catchments (Figure 4.14), this is not reflected in the measured data. This could be as a result of the worst-case scenario DT_{50} values used in the model. This results in a slower rate of degradation and therefore pesticide mass is still available for transport in the soil, and as discussed previously, this period in 2007 was the wettest on record since 1912 (Marsh and Hannaford, 2007) which caused the initiation of drain flow in the model in all catchments. Pesticide in drain flow in the late spring has also been observed by Brown *et al.* (2004) for sulfosulfuron, a post emergence herbicide which was applied to winter wheat on the 16th May 2000 and was measured in drain flow 10 days after application. Subsequent losses were not seen as there was a gap in drain flow between June and September 2000 (Brown *et al.*, 2004). Note that due to the scale of concentration in the Waveney catchment, due to large peaks in predicted concentrations in November and December, the increase in concentration in May and June is not visible (Figure 4.14c).

The results presented above compared predicted propyzamide concentrations with measured propyzamide concentrations. The same observations can be seen for the other four autumn –applied herbicides considered in Section 4.5 (carbetamide, chlorotoluron, mecorprop and isoproturon) and are presented in Appendix H.

For spring applied pesticides (2,4-D, clopyralid and MCPA) concentrations are predicted between May, June and July 2007 which is reflected in the measured data (Appendix H).

4.6.1. Discussion of hydrological pathways and pesticide concentrations

Catchment hydrological response plays a critical role in determining how pesticides are transported from land to water (Holvoet *et al.*, 2005). The contribution of diffuse pollution to the catchment outlet is a complicated function of soil type, climate, hydrology, topography, land use and land management, leading to multiple loss pathways (Heathwaite *et al.*, 2005).

Rainfall events following application are considered critical for transporting pesticides to surface water bodies, particularly if the soil is at or close to field capacity (Capel *et al.*, 2001; Leu *et al.*, 2004a; Nolan *et al.*, 2008).

Concentration patterns of pesticides in surface water can be linked to the rising limb and peak flows in the hydrograph (Müller *et al.*, 2003; Leu *et al.*, 2004a; Taghavi *et al.*, 2010; Taghavi *et al.*, 2011). For autumn-applied herbicides hydrograph predictions in the autumn and winter are important and for spring-applied herbicides summer peaks are important.

The hydrograph predictions between October and March, compared with the measured flow, for the timing and magnitude of hydrograph peaks are in general very good in the Lugg, Teme, Waveney and Yare (Figure 4.8a,b and Figure 4.10a,c Section 4.5). In the Wensum catchment, although the magnitude of peak events is not simulated well the predicted timing of the rising limb of the hydrograph for events between October and March is generally good when compared with the measured data (Figure 4.10b). This could explain why the timing of pesticide concentrations at the catchment outlet is well predicted in the Wensum.

Drain flow can be the dominant hydrological pathway in the autumn and winter, as seen in the field by Williams *et al.* (1996) in a study catchment in Herefordshire between 1987 and 1993, where the authors concluded that the transport of pesticides occurred by preferential flow to field drains between November and April. Tediosi *et al.*, (2012 and 2013) in the upper Cherwell demonstrated that once drain flow is initiated significant pesticide concentrations can be observed for several weeks after the initial application.

In the spring and summer the hydrograph predictions are not as good, often missing events in the hydrograph (Figure 4.8a,b and Figure 4.10a,b,c Section 4.5). This is most likely due to an under-estimation in overland flow which has consequences for predictions of pesticide concentrations as the pesticide fate and transport model requires both a rainfall event and hydrologically active pathway before pesticide transport can take place.

In a study by Logan *et al.* (1994) at a field site in NW Ohio surface runoff was found to have greater annual loads of pesticides than tile drains for spring applied pesticides reflecting that surface runoff was the dominant hydrological pathway in April to June and July to September.

4.7. Conclusions

This chapter has described the application of the pesticide fate model to five case-study catchments with varying pesticide-land use combinations. The hydrological model was calibrated for seven parameters and validated using NSE and PBIAS as goodness-of-fit criteria. It was shown to reproduce the hydrographs at the catchment outlet with acceptable fit to the observed data for four of the five catchments. This suggests that the representation of key hydrological pathways by the model may be adequate.

Outputs from the pesticide fate model are also reasonable in terms of the frequency of detection greater than $0.1 \mu\text{g L}^{-1}$ and the 90th percentile concentration compared with measured data, although performance is better for some catchment-pesticide-land use combinations than for others. When comparing measured and predicted time-series the simulations tend to predict the presence of pesticides at the catchment outlet sooner than the measured data. There are, however, uncertainties present in model predictions with respect to the assumptions regarding pesticide treated area, application rate and timing of application as well as uncertainty associated with the measured grab samples.

In conclusion, the pesticide fate and transport model developed has demonstrated that a broad-scale, processes-based model can generate acceptable reproductions of both hydrograph response and pesticide concentrations at the catchment outlet.

[This page is left intentionally blank]

Chapter 5. Conceptual Model of Pesticide Fate and Transport in the Unsaturated Zone

5.1. Introduction

The principal pathway of diffuse agricultural contaminants to groundwater is by the recharging water (Carsel *et al.*, 1985; Foster, 1998; Lapworth *et al.*, 2006). Transport mechanisms in the unsaturated zone which include intergranular matrix and preferential flow (which includes movement via macropores and fractures; Nimmo, 2012), affect both timing and magnitude of pesticide concentrations at the water table. For example, if pesticides were present within the percolating water that flowed into the fissure network there is potential that it could reach the water table very quickly (Brouyère *et al.*, 2004). On the other hand, intergranular matrix flow of pesticides through the unsaturated zone could lead to very long travel times (Adams *et al.*, 2000) and potentially a significant delay, as seen for nitrates (Howden *et al.*, 2011; Wang *et al.*, 2013).

The unsaturated zone can be composed of solid geologies, for example chalk, limestone or sandstone, or solid geologies overlain by superficial deposits. Superficial deposits (sometimes referred to as drift) are defined by the British Geological Survey (BGS) as geological deposits formed during the Quaternary period (BGS, 2013). Superficial deposits can range from glaciofluvial sands and gravels through to till (boulder clay). The presence and nature of superficial deposits can significantly influence the timing and volume of recharge reaching the water table (Hulme *et al.*, 2001; Marks *et al.*, 2001a; Goody and Darling, 2009; Griffiths *et al.*, 2011) and, therefore, in turn influence pesticide movement in the unsaturated zone to the water table. It is estimated that approximately 90% of the UK is covered by superficial deposits (Griffiths *et al.*, 2011).

There is an unoccupied niche for a pesticide fate and transport model to explicitly account for these key unsaturated zone processes which could affect the timing and magnitude of pesticide transfers to the water table, whilst also being applicable to a broad range of hydrogeological settings present in the UK.

Models such as MIKE-SHE (Christiansen *et al.*, 2004) and TRACE/3DLEWASTE (Herbst *et al.*, 2005) which have considered pesticide fate and transport to groundwater, however they tend to require a large amount of parameters and take a long time to set up and run.

This chapter outlines a conceptual model and mathematical description for an unsaturated zone pesticide fate and transport model. The predictions of percolation and pesticide mass flux from the soil zone that enters the unsaturated zone model are made with the soil water balance model and pesticide fate model described in Chapter 3, utilising the boundary condition at the interface between the subsoil and unsaturated zone (Section 3.3).

The overall aim of the unsaturated zone model is to aid water company risk assessment by determining pesticides that could reach the water table above $0.1 \mu\text{g L}^{-1}$ and the associated travel time. Therefore, the model outputs relate to the predicted peak concentrations at the water table and travel time of the peak concentration to the water table. This model only considers pesticide fate and transport through the unsaturated zone to the water table, and does not account for further movement in the saturated zone to the borehole or surface water resources.

5.2. Hydrogeological settings, transport pathways and pesticide fate

In order to incorporate a wide range of unsaturated zone scenarios that could influence the timing and magnitude of pesticide concentrations at the water table, three broad hydrogeological settings have been identified that occur in the UK. These are: (i) aquifer at outcrop, (ii) aquifer overlain by permeable superficial deposits and (iii) aquifer overlain by low permeability deposits (Figure 5.1). As the unsaturated zone model considers pesticide concentrations in drinking water resources only principal aquifers are considered. In most cases, principal aquifers were previously designated as major aquifers (EA, 2013b).

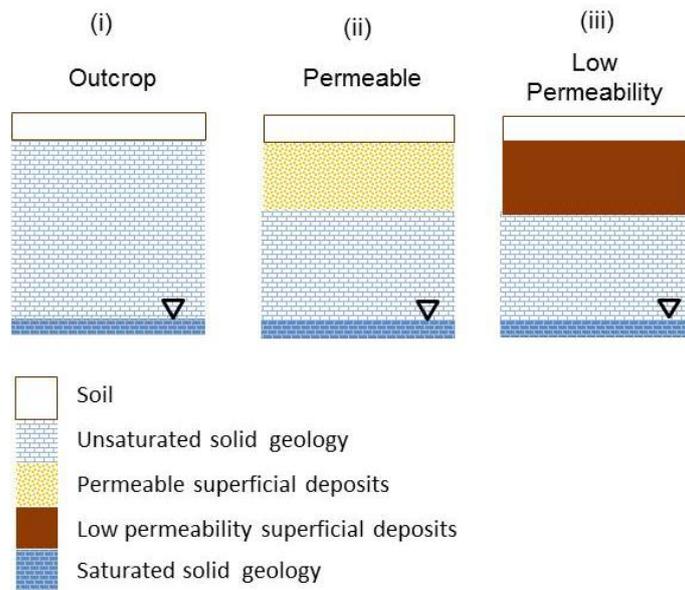


Figure 5.1. Schematic diagram of the three broad hydrogeological settings considered in the unsaturated zone model.

The hydrogeological settings only considering vertical transport through the unsaturated zone and only simulate transport to a principal aquifer with no account for perched water tables.

5.2.1. Aquifer at outcrop

This hydrogeological setting describes a situation where the soil directly overlies the solid geology with no superficial deposits present in the unsaturated zone (Figure 5.2). Water movement in the unsaturated zone can be as intergranular matrix flow, fracture flow or dual permeability (assuming transport in the matrix and the fracture); although the importance of each pathway varies between geological formations. For example the Lower Greensand is considered to have very minor fracturing and the flow will principally be intergranular (Allen *et al.*, 1997). On the other hand, in limestone geologies flow is more likely to be principally via the fractures (Grey *et al.*, 1995).

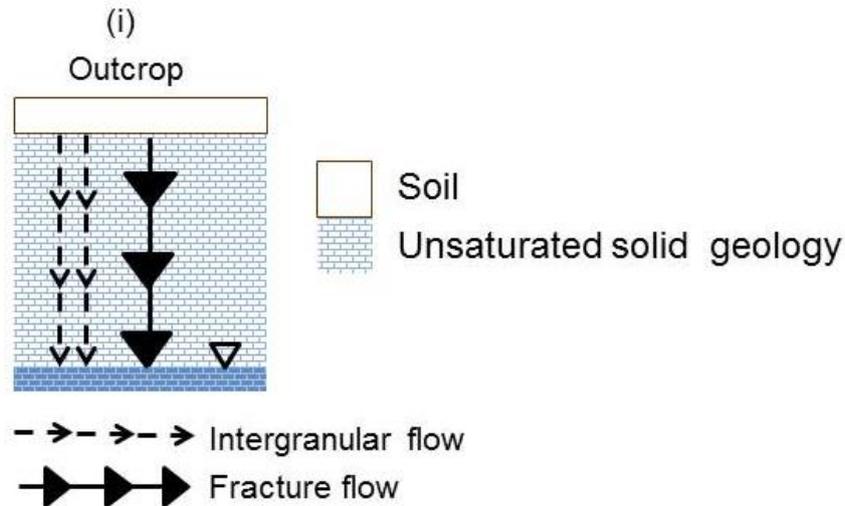


Figure 5.2. Schematic diagram of solute transport pathways in hydrogeological setting (i) aquifer at outcrop.

5.2.1.1. Intergranular matrix flow

Movement of solutes through the intergranular matrix in the unsaturated zone will be subject to advective transport (movement with the bulk flow), dispersive transport (dispersion of a solute at different rates as a result of variations in pore water velocity, which can in turn be as a result of differences in pore shapes and grain sizes; Batu, 2006) and diffusive transport (solute spreading as a result of a concentration gradient). In the unsaturated zone advective and dispersive transport are considered to be the dominant mechanisms (Spitz and Moreno, 1996).

To describe the transport of solutes through the intergranular matrix of the unsaturated zone an analytical solution of the advection-dispersion equation (ADE) is used (Hunt, 1983; Zheng and Bennett, 2002), assuming a single-source pulse of pesticide entering the top of the unsaturated zone. This was considered to be more suitable than assuming a continuous source as leaching is episodic and because pesticide degradation in the soil between application and a rainfall event will reduce the pesticide mass between percolation events and thus reinforces the non-continuous nature of the source.

As the model only considers vertical movement of solutes and water, only longitudinal dispersion is included, although in reality transverse dispersion is also possible. The solution employed (Hunt, 1983; Zheng and Bennett, 2002) can be written:

$$C_{ADE} = \frac{J_{UZ}}{2 \times \phi \times \sqrt{\pi \times D \times t_{UZ}}} \times \exp\left[-\frac{(Z_{UZ} - Fw \times t_{UZ})^2}{4 \times D \times t_{UZ}}\right] \quad (5.1)$$

where C_{ADE} is the predicted peak intergranular matrix concentration at the base of the hydrogeological unit being considered ($\mu\text{g m}^{-3}$), J_{UZ} is the initial mass flux entering the hydrogeological unit from the base of the soil zone at $t = 0$ ($\mu\text{g m}^{-2} \text{day}^{-1}$), ϕ is the total porosity of the hydrogeological unit (-), D is the dispersion coefficient ($\text{m}^2 \text{day}^{-1}$), t_{UZ} is time from the mass being added to the hydrogeological unit (days), Z_{UZ} is the thickness of the hydrogeological unit (m), and Fw is the pore water velocity (m day^{-1}). To convert the predicted concentration from $\mu\text{g m}^{-3}$ to $\mu\text{g L}^{-1}$ the output is divided by 1,000.

Fw is calculated from (Holman *et al.*, 2004):

$$Fw = \frac{K_{matrix}}{\phi} \quad (5.2)$$

in which K_{matrix} is the hydraulic conductivity of the matrix (m day^{-1}).

Dispersion results in a spreading out of a contaminant as it travels through the unsaturated zone. The dispersion coefficient is described as:

$$D = \alpha_L \times Fw \quad (5.3)$$

where α_L is the longitudinal dispersivity (m). The smaller the value of D the less pesticide mass will be spread out longitudinally (i.e. along the flow path).

It is worth noting that sorption and degradation processes are included during transport in the intergranular matrix. To account for degradation and sorption the analytical solution of the advection dispersion equation (Equation 5.1) can be extended to (Pang and Hunt, 2001):

$$C_{ADE} = \frac{J}{2 \times \theta \times RF_{UZ} \times \sqrt{\frac{\pi \times D \times t_{uz}}{RF}}} \times \exp\left[-\frac{\left(Z_{uz} - \frac{Fw \times t_{uz}}{RF}\right)^2}{\frac{4 \times D \times t_{uz}}{RF}}\right] \times \exp(-\lambda \times t_{uz}) \quad (5.4)$$

where RF_{UZ} is a dimensionless retardation factor in the unsaturated zone and λ is a degradation rate constant (days^{-1}).

RF_{UZ} is defined as:

$$RF_{UZ} = 1 + \left(\frac{(K_{OC} \times OC_{unsat}) \times \rho_{b,uz}}{\Phi} \right) \quad (5.5)$$

where OC_{unsat} is the organic carbon content of the unsaturated zone (-) and $\rho_{b,uz}$ is the bulk density of the unsaturated zone (g cm^{-3}).

The rate constant is calculated from:

$$\lambda = \frac{\ln(2)}{DT_{50(UZ)}} \quad (5.6)$$

where $DT_{50(UZ)}$ is the half-life in the unsaturated zone (days). The DT_{50} in the unsaturated zone is assumed to increase as a function of the lower organic carbon content in relation to the topsoil (Holman *et al.*, 2004) as follows:

$$DT_{50(UZ)} = DT_{50} \times \left(\frac{OC_{soil}}{OC_{UZ}} \right) \quad (5.7)$$

where OC_{soil} is the organic carbon of the topsoil (%) and OC_{UZ} is the organic carbon content of the unsaturated zone (%).

5.2.1.2. Fracture flow

The importance of fracture flow in order to enable preferential flow of pesticides past the bulk of the unsaturated zone matrix to the water table has been demonstrated in the field (e.g. Johnson *et al.*, 2001; Haria *et al.*, 2003; Brouyère *et al.*, 2004). Pesticide transport in fractures is described using an advection-only equation, which assumes that the solute is transported with the bulk flow of the water.

$$C_f = \frac{J_{UZ}}{qP} \quad (5.8)$$

where C_f is the concentration at the base of the fracture ($\mu\text{g l}^{-1}$).

The fractures are assumed to penetrate vertically through the full unsaturated zone thickness. In the unconfined north Norfolk chalk, fractures can penetrate to a depth of 20 m (Hiscock, 1993; Ireson *et al.*, 2012). The rapid movement through the fracture means that there is assumed to be insufficient time for solute exchange between the fracture and matrix or for degradation (Foster, 1998).

Fracture flow travel time through the hydrogeological unit is calculated as:

$$t_f = \frac{Z_{uz}}{K_f} \quad (5.9)$$

where t_f is the travel time through the fracture (days) and K_f is the hydraulic conductivity of the fracture (m day^{-1}).

5.2.1.3. Dual permeability

In dual permeability geologies, such as the chalk (Mathias *et al.*, 2006), fracture flow is episodic (Wheater *et al.*, 2006). The flux of water from the soil is one of the major controlling factors in the initiation of fracture flow (Jones and Cooper, 1998). The initiation of fracture flow has been postulated by several researchers to be as a result of the inability of the intergranular matrix to accept incoming water, i.e. the water flux entering the intergranular matrix is greater than the saturated matrix hydraulic conductivity, (Reeves, 1979; Wellings, 1984; Lee *et al.*, 2006). Lee *et al.* (2006) found that periods likely to have contained fracture flow all had a maximum daily rainfall intensity of more than 5 mm day^{-1} , which was greater than the saturated intergranular matrix hydraulic conductivity assumed for the chalk ($3 - 5 \text{ mm day}^{-1}$). In a tracer experiment in a chalk aquifer in France, Brouyère *et al.* (2004) concluded that fractures were inactive under natural recharge conditions and tracer movement was postulated to be

through the matrix. However, under a constant rate of water being added, fracture flow was initiated and rapid transport of the tracer was observed.

In the model, if percolation from the soil zone (as calculated in Section 3.2.7) entering the unsaturated zone is assumed to be greater than the saturated matrix hydraulic conductivity then transport occurs in both the intergranular matrix (up to the matrix saturated hydraulic conductivity) and the fracture. If percolation is less than saturated matrix hydraulic conductivity then only intergranular matrix flow is assumed. These assumptions have been used by Jones and Cooper (1998) and Van der Daele *et al.* (2007).

If transport via the intergranular matrix and fracture occurs then the pesticide mass flux is split according to the proportional hydrological contribution of the two flow domains as follows:

$$f_{fractures} = \frac{(qP - K_{matrix})}{qP} \quad (5.10)$$

$$f_{matrix} = 1 - f_{fractures}$$

where $f_{fracture}$ is the fraction of flow via the fracture and f_{matrix} is fraction of flow via the intergranular matrix.

For example, if the hydraulic conductivity of the intergranular matrix was 0.01 m day⁻¹ and the percolation event from the soil zone was 0.025 m day⁻¹ then the fraction of pesticide mass being transported by the fracture would be calculated as:

$$\frac{(0.025 - 0.01)}{0.025} * 100 = 60 \% \quad (5.11)$$

If the intergranular matrix hydraulic conductivity was 0.001 m day⁻¹ and the water flux remained the same then the fraction being transported by the fracture would now be:

$$\frac{(0.025 - 0.001)}{0.025} * 100 = 96 \% \quad (5.12)$$

5.2.2. Aquifer overlain by permeable superficial deposits

The recharge reaching the water table, and therefore the solutes transported, will depend on the lithology of the superficial deposits (Marks *et al.*, 2004a). More permeable superficial deposits, such as glaciofluvial sands and gravels will have higher rates of water movement in contrast to low permeability till. Fracturing in superficial deposits is not incorporated in the model due to uncertainty regarding how extensive fracturing is in low permeability deposits and difficulties in parameterising fracture flow in this lithology. Intergranular matrix flow is assumed to be the dominant pathway through superficial deposits (Allen *et al.*, 1997; Marks *et al.*, 2001a). Pesticide transport through the superficial deposits is predicted using the analytical solution of the ADE, still considering sorption and degradation (Equation 5.4).

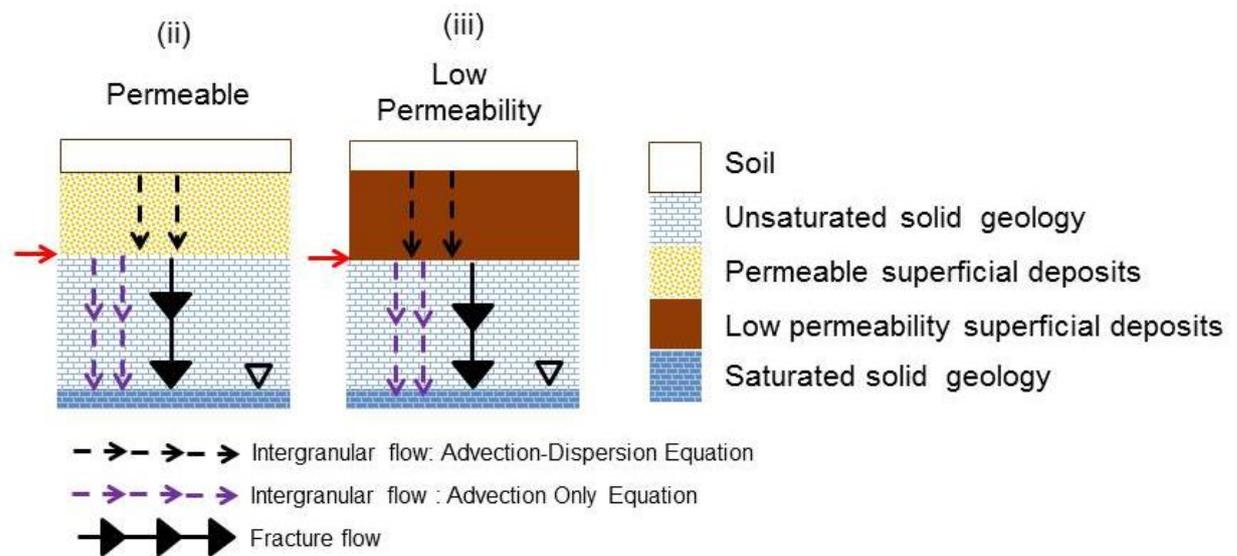


Figure 5.3. Schematic diagram of solute transport pathways in hydrogeological settings (ii) permeable superficial deposits and (iii) low permeability superficial deposits.

From the base of the superficial deposits to the water table (marked with the red arrow in Figure 5.3) the pesticide is transported through the unsaturated solid geology aquifer. If intergranular matrix flow is assumed in the solid geology, pesticide movement to the water table is described using an advection-only equation under unit hydraulic gradient (Equation 5.13). This is because the assumptions for a single-source pulse input upon which the ADE solution is based are no longer valid due to the dispersion of the pesticide in the superficial deposits.

$$C_{AO} = C_{ADE,peak} \times AF \quad (5.13)$$

where C_{AO} is the predicted intergranular matrix concentration at the base of the unsaturated zone ($\mu\text{g L}^{-1}$), $C_{ADE,peak}$ is the predicted peak intergranular matrix concentration from the ADE at the base of the superficial deposits ($\mu\text{g L}^{-1}$), and AF is a first-order attenuation factor (-) to account for degradation during transport, from Holman *et al.* (2004).

$$AF = \text{Exp} \left[-t_m \times \left(\frac{\ln(2)}{DT_{50(UZ)}} \right) \right] \quad (5.14)$$

where t_m is the travel time through the intergranular matrix (days) which is calculated using:

$$t_m = \frac{Z_{UZ} \times RF_{UZ}}{F_w} \quad (5.15)$$

If fracture flow is assumed in the solid geology below the superficial deposits, then the concentration at the water table is assumed to be equal to $C_{ADE,peak}$ (Equation 5.4) calculated at the base of the superficial deposits. This is as a result of the assumption that pesticides are not subject to degradation or sorption in the fractures.

For dual permeability solid geologies the initiation of fracture flow in the solid geology, when it is overlain by superficial deposits, is a function of the matrix hydraulic conductivity of the superficial deposits and the underlying solid geology aquifer. For example, if the intergranular matrix hydraulic conductivity

of glaciofluvial sands and gravels deposits was assumed to be 1 m day^{-1} and the intergranular matrix hydraulic conductivity of a chalk aquifer was 0.1 m day^{-1} then fracture flow could be initiated and would then be a function of the water flux through the superficial deposits. If, on the other hand, the intergranular matrix hydraulic conductivity of till superficial deposits was 0.01 m day^{-1} , then fracture flow would not be initiated.

5.2.3. Pesticide fate in the unsaturated zone

Pesticide fate in the unsaturated zone, as in the soil, is controlled by sorption to the solid phase and degradation processes (Farlin *et al.*, 2012). There is limited knowledge regarding sorption processes in the unsaturated zone. In a study exploring sorption in unsaturated zone material in France, Coquet (2003) found that although sorption did occur, it was highly variable.

Pesticide degradation in the unsaturated zone occurs at a slower rate than in the soil zone (Cavalier *et al.*, 1991; Chilton *et al.*, 1998; Issa and Wood, 1999). Issa and Wood (1999) studied the potential of the unsaturated zone to degrade atrazine and isoproturon and found a high degree of variability. In some samples atrazine half-lives ranged between 2 to 4 months and in others it was suggested that a decade could be required before significant degradation was seen. The factors controlling degradation rate was suggested to be the presence of microbial populations (Issa and Wood, 1999), and for most pesticides this is the primary degradation mechanism (Bloomfield *et al.*, 2006b). It is worth remembering that some unsaturated zone environments, such as superficial deposits, may contain significant microbial numbers and activity (Konopka and Turco, 1991), particularly where the organic matter content is high (Issa and Wood, 1999).

5.4. Conclusions

This chapter has outlined the development of a broad-scale conceptual model for pesticide fate and transport in the unsaturated zone to the water table. Two flow domains have been considered: intergranular matrix flow and fracture flow, with the option of dual permeability flow in the solid aquifer geology if required. Three hydrogeological settings have been identified: (i) aquifer at outcrop, (ii) aquifer overlain by permeable superficial deposits, and (iii) aquifer overlain by low permeability deposits. Pesticides are subject to degradation and sorption in the intergranular matrix flow pathway of the unsaturated zone, but not in the fractures. The hydrogeological settings can be parameterised to represent a variety of unsaturated zone aquifer scenarios.

Chapter 6. Application of the Unsaturated Zone Pesticide Fate and Transport Model

6.1. Introduction

This chapter covers the application of the unsaturated zone model outlined in Chapter 5 in order to investigate the role of unsaturated zone processes in affecting the timing and magnitude of pesticide transfers to the water table, considering the presence and permeability of superficial deposits. The three hydrogeological settings (identified and described in Chapter 5), (i) aquifer at outcrop (ii) aquifer overlain by permeable superficial deposits, and (iii) aquifer overlain by low permeability deposits, were parameterised for three principal UK aquifers (chalk, limestone and sandstone). The chalk represents a dual permeability aquifer, the sandstone an intergranular aquifer and the limestone a fractured aquifer. Sands and gravels represent permeable superficial deposits and till represents low permeability superficial deposits.

The chapter is split into four sections:

- Section 6.2 outlines the model set-up, including the parameterisation of the soil water balance and pesticide fate and transport model (described in Chapter 3) to provide predictions of pesticide mass flux at the top of the unsaturated zone and the derivation of unsaturated zone parameter values.
- Section 6.3 describes the results of the unsaturated zone model, presented as peak predicted pesticide concentrations and travel time to peak concentrations at the water table in all three hydrogeological settings.
- Section 6.4 provides a discussion of the significant role which the unsaturated zone plays in the timing and magnitude of pesticide exposure at the water table.
- Section 6.5 presents the conclusions to the chapter.

6.2. Methodology for unsaturated zone model setup

This section describes the model set-up for three hydrogeological settings in three principal aquifers chalk; limestone and sandstone. Before the unsaturated zone model can be executed, the soil water balance model and the pesticide fate model must be parameterised to provide a prediction of percolation and pesticide mass flux entering the top of the unsaturated zone (Chapter 3). Note, the model could be run in a semi-distributed manner for the whole recharge zone, as for the surface water catchments (Chapter 4). However, the main aim here is to explore the role which unsaturated zone processes play in controlling pesticide exposure at the water table.

6.2.1. Weather, soil and land use

The soil water balance model was run daily from 1989 – 2010 using rainfall and temperature data (for calculating evapotranspiration) from Santon Downham weather station in East Anglia (Section 4.3.1). This station is representative of climatic conditions in a predominantly agricultural area, but its selection was arbitrary. A representative soil was chosen for each aquifer and superficial deposit combination (Figure 6.1) by choosing a soil from a HOST class that best fits this combination (for a more detailed explanation of HOST see Section 3.3). Gustard *et al.* (1992) identified 34 hydrogeological units and assigned HOST classes to each one. For example, HOST class 1, 8 or 12 could represent a chalk aquifer at outcrop.

The bottom boundary hydraulic conductivity assigned to each representative soil (Table 6.1) is based on HOST class, as described in Section 3.3. For HOST classes 1 – 7 the value is from the SEISMIC database for the final soil layer (Section 3.3.2). For HOST 24 (Table 6.1) the bottom boundary hydraulic conductivity is set to 0.08 mm day^{-1} after Evans *et al.* (1999).

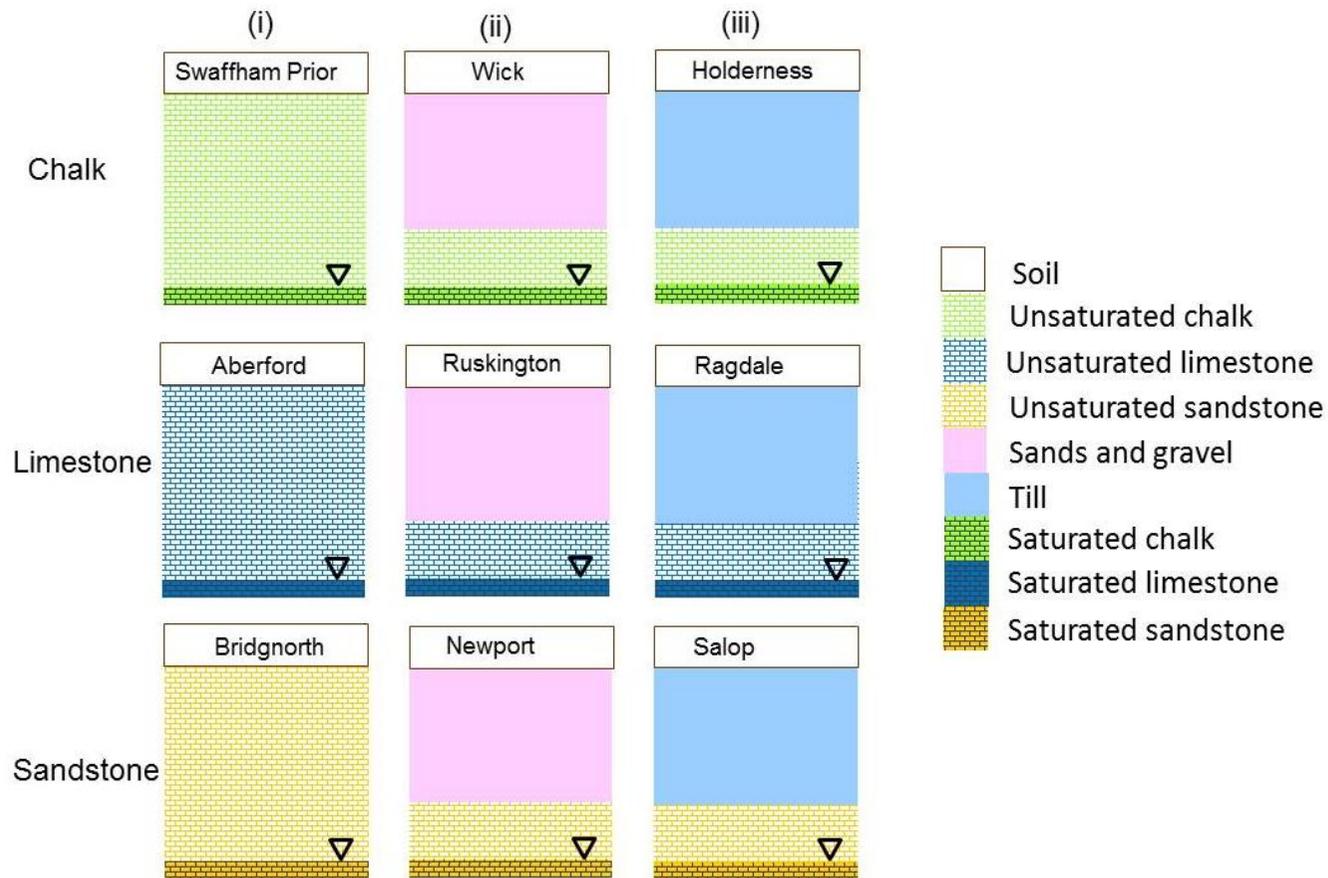


Figure 6.1. Diagram of the unsaturated zone model for different hydrogeological settings including the representative soil for each setting: (i) aquifer at outcrop; (ii) aquifer overlain by permeable superficial deposits; and (iii) aquifer overlain by low permeability deposits, for three principal aquifers: chalk; limestone; and sandstone.

Table 6.1. Properties of the representative soils used in the unsaturated zone model.

	Saturated sub-vertical hydraulic conductivity of lowest soil layer (mm day⁻¹)	HOST class	Hydrogeological unit (Gustard <i>et al.</i>, 1992)
Swaffham Prior	3109*	1	Chalk
Wick	3956*	5	Gravel, loamy drift
Holderness	0.08	24	Very soft massive clays
Aberford	2860*	2	Limestone
Ruskington	3187*	7	Loamy drift, river alluvium
Ragdale	0.08	24	Very soft massive clays
Bridgnorth	5589*	3	Sandstone
Newport	6774*	5	Gravel, loamy drift
Salop	0.08	24	Very soft massive clays

*Values from the SEISMIC database for arable land use.

The land use is assumed to be winter wheat and each pesticide (designated by a K_{OC} and DT_{50} combination) is assumed to be applied, arbitrarily, at a rate of 2 kg ha⁻¹. Only one application is considered, on the 1st of October (starting in 1991 to allow for a warm-up period in the water balance). Since the principal aim here is to understand the role which the unsaturated zone plays in pesticide transfers to the water table a more detailed explanation of pesticide application is not required.

6.2.2. Pesticide properties

K_{OC} and DT_{50} are the pesticide properties which most influence predictions of pesticide loss (Dubus *et al.*, 2003). The pesticide fate model was run for a range of K_{OC} (1 – 1,000 L kg⁻¹) and DT_{50} (1 – 350 days) values, to capture a range of possible pesticide properties. This resulted in 192 combinations. Note that the DT_{50} values are always quoted for the topsoil (unless otherwise stated).

The peak daily pesticide mass flux from the base of the soil zone from each K_{OC} and DT_{50} combination is assumed to enter the top of the unsaturated zone (i.e. the start of the unsaturated zone model) and be transported to the water table via intergranular matrix flow and/or fracture flow. The transport pathway depends on the aquifer geology (chalk, limestone or sandstone) and the presence/absence of superficial deposits (Figure 6.1).

The ADE used for predicting pesticide concentrations at the water table from the intergranular matrix flow pathway is set-up to run between $t = 1$ and $t = 100,000$ (i.e. 274 years), where $t =$ time (days). The day that the pesticide enters the unsaturated zone is assumed to be $t = 1$.

6.2.3. Unsaturated zone parameter values

The unsaturated zone model was run for a single set of parameter values chosen to be representative of each aquifer and its superficial deposits (Table 6.2). The parameter values were derived from published literature where possible, as described below.

Table 6.2. Parameter values used for each geological unit considered in the unsaturated zone model.

	Chalk	Sandstone	Limestone	Sands and Gravels	Till
Organic carbon (OC_{UZ}; %)	0.05*	0.05*	n/a	0.01*	0.1*
Saturated intergranular matrix hydraulic conductivity (K_{matrix}; m day⁻¹)	0.001	0.5	n/a	1.5	0.00001
Fracture hydraulic conductivity (K_f; m day⁻¹)	5	n/a	10	n/a	n/a
Bulk density (ρ_b; g cm⁻³)	1.6	2.11	n/a	1.8*	2
Total porosity (-)	0.3	0.26	n/a	0.25	0.32

* assumed

Note, that in the unsaturated zone model, total porosity (defined as the proportion of the air space in the rock; Grey *et al.*, 1995) is used when calculating solute movement through the intergranular matrix (Section 5.2.2) rather than effective porosity (defined as the proportion of interconnected pores available for flow in the total volume, which therefore excludes dead-end pores; Todd and Mays, 2005). This is because the effective porosity is rarely measured in the unsaturated zone.

In the Jurassic limestone aquifer, movement is typically through the fractures (Grey *et al.*, 1995), and has been estimated to be up to 30 m day⁻¹ (Andrews and Kay, 1982). Values in the limestone for organic carbon, porosity, bulk density and intergranular matrix hydraulic conductivity are not required as the solute transport pathway is assumed to be entirely via the fractures and, therefore, in the model not subject to sorption or degradation (Section 5.2.1.2).

Flow in the sandstone aquifer is assumed to be in the intergranular matrix only. Hydraulic conductivities of sandstone formations are highly variable and range over four orders of magnitude ($10^{-4} - 10 \text{ m day}^{-1}$; Allen *et al.*, 1997). Typically the porosity for sandstone is high (median values of 19 % – 31 %; Allen *et al.*, 1997). The bulk density ranges between 1.94 – 2.51 (Bloomfield *et al.*, 2006a).

The chalk is an example of a dual permeability aquifer (Mathias *et al.*, 2006). The intergranular chalk matrix, particularly the Upper and Middle Chalk found in eastern England, typically has a high porosity (25 – 45 %) and a low matrix hydraulic conductivity ($10^{-4} \text{ m day}^{-1}$ to $10^{-2} \text{ m day}^{-1}$; Price *et al.*, 1993). The bulk density of the chalk is generally between 1.5 and 1.6 g cm^{-3} (Bloomfield *et al.*, 1995). Fracture hydraulic conductivity of the chalk can be up to 10 m day^{-1} (UNESCO, 1984 IN Singhal and Gupta, 2010; Allen *et al.*, 1997).

Flow in both the permeable and low permeability superficial deposits is assumed to be intergranular matrix flow (Grey *et al.*, 1995). Field hydraulic conductivity values for sand and gravel superficial deposits in Norfolk were measured between 0.1 and 8 m day^{-1} (Klinck *et al.*, 1996). The porosity can range between 25 and 40 % (Sniffer, 2006). The intergranular matrix hydraulic conductivity of till is typically low; for example, in Norfolk hydraulic conductivity of the till was measured between $1 \times 10^{-6} \text{ m day}^{-1}$ to $1 \times 10^{-3} \text{ m day}^{-1}$ (Klinck *et al.*, 1996). From cored boreholes in the Lowestoft Till in eastern England estimates of bulk density range from 1.39 to 2.27 g cm^{-3} and porosity from 0.28 to 0.38 (Hiscock and Najafi, 2011).

For the longitudinal dispersivity parameter (αL), required for the ADE (Section 5.2.1), an approximation of 0.1 m is assumed, as Jørgensen *et al.* (1998), Jørgensen *et al.* (2004) and Chambon *et al.* (2011).

Two static water table depths were considered to investigate the effect of longer travel times and associated degradation on pesticide transfers; 4 mbgl (shallow) and 20 mbgl (deep). The superficial deposits overlying the aquifer beneath the soil profile, in hydrogeological settings (ii) and (iii) are assumed to be 2 m thick (Figure 6.2). For most representative soils, the soil thickness was 1.5 m, which

results in an unsaturated aquifer thickness of 0.5 m when the water table is 4 mbgl and 16.5 m when the water table is 20 mbgl. There were two exceptions where the soil was assumed to be shallower: Aberford (0.55 m) and Bridgnorth (0.7 m). In these two cases a reduction in the soil thickness was compensated by an increase in the unsaturated aquifer thickness.

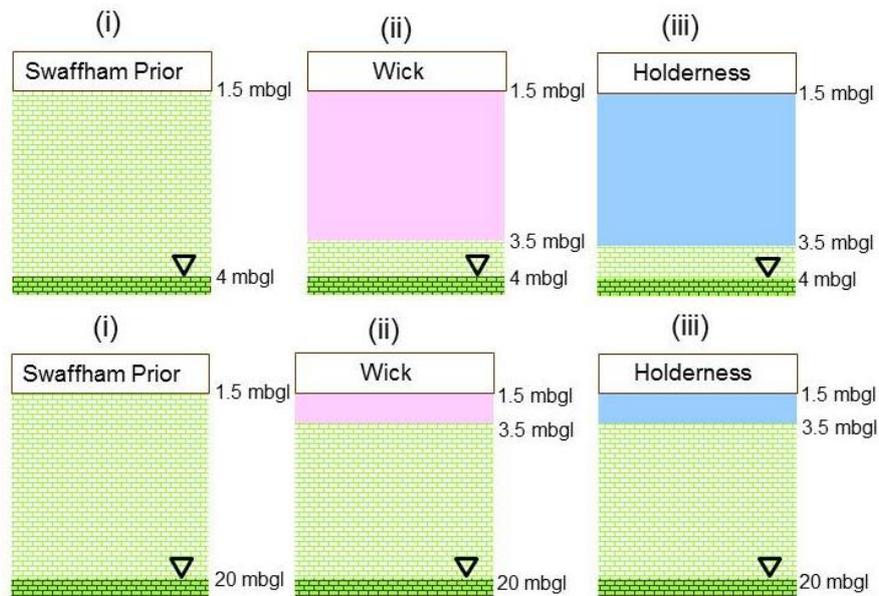


Figure 6.2. Example of hydrogeological unit thicknesses assumed in the unsaturated zone model in a chalk aquifer, for a water table depth of 4 mbgl and 20 mbgl.

6.3. Results for pesticide concentration and travel time to the water table

All results are presented as peak concentrations at the water table and the associated travel time from the start of the unsaturated zone. Peak concentrations can be considered are assessed with reference to the $0.1 \mu\text{g L}^{-1}$ MAC for drinking water.

6.3.1. Peak pesticide concentrations and travel time to the water table in a limestone aquifer

6.3.1.1. Limestone aquifer at outcrop

Predicted peak concentrations at the water table are all greater than $0.1 \mu\text{g L}^{-1}$ when the limestone aquifer is at outcrop (Figure 6.3). The pesticides are assumed to be travelling quickly via the fracture network to reach the water table (Table 6.3), as a result of the high fracture hydraulic conductivity and the assumption in the model that no sorption, degradation or dispersion occurs during transport, the peak concentrations at 4 mbgl and 20 mbgl are exactly the same. The change in depth does affect travel time to peak concentration, but the difference is small as the peak concentration reaches the water table in less than a day when the water table is 4 mbgl and in approximately two days when the water table is 20 mbgl (Table 6.3).

6.3.1.2. Limestone aquifer overlain by superficial deposits

When sand and gravel deposits overly the limestone aquifer, peak concentrations are reduced compared to when the limestone is at outcrop (Figure 6.3). This is due to the dispersion assumed in the sands and gravels. Over half (58 %) of the K_{OC} and DT_{50} combinations have predicted peak concentrations over $0.1 \mu\text{g L}^{-1}$ (i.e. when the K_{OC} is less than 500 L kg^{-1} ; Figure 6.3). The travel time through the sands and gravels and underlying limestone to the water table is quick, taking less than a day when the water table is 4 mbgl and less than three days when the water table is 20 mbgl (Table 6.3). This is due to the large hydraulic conductivity assumed for the sand and gravel deposits.

When till overlies the limestone aquifer predicted peak concentrations are all below $0.01 \mu\text{g L}^{-1}$ when the water table is at 4 mbgl (Figure 6.3) and 20 mbgl (not shown). These concentrations are a reflection of the long travel times, allowing opportunity for degradation, with the quickest peak reaching the water table after 18 years (Table 6.3). The longest predicted travel time is 274 years

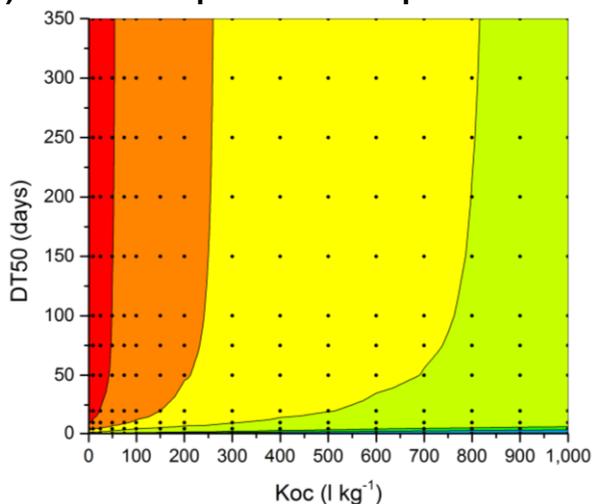
and represents the limit of the number of days in the ADE assumed in the model set-up (100,000).

Table 6.3. Maximum and minimum predicted travel time to peak concentration for the full range of K_{OC} and DT_{50} combinations, for water tables at 4 mbgl and 20 mbgl, and for three hydrogeological settings, assuming a limestone aquifer.

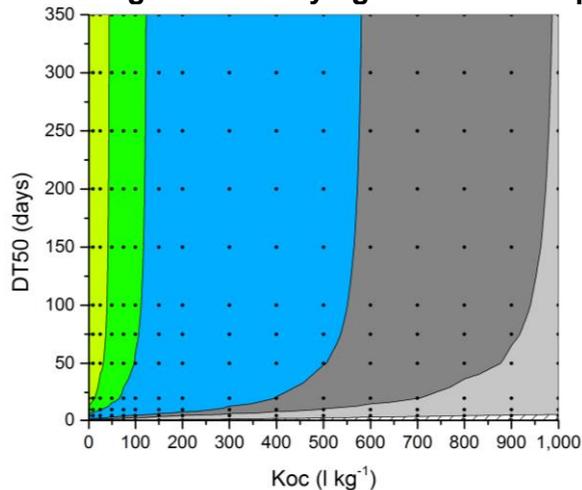
Hydrogeological setting	Travel time to water table: 4 mbgl	Travel time to water table 20: mbgl
(i) limestone aquifer at outcrop	0.3 days*	2 days*
(ii) sands and gravels over a limestone aquifer	0.3 – 0.7 days	2 – 2.5 days
(iii) till over a limestone aquifer	18 years – 274 years	18 years – 274 years

*Due to the flow domain being entirely dominated by the fractures there is no range available as the pesticide properties have no effect on travel time in this situation.

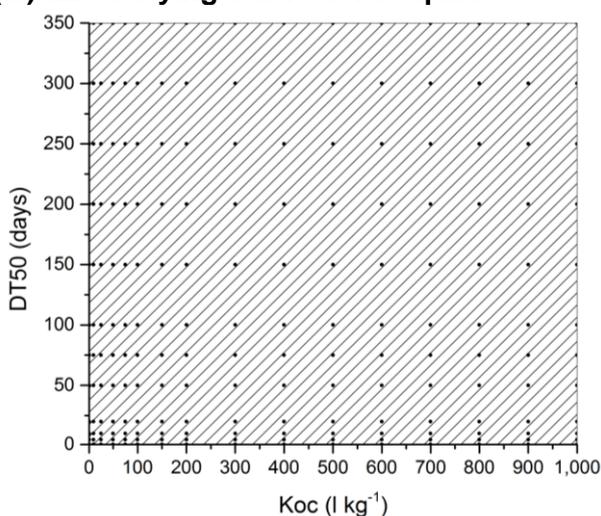
i) limestone aquifer at outcrop



(ii) sands and gravels overlying a limestone aquifer



(iii) till overlying a limestone aquifer



Key: peak concentrations (µg L⁻¹)

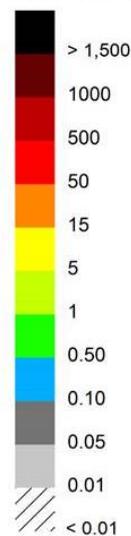


Figure 6.3. Predicted peak concentrations at the water table (4 mbgl) for three hydrogeological settings in a limestone aquifer. The dots represent the model run points.

6.3.2. Peak pesticide concentrations and travel time to the water table in a sandstone aquifer

6.3.2.1. Sandstone aquifer at outcrop

When the sandstone aquifer is at outcrop and the water table is at 4 mbgl, 77% of the peak concentrations are predicted to be greater than 0.1 µg L⁻¹ (Figure 6.4). This is a reflection of the intergranular matrix hydraulic conductivity resulting in a quick travel time (2 – 4 days; Table 6.4). When the water table is

at 20 mbgl, 55 % of the peak concentrations are predicted to be greater than $0.1 \mu\text{g L}^{-1}$ (Figure 6.5), but the travel time is only marginally slower (9 - 23 days; Table 6.4). The reduced predicted peak concentration between the two water table depths is due to the spreading of pesticide mass due to dispersion (as described in the ADE) during transport to a greater depth (Figure 6.6).

Table 6.4. Maximum and minimum predicted travel time to peak concentration for the full range of K_{OC} and DT_{50} combinations, for water tables at 4 mbgl and 20 mbgl, and for three hydrogeological settings, assuming a sandstone aquifer.

Hydrogeological setting	Travel time to water table: 4 mbgl	Travel time to water table: 20 mbgl
(i) sandstone aquifer at outcrop	2 – 4 days	9 – 23 days
(ii) sands and gravels over a sandstone aquifer	0.5 – 1 day	8 – 20 days
(iii) till over a sandstone aquifer	18 – 274 years	18 – 274 years

6.3.2.2. Sandstone aquifer overlain by superficial deposits

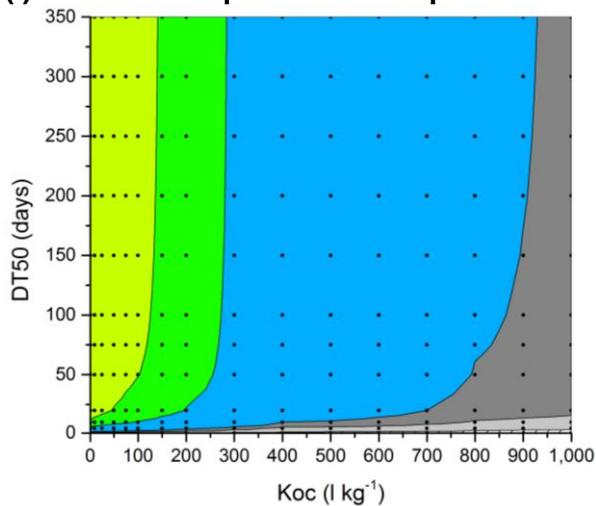
When sands and gravels overlie the sandstone aquifer, the predicted peak concentrations at the water table are reduced in comparison to when the sandstone is at outcrop, with only 3% greater than $0.1 \mu\text{g L}^{-1}$ (Figure 6.4). The travel time, however, is quicker than when at outcrop (approximately less than 1 day; Table 6.4). This is a result of the difference in predictions of mass flux, made by the soil water balance and pesticide fate model, for the representative soil for each hydrogeological setting (Figure 6.1). The mass flux from the Bridgnorth soil type entering the top of the sandstone aquifer at outcrop is larger than the mass flux from the Newport soil type entering the sand and gravels overlying the sandstone aquifer. The mass is smaller as a result of a larger $K_{(\theta)}:K_{sat}$ ratio (i.e. the difference between the two values is bigger) which results

in less pesticide displacement in the Newport soil (soil overlying sands and gravels) than the Bridgnorth soil (sandstone at outcrop). Hence the higher concentrations when the sandstone is at outcrop.

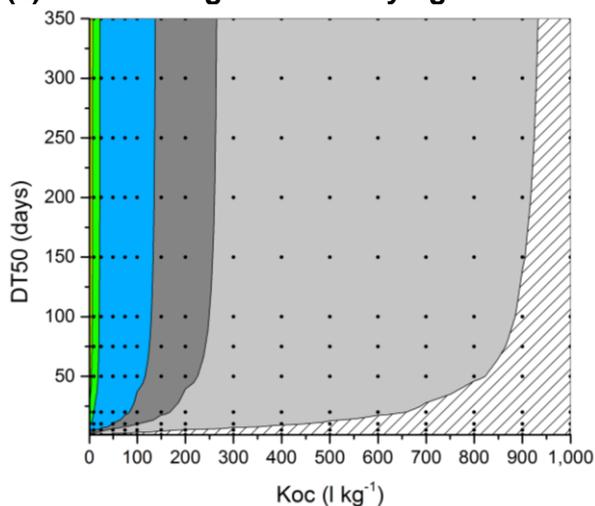
When the water table is at 20 mbgl peak concentrations greater than $0.1 \mu\text{g L}^{-1}$ are still predicted to be 3 % (Figure 6.5). A reduction in predicted concentration with an increase in depth is not seen (as it is when the sandstone aquifer is at outcrop). This is because when the sandstone aquifer is at outcrop the ADE equation is used, but when sand and gravel deposits overlie the sandstone the ADE equation is used in the deposits and the advection-only equation in the sandstone. This is because the assumptions for the analytical solution to the ADE for a single-pulse input are no longer valid (Section 5.2.1).

When till overlies a sandstone aquifer and the water table is 4 mbgl, the predicted peak pesticide concentrations are all below $0.01 \mu\text{g L}^{-1}$ (Figure 6.4). As when till overlies limestone, travel times when there is till are much longer than when the aquifer is at outcrop or when permeable deposits are present (Table 6.4).

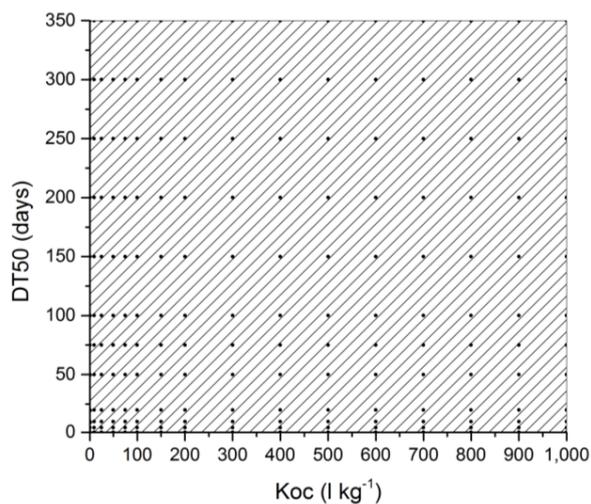
(i) sandstone aquifer at outcrop



(ii) sands and gravels overlying a sandstone aquifer



(iii) till overlying a sandstone



Key: peak concentrations ($\mu\text{g L}^{-1}$)

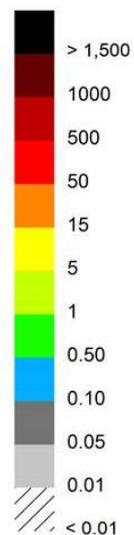
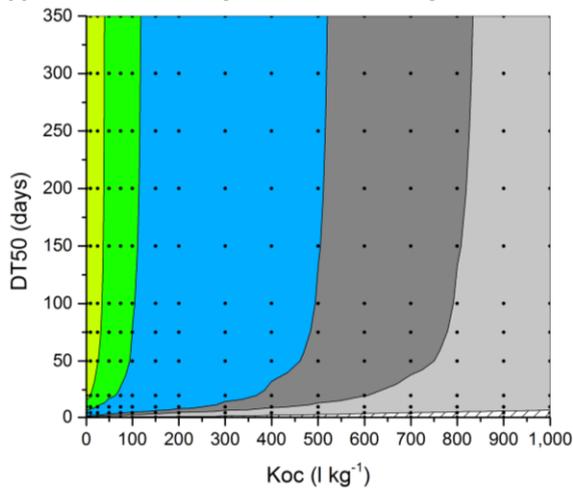
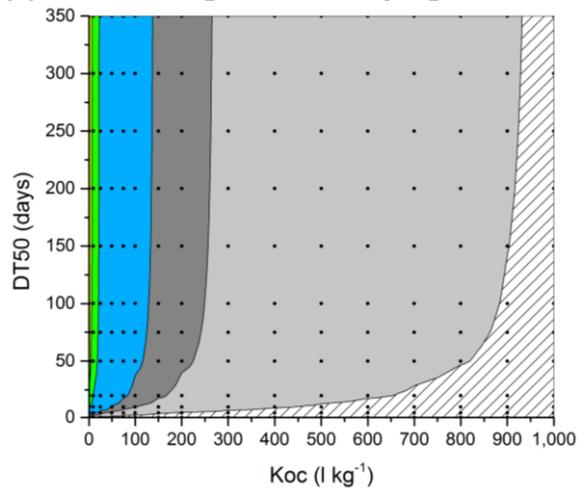


Figure 6.4. Predicted peak concentrations at the water table (4 mbgl) for three hydrogeological settings assuming a sandstone aquifer.

(i) sandstone aquifer at outcrop



(ii) sands and gravels overlying a sandstone aquifer



Key: peak concentrations ($\mu\text{g L}^{-1}$)

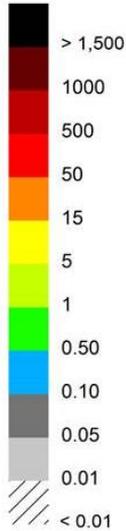


Figure 6.5. Predicted peak concentrations at the water table (20 mbgl) for two hydrogeological settings assuming a sandstone aquifer.

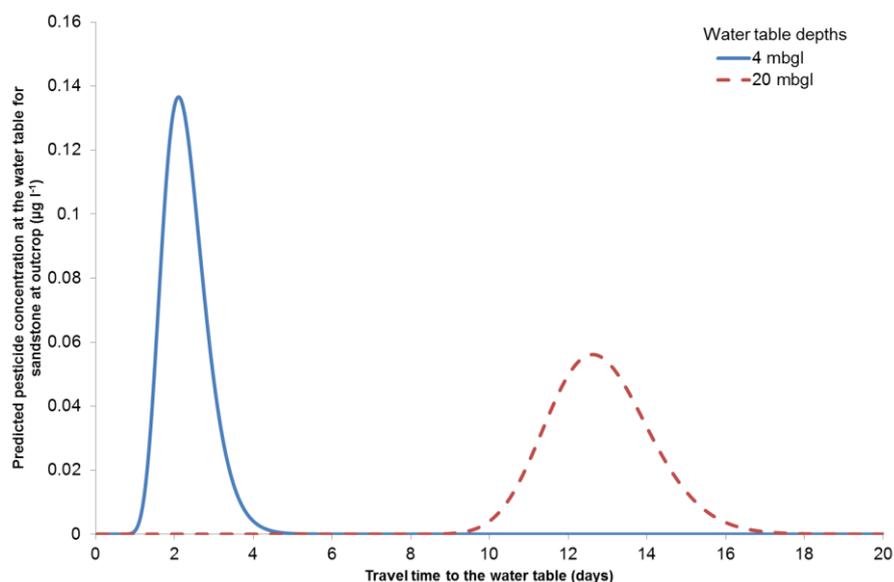


Figure 6.6. Predicted pesticide concentration at the water table when the water table is 4 mbgl and 20 mbgl, calculated with the advection dispersion equation assuming a sandstone aquifer at outcrop.

6.3.3. Peak pesticide concentrations and travel time to the water table in a chalk aquifer

6.3.3.1. Chalk aquifer at outcrop

The chalk is assumed to be dual permeability and at outcrop the predicted peak fracture concentration at the water table (4 mbgl) is higher than the peak intergranular matrix concentration (Figure 6.7). When the water table is 20 mbgl fracture concentration is the same as that predicted at 4 mbgl (as previously discussed when limestone is at outcrop; Section 6.3.1.1). However, the predicted peak intergranular matrix concentration reduces between the two water table depths (31% of predictions greater than $0.1 \mu\text{g L}^{-1}$ when the water table is 4 mbgl to 9 % when the water table is 20 mbgl). This 9 % of predictions greater than $0.1 \mu\text{g L}^{-1}$ represents pesticides with $K_{OC} < 25 \text{ L kg}^{-1}$ and $DT_{50} > 100$ days. This narrow range of K_{OC} and DT_{50} combinations is unlikely to occur in modern plant protection products (Holman *et al.*, 2004), as this combination has a high likelihood of leaching to water resources as well as the potential to be persistent in the environment.

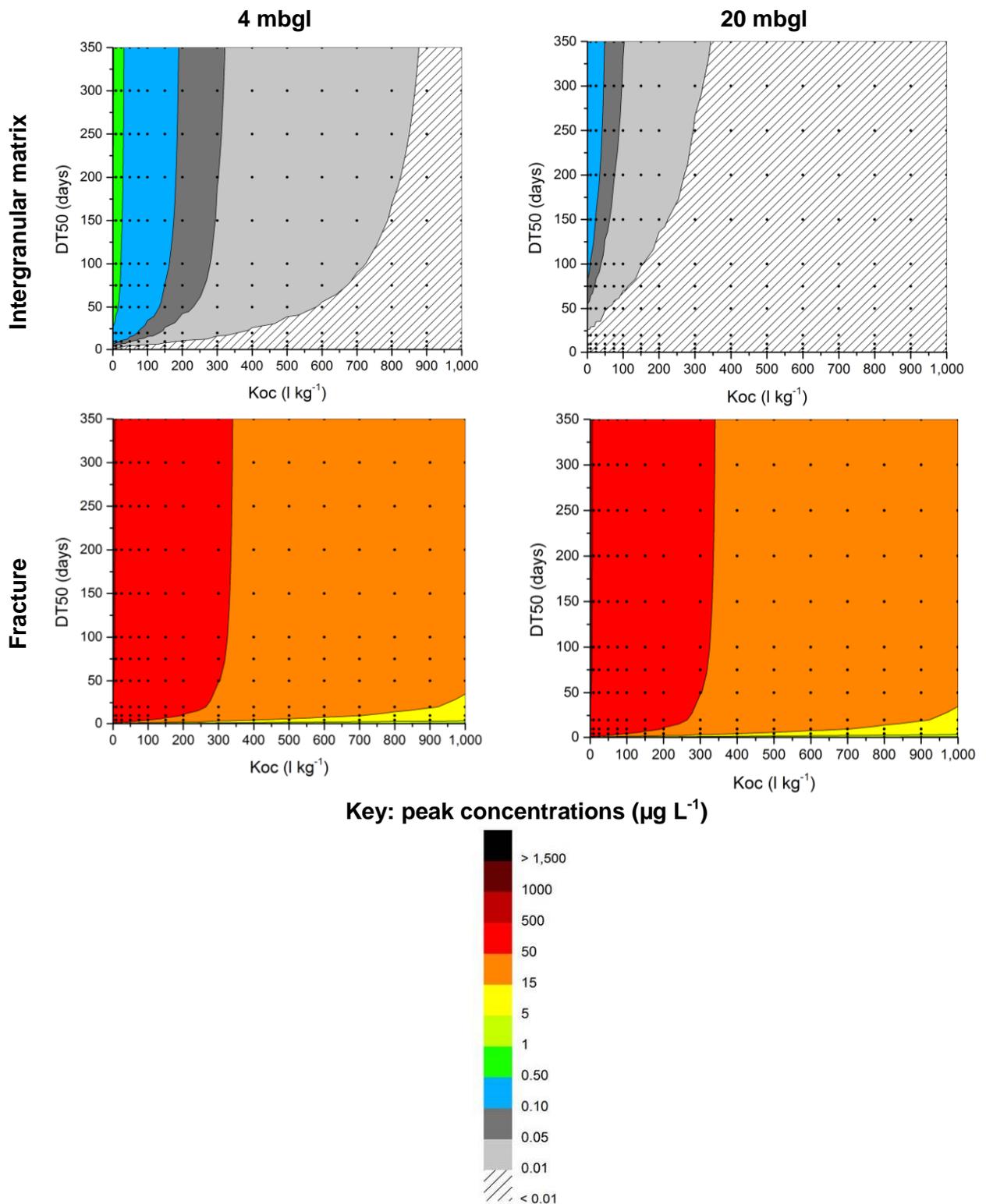


Figure 6.7. Predicted peak concentrations with the water table 4 mbgl assuming a chalk aquifer at outcrop and two flow pathways: intergranular matrix flow and fracture flow.

6.3.3.2. Chalk aquifer overlain by superficial deposits

Sand and gravel deposits overlying a chalk aquifer causes a decrease in predicted peak pesticide concentrations from the fractures at the water table, compared to fracture concentrations at outcrop (Figure 6.8). In the intergranular matrix flow pathway, the presence of sands and gravels increases the predicted peak water table concentration at both 4 mbgl and 20 mbgl (Figure 6.8) in comparison to chalk concentrations at outcrop. The predicted peak concentrations in the intergranular matrix are smaller in the chalk aquifer than the sandstone aquifer when both overlain by permeable superficial deposits. This is a result of a lower matrix hydraulic conductivity assumed in the chalk than the sandstone. As seen in the sandstone aquifer, the travel time to the water table when sands and gravel deposits are present is generally quicker when the chalk is at outcrop (Table 6.5). This is due to the higher matrix hydraulic conductivity of the sand and gravel deposits in comparison to the solid geology.

When till superficial deposits overly the chalk, predicted peak concentrations are always predicted to be less than $0.01 \mu\text{g L}^{-1}$ when the water table is 4 mbgl and 20 mbgl, as seen for limestone and sandstone aquifers (Figures 6.3 and 6.4), and is therefore not shown here. The travel time through till deposits is longer in comparison than when the aquifer is at outcrop or when there are permeable deposits present (Table 6.5). Fracture flow is not initiated in the chalk underlying the till because the matrix hydraulic conductivity of the till is less than the matrix hydraulic conductivity of the chalk.

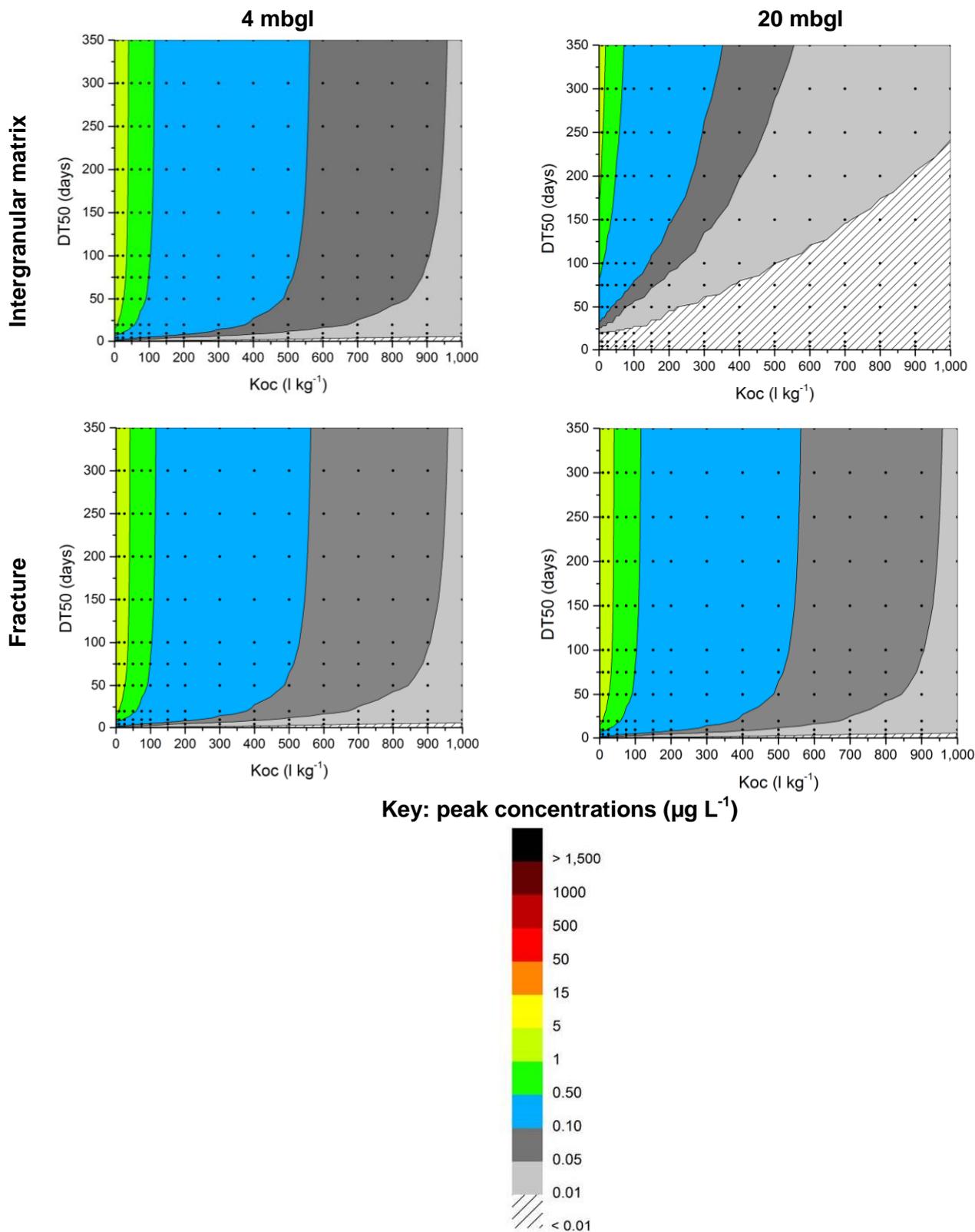


Figure 6.8. Predicted peak concentrations when the water table is 20 mbgl when the sands and gravels are overlying an unsaturated chalk aquifer and two flow pathways: intergranular matrix flow and fracture flow.

Table 6.5. Maximum and minimum predicted travel time to peak concentration in the intergranular matrix and fracture for the full range of K_{OC} and DT_{50} combinations, for the water table 4 mbgl and 20 mbgl, and for three hydrogeological settings, assuming a chalk aquifer.

Hydrogeological setting	Travel time to water table: 4 mbgl		Travel time to water table 20: mbgl	
	Intergranular matrix	Fracture	Intergranular matrix	Fracture
(i) chalk aquifer at outcrop	1 – 7 years	0.5 days	8 – 55 years	16.5 days
(ii) sands and gravels over a chalk aquifer	0.5 – 1.5 years	0.4 days	13 – 50 years	3.3 – 3.8 days
(iii) till over a chalk aquifer	16 – 276 years	n/a*	29 – 276 years	n/a*

*Fracture flow is not predicted to occur in the chalk as the potential recharge through the till is less than the intergranular matrix hydraulic conductivity of the chalk.

6.4. Discussion

6.4.1. The role of fractures in the unsaturated zone

The results generated by the unsaturated zone model suggest that fracture flow can lead to the appearance of high peak concentrations very quickly in comparison to intergranular matrix flow. This highlights the potentially significant role of preferential flow in transporting pesticides from the top of the unsaturated zone to the water table. Preferential flow via fractures to the water table was demonstrated in the chalk of southern England (water table 4 – 5 mbgl) by Johnson *et al.* (2001) where concentrations of isoproturon and chlorotoluron increased from background concentrations quickly after a large rainfall event. Similarly, Brouyère *et al.* (2004) showed that the peak tracer concentrations

resulting from artificial recharge in a chalk aquifer in Belgium with an unsaturated zone thickness of 8.5 m were reached in just eleven hours as a consequence of fracture flow. When a second experiment was carried out under natural recharge conditions (i.e. no artificial addition of water), the tracer was not detected after 700 days (which marked the end of the monitoring campaign). The authors suggest that fracture flow was not activated under the natural recharge conditions experienced during the experiment, and that transport was predominantly via the intergranular matrix.

One of the main assumptions in the unsaturated zone model is that fractures, if present in the solid geology, penetrate through the full unsaturated zone thickness and are interconnected. Not all fractures may connect to the water table, which could result in an over-prediction of the importance of fracture flow in some geological situations. Note that dead-end fractures can still play an important role in preferentially transferring pesticides deeper into the unsaturated zone. Once at a dead-end, water and solute within a fracture can infiltrate into the surrounding matrix and continue to travel to the water table (Su *et al.*, 2003). This would lead to a quicker breakthrough than expected by intergranular matrix flow alone.

Another assumption that could affect peak fracture concentrations in the unsaturated zone model is the assumption of no solute transfer between the fractures and the matrix. This process could potentially reduce concentrations at the water table. In the model it is assumed that the fracture hydraulic conductivity is too high to allow sufficient time for water and solute absorption into the surrounding matrix. In reality, however, this interaction will depend on the matrix potential and hydraulic conductivity of the matrix, as well as the flow rate in the fractures (Beven and Germann, 1982).

6.4.2. Travel time to the water table via the intergranular matrix

Travel time in the intergranular matrix is a significant factor in influencing pesticide concentrations at the water table. In the unsaturated zone model, the key physical properties that affect travel time are: intergranular matrix hydraulic conductivity, organic carbon content, the K_{OC} of the pesticide under consideration and the unsaturated zone thickness.

6.4.2.1. Intergranular matrix hydraulic conductivity

As the intergranular matrix hydraulic conductivity decreases there is a two-fold consequence to an increase in travel time; this allows more opportunity for degradation and it allows for greater dispersion. The effect of dispersion on solute breakthrough when hydraulic conductivity in the intergranular matrix is reduced is illustrated in Figure 6.9. In this example, we assumed that the aquifer is at outcrop, the pesticide has a K_{OC} of 100 L kg^{-1} and a DT_{50} of 5 days (i.e. in the topsoil, resulting in a DT_{50} of 675 days in the unsaturated zone), the water table is at 4 mbgl (3.5 m of unsaturated zone material) and the pesticide load at the top of the unsaturated zone, entering as an instantaneous spike, is $100 \mu\text{g m}^{-2}$.

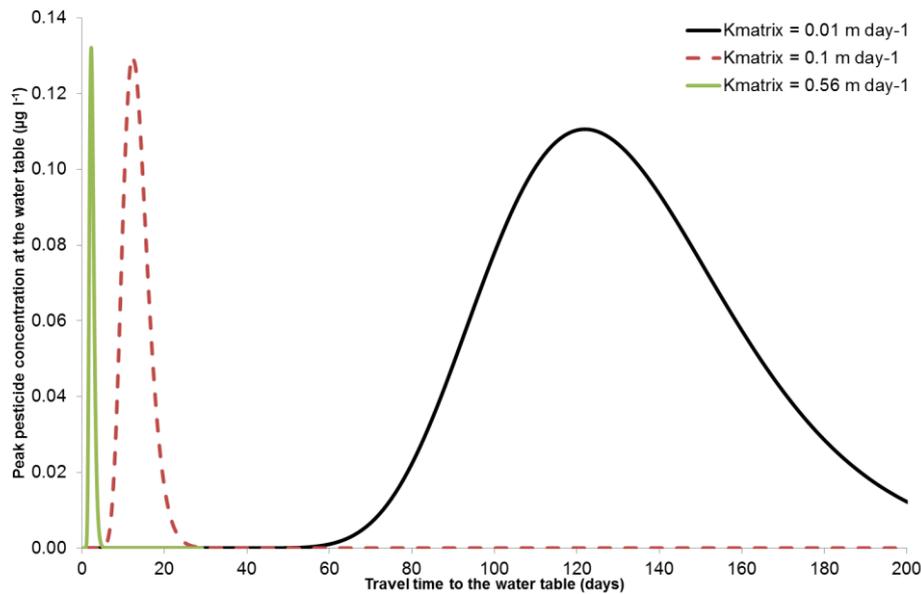


Figure 6.9. Illustrative predicted peak pesticide concentrations and travel time to the water table using the advection-dispersion equation for three different intergranular matrix hydraulic conductivities. For details of assumptions see text.

6.4.2.2. Organic carbon content and sorption

A change in pesticide travel time with changes in organic carbon content is linked to the calculation of retardation in the unsaturated zone. As the organic carbon content increases, the retardation of a pesticide as it moves through the intergranular matrix is also predicted to increase as a result of greater sorption hence, travel time increases. Some studies suggest that at low organic carbon contents (e.g. less than 1%), as seen in many unsaturated zones, sorption to organic carbon may not be the primary sorption process for some compounds, and instead sorption will primarily be to mineral surfaces (Fetter, 1993; Ghafoor *et al.*, 2013). In a series of experiments on unsaturated zone materials (including limestone, clays and sands) with three pesticides (atrazine, isoproturon and met amitron), Coquet (2001) determined that the distribution coefficient (K_d ; the ratio of sorbed chemical concentration to the concentration in the liquid phase) was strongly correlated to clay content. However, the sparse

data available for unsaturated zone clay content means that estimating sorption based on clay content is currently problematic.

6.4.2.3. *Unsaturated zone thickness*

Unsaturated zone thickness is a significant factor for determining travel times through the intergranular matrix in the unsaturated zone model. As the unsaturated zone thickens lower peak concentrations and longer travel times are predicted, particularly when the intergranular matrix hydraulic conductivity is low the reduction in concentration with depth is more marked (e.g. in a chalk aquifer in comparison to a sandstone aquifer). When studying spatial and temporal trends of pesticide exposure in the Triassic Sherwood Sandstone aquifer of South Yorkshire, Lapworth *et al.* (2006) concluded that significant concentrations were observed in the shallow part of the aquifer, but that longer term monitoring was required, between 5 – 10 years, to determine further temporal trends in pesticide concentrations.

The unsaturated zone model assumes that the water table is fixed and that, therefore, the unsaturated zone thickness is fixed. In reality, water tables will fluctuate. If water tables rise, pesticides in the unsaturated zone can be mobilised (i.e. flushed from the matrix), which will decrease the effective travel time to the saturated zone. A rise in the water table has been linked to peak concentrations of 1.2 $\mu\text{g l}^{-1}$ of diruon in a borehole in south-east England (Lapworth and Goody, 2006). Water table fluctuations can occur naturally, for example as a result of recharge, but they can also be artificially influenced, for example via local abstractions (Lapworth *et al.*, 2006).

6.4.3. Degradation in the unsaturated zone

Pesticides are assumed to undergo degradation during transport. Therefore, the longer the travel time the greater the opportunity for degradation. The lower the degradation rate assumed, the higher the peak intergranular matrix concentration predicted.

The choice of degradation rate constant derived from DT_{50} , therefore, has implications for the predicted arrival of pesticides used historically (including so called “legacy” compounds which have now been banned but which could still be moving slowly towards the aquifer in some systems). Evidence for long unsaturated zone travel time potential in the Triassic Sandstone of south Yorkshire has been presented by Goody *et al.* (2005) who discovered that mecoprop was present in both its R and S forms, indicating that it is likely to more than 20 years old. Assuming a degradation rate that is too rapid would result in an under estimation of the potential for a pesticide to appear at the water table at measurable concentrations years after application. On the other hand, assuming too low a degradation would lead to an over estimation of legacy pesticide exposure.

6.4.4 Superficial deposits

Application of the unsaturated zone model has highlighted the potentially significant role that superficial deposits can have in the prediction of pesticide exposure and travel times to the water table. Permeable sand and gravel deposits generally result in an increase in predicted concentrations at the water table in aquifers where flow is via the intergranular matrix, as the hydraulic conductivity is typically greater than that of the underlying aquifer. On the other hand, when sands and gravels overlie fractured aquifers, the deposits can provide a degree of protection relative to situations when the aquifer is at outcrop.

Low permeability superficial deposits are predicted to provide a degree of protection to underlying aquifers by increasing travel times and allowing time for degradation. However, weathering in low permeability superficial till deposits can cause fracturing and, therefore, the potential for faster transport (Klinck *et al.*, 1996; Marks *et al.*, 2001a; Hiscock *et al.*, 2011). The most intensely weathered zone is typically developed close to the till surface and is often only 2 – 4 m thick (Marks *et al.*, 2004a), although it can reach up to 10 m (Griffiths *et al.*, 2011). However, it is often underlain by unweathered till (Marks *et al.*,

2004b; Hiscock *et al.*, 2011). Fracturing in low permeability deposits is not accounted for in the model described here, but could potentially increase the vulnerability of underlying aquifers. It is worth remembering that the mass flux predicted to enter the unsaturated zone is based on the boundary conditions between the subsoil and the unsaturated zone. When till deposits are present, the primary pathway for pesticide mass leaching from the soil zone is laterally, typically via artificial field drains (Soley and Heathcote, 1998). Therefore, the mass assumed to enter the top of the unsaturated zone is smaller than when sand and gravel deposits are present.

6.5. Conclusions

In this chapter the unsaturated zone model was used to illustrate the potentially significant role that unsaturated zone processes can play in controlling the timing and magnitude of pesticide transfers to the water table. The vulnerability of the water table to meaningful pesticide exposure (e.g. concentrations greater than $0.1 \mu\text{g L}^{-1}$) is considerably influenced by pesticide properties (K_{OC} and DT_{50}), the transport pathways assumed to be active (along with associated physical properties such as hydraulic conductivity), the thickness of the unsaturated zone and the presence and nature of superficial deposits. Importantly, the travel time to peak concentrations will affect whether or not persistent 'legacy' chemicals are still likely to appear in groundwater bodies as a consequence of slow unsaturated zone travel times. If the history of pesticide use can be estimated in a groundwater recharge zone, good travel time estimation could also be used to predict the timing of exposure in abstracted water and, hence, guide the choice of pesticides requiring monitoring by water companies.

Chapter 7. Scenario Modelling at the Catchment Scale in Surface Water Resources

7.1. Introduction

To illustrate the predictive ability of the pesticide fate and transport model developed in Chapter 3, the model was applied to a set of case study mitigation scenarios designed to reduce pesticide concentrations to below $0.1 \mu\text{g L}^{-1}$ at the catchment outlet. The mitigation scenarios considered can be split into three broad categories:

- Temporal restriction on the timing of application with respect to drain flow.
- Spatial targeting of pesticide application (e.g. restriction of application on vulnerable soils, such as those where artificial drains are likely to have been installed).
- Change in crop area (e.g. a shift from winter-sown to spring-sown crops).

The chapter is split into four sections:

- Section 7.2 outlines the case study mitigation scenarios to be explored using the model and the set-up of the model for two contrasting catchments.
- Section 7.3 presents the results of the case study mitigation scenarios with respect to a baseline (i.e. current cropping and pesticide use).
- Section 7.4 provides a discussion on the effectiveness of each case-study mitigation intervention in terms of reducing pesticide concentrations at the catchment outlet.
- Section 7.5 presents the conclusion to the chapter.

7.2. Methodology

The model was applied to two contrasting catchments to explore the effect of different example mitigation scenarios (based on previous work presented by Garrett and Kennedy, 2006; Reichenberger *et al.* 2007) on pesticide concentrations at the catchment outlet. Propyzamide was chosen as a representative pesticide, with the Lugg and the Yare as representative catchments. These catchments represent different catchment sizes, climates, soils, geologies and arable land use area (see Table 4.1 and Table 4.5 in Section 4.2).

The mitigation scenarios were compared to a baseline scenario in which the application window for propyzamide on winter OSR was assumed to be 17 weeks from the 1st October to the 31st January, application was assumed to be at the maximum dose rate and loading evenly spread across the 17 weeks (as described in Section 4.3.7). If rainfall on a proposed day of application was more than 0.5 mm day⁻¹ then it is assumed that spraying does not occur and the application moves forward to the next day. Unless otherwise stated all the assumptions and parameters for each case-study mitigation scenario are the same as the baseline scenario.

7.2.1. Temporal restrictions of application

Temporal restriction of propyzamide application with respect to drain flow was explored with two scenarios. In the first scenario application was restricted when drains are flowing such that the application day is moved forward until a day is identified when there is no drain flow. Proxy-zero values (0.5 mm and 0.1 mm day⁻¹) are required as predictions of drain flow are rarely zero, this is a result of the exponential equation used to calculate drain flow (Section 3.2.5). This is in accordance with actual drainage systems for which flow is positive during the whole of the winter period (e.g. Tediosi *et al.*, 2012).

In the second scenario, propyzamide application is restricted to September only (Garrett and Kennedy, 2006; Reichenberger *et al.*, 2007), before the typical

expected onset of drain flow. This restriction is designed to increase the interval between application and initiation of drain flow, thereby allowing more time for degradation and sorption (Carter, 2000b; Brown and van Beinum, 2009). The application window is now assumed to be across four weeks, from the 1st September to the 30th September. As a result of the shorter application window a greater loading of pesticide will be applied each week. Note there is no change to the assumed planting date of winter oilseed rape (31st August). In both scenarios outlined above it is assumed that 100 % of farmers in each catchment participate.

7.2.2. Spatial targeting of pesticide application

The third scenario explores spatial targeting of propyzamide application with a restriction of use to “vulnerable soils”, such as those with artificial drains installed (Garratt and Kennedy, 2006; FOCUS, 2007; Reichenberger *et al.*, 2007; Brown and van Benium, 2009). In the soil water balance model, the soil types with a high likelihood of artificial field drains are assigned to boundary condition B at the interface between the subsoil and the unsaturated zone (Table 3.1 Section 3.3). Restrictions of application are assumed to be via reductions in treated areas on these vulnerable soils: 75 %, 50 % and 25 % through to a complete ban (0 %). This range is intended to identify the level of restrictions required to bring concentrations below 0.1 µg L⁻¹. Soils that are not assumed to be artificially drained face no restriction to application.

7.2.3. Change in area of winter oilseed rape grown

The final scenario explores the effect of changing cropping from winter OSR (assumed to receive propyzamide) to spring OSR (assumed to be receiving metazachlor; applied to spring OSR as a post-emergence herbicide). Propyzamide and metazachlor were chosen as representative pesticides in order to explore how a switch from one crop to another can affect the total frequency of pesticide concentrations at the catchment outlet.

The percentage of arable land in the Lugg and Yare catchment growing winter OSR was varied in a one-at-a-time, step-wise, manner with direct substitution of winter OSR for spring OSR (Table 7.1). In this way we can specifically investigate the potential for “pollution swapping”. Pollution swapping can occur when a mitigation option brings about an increase in concentrations of a different pollutant (Stevens and Quinton, 2009). Note, the maximum amount of oilseed rape (winter or spring) grown in either catchment is assumed to be 10 %. This is based on the DEFRA June Survey statistics for the area of winter OSR typically grown at a county level (DEFRA, 2010).

Table 7.1. Percentages of arable land in the Lugg and Yare catchment growing winter OSR and spring OSR for the case study mitigation scenario exploring the effect of change in cropping, considering a step-wise approach.

	Scenario						
	4a	4b	4c	4d	4e	4f	4g
Percentage of winter OSR	10 %	8 %	6 %	4 %	2 %	1 %	0 %
Percentage of spring OSR	0 %	2 %	4 %	6 %	8 %	9 %	10 %

In Chapter 4, the crop treated area was estimated and fixed (Table 4.11 in Section 4.3.7). To capture the uncertainty associated with fixing the crop treated area, the percentage of winter and spring OSR receiving either propyzamide or metazachlor will vary from 0% to 100%.

7.2.4. Input data

For all model case study scenarios, only the worst case pesticide K_{OC} and DT_{50} values were used for each substance. “Worst case” values represent the highest DT_{50} and the lowest K_{OC} reported in the literature. Predicted concentrations obtained using the “best case” values for propyzamide were less the LOQ in both catchments (Table 4.17, Section 4.5.2.1). The crop parameters

required with the soil water balance model for spring oilseed rape are detailed in Table 7.2 and are taken from Holman *et al.* (2005).

The application rate for metazachlor is assumed to be at the maximum label rate of 0.75 kg ha⁻¹ (Appendix E) and the application window is assumed to cover 3 weeks between emergence (24th April) and 10 % crop cover (14th May). Metazachlor K_{OC} (134 L kg⁻¹) and DT_{50} (29 days) values are from the CatchIS database (CatchIS, 2013). K_{OC} and DT_{50} values for propyzamide can be found in Table 4.10 Section 4.3.6.

Table 7.2. Crop parameters and crop dates assumed for spring oilseed rape.

	Spring OSR*
Rooting depth at emergence (m)	0.025
Maximum rooting depth (m)	1.2
K_c initial	1
K_c middle	1.05
K_c end	0.3
Depletion factor (p ; -)	0.7
Planting date	9 th April
Emergence (days)	15
10 % cover (days)	21
100 % cover (days)	10
Senescence (days)	92
Harvest date	9 th September

* Parameters from Holman *et al.* (2005).

The pesticide fate and transport model was run for all four mitigation scenarios in both catchments. Results are presented for three winter OSR crop years: Year 1: September 2006 – August 2007, Year 2: September 2007 – August 2008, and Year 3: September 2008 to August 2009. The results are presented as the 90th percentile concentration and the frequency of predictions greater than 0.1 µg L⁻¹; this is to be consistent with the result presented in Chapter 4.

Calibrated flow parameters for the Lugg and the Yare catchments remain unchanged (Table 4.14 in Section 4.4.2).

7.3. Mitigation scenario results

7.3.1. Temporal restrictions on the timing of application

7.3.1.1. Restricting propyzamide application when drains are flowing

Restricting application in the Yare catchment to when drain flow is less than 0.5 mm day⁻¹ results in only a small change from the baseline in the 90th percentile concentration and the frequency of detection > 0.1 µg L⁻¹ (Table 7.3). This occurred in all crop years considered between September 2006 and August 2009 (Table 7.3). The same restriction in the Lugg catchment, in contrast, produces a reduction in the 90th percentile concentration to less than LOQ, and no concentrations greater than 0.1 µg L⁻¹ were predicted in Year 1 or Year 3 (Table 7.4). The 0.27 % of predictions greater than 0.1 µg L⁻¹ in Year 2 (Table 7.4) is a result of the other flow pathways available for pesticide transport in the catchment (surface runoff and lateral throughflow).

The difference between the two catchments is a consequence of the number of days when application is assumed to occur as a result of the temporal restriction. For example, from October 2006 to January 2007 in the baseline scenario, propyzamide application occurs every week (i.e. the loading is spread evenly over the application period) in both catchments. In comparison, when the application day is moved forward until drain flow is less than 0.5 mm day⁻¹ (keeping the total application to each catchment constant) then only two application days are possible in the Yare catchment (20th October 2006 and the 29th December 2006; Figure 7.1). On the 20th October 2006 three weeks of propyzamide loadings are made (i.e. the applications delayed between the 01st October 2006 and 19th October 2006). On the 29th December 2006 ten weeks of delayed application is assumed to be applied (from the 21st October 2006 to

28th December 2006). Therefore, loading increases on days when application is possible, resulting in much higher propyzamide concentrations in the drain flow events following application compared to the baseline scenario (Figure 7.1). These conclusions are repeated in Year 2 and Year 3.

In the Lugg catchment there is only one day in the application window which is suitable (03rd October 2006). This is in the first week in the application window and therefore in the model only one propyzamide application in the available 17-week window is assumed. In both the Yare and the Lugg catchments restricting application to when drain flow is less than 0.1 mm day⁻¹ resulted in a reduction in predicted concentrations to less than LOQ at the 90th percentile for all crop years (Table 7.3 and Table 7.4). In addition, in this scenario there are no modelled concentrations greater than 0.1 µg L⁻¹. This is a consequence of no propyzamide being applied in either catchment in the model.

Table 7.3. Predicted 90th percentile concentrations and frequency of detections greater than 0.1 µg L⁻¹ at the catchment outlet in the Yare catchment for the baseline and three temporal restriction mitigation scenarios, by crop year from September 2006 to August 2009.

Scenario	Year	Baseline	Restriction in timing of application		
			< 0.5 mm day ⁻¹ drain flow	< 0.1 mm day ⁻¹ drain flow	Application in September only
90th percentile concentration (µg L⁻¹)	1 (2006/2007)	0.24	0.20	< LOQ	0.20
	2 (2007/2008)	0.15	0.14	< LOQ	0.10
	3 (2008/2009)	0.20	0.18	< LOQ	0.18
Frequency of detections greater than 0.1 µg L⁻¹ (%)	1 (2006/2007)	22 %	19 %	0 %	18 %
	2 (2007/2008)	16 %	14 %	0 %	11 %
	3 (2008/2009)	17 %	16 %	0 %	14 %

Table 7.4. Predicted 90th percentile concentrations and frequency of detections greater than 0.1 µg L⁻¹ at the catchment outlet in the Lugg catchment for the baseline and three temporal restriction mitigation scenarios, by crop year from September 2006 to August 2009.

Scenario	Year	Baseline	Restriction in timing of application		
			< 0.5 mm day ⁻¹ drain flow	< 0.1 mm day ⁻¹ drain flow	Application in September only
90th percentile concentration (µg L⁻¹)	1 (2006/2007)	0.16	< LOQ	<LOQ	0.15
	2 (2007/2008)	0.14	< LOQ	< LOQ	< LOQ
	3 (2008/2009)	0.06	< LOQ	< LOQ	< LOQ
Frequency of detections greater than 0.1 µg L⁻¹ (%)	1 (2006/2007)	19 %	0 %	0 %	15 %
	2 (2007/2008)	14 %	0.27 %	0.27 %	0.27 %
	3 (2008/2009)	7 %	0 %	0 %	0 %

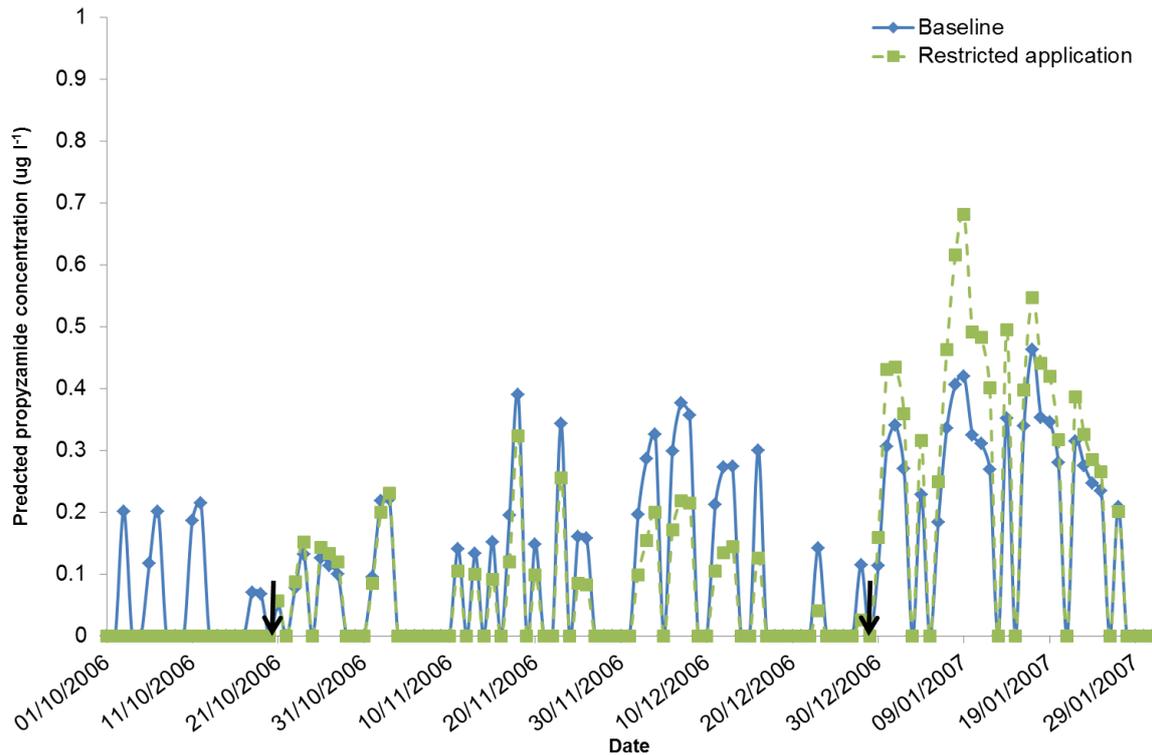


Figure 7.1. Predicted propyzamide concentrations in the baseline scenario and predicted concentrations when restricting application when drain flow is greater than 0.5 mm day^{-1} in the Yare catchment between October 2006 and January 2007. Available application days in the mitigation scenario are shown with the black arrows.

7.3.1.2. September only propyzamide application

Restricting propyzamide application to September resulted in a small reduction in the predicted 90th percentile propyzamide concentration and the frequency of detection greater than $0.1 \mu\text{g L}^{-1}$ in the Yare and Lugg catchments in all years considered (Table 7.3 and Table 7.4). As Figure 7.2 demonstrates when drain flow is initiated, towards the end of September 2006, and pesticide displacement is possible, concentrations are predicted to be higher than in the baseline scenario at the catchment outlet. This is because it is assumed that all of the farmers growing oilseed rape in the catchment are assumed to switch to applying propyzamide in September and as a result this concentrates the application of pesticide to a four-week window. Therefore, when drain flow is initiated the mass in the soil available for displacement is larger than when the

application is spread over 17 weeks. Concentrations at the end of September and the start of October are, therefore, higher than those predicted for the baseline (Figure 7.2).

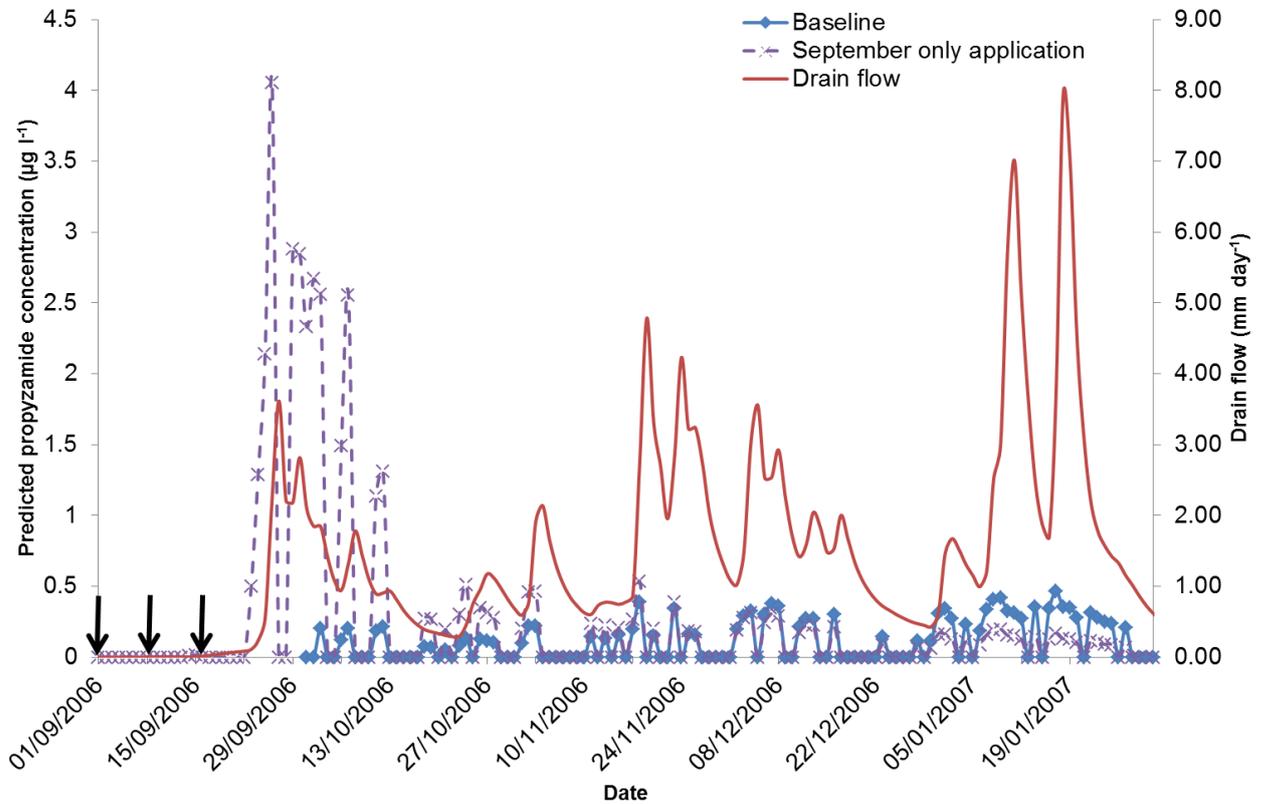


Figure 7.2. Predicted propyzamide concentrations in the baseline scenario and predicted concentrations with a September-only application window in the Yare catchment between September 2006 and January 2007. Also shown is predicted drain flow from the Beccles soil type. Application days in the mitigation scenario are shown with black arrows.

7.3.2. Spatial targeting of pesticide application

A consistent reduction in propyzamide concentration, at the predicted 90th percentile, is seen in both catchments in all crop years, as a consequence of increasing levels of spatial targeting of application on vulnerable soils (Table 7.5 and Table 7.6). In the Yare catchment (Table 7.5) a greater proportion of the soil is assumed to be artificially drained (87 %) and, therefore, a greater spatial restriction of application on vulnerable drained soils is required to bring the 90th percentile concentration below 0.1 $\mu\text{g L}^{-1}$ compared with the Lugg (Table 7.6).

In both catchments, the predicted frequency of detections greater than 0.1 $\mu\text{g L}^{-1}$ does not show the same consistent decrease compared to the 90th percentile concentrations (Table 7.5 and Table 7.6). This is because although the concentrations are predicted to be reduced as the spatial restriction of application increases, the predicted concentration are still greater than 0.1 $\mu\text{g L}^{-1}$.

Table 7.5. Predicted 90th percentile propyzamide concentrations and the frequency of detections greater than 0.1 µg L⁻¹ in the Yare for the baseline scenario and mitigation scenario restricting the area of application on the most vulnerable soils, September 2006 to August 2009.

Scenario	Year	Baseline	Restricted application on vulnerable soils (%)			
			25 %	50 %	75 %	100 %
90th percentile concentration (µg L⁻¹)	1 (2006/2007)	0.24	0.18	0.12	0.06	< LOQ
	2 (2007/2008)	0.15	0.10	0.07	< LOQ	< LOQ
	3 (2008/2009)	0.20	0.15	0.10	0.05	< LOQ
Frequency of detections greater than 0.1 µg L⁻¹ (%)	1 (2006/2007)	22 %	19 %	14 %	2 %	0 %
	2 (2007/2008)	16 %	11 %	6 %	0 %	0 %
	3 (2008/2009)	17 %	16 %	12 %	0 %	0 %

Table 7.6. Predicted 90th percentile propyzamide concentrations and the frequency of detections greater than 0.1 µg L⁻¹ in the Lugg for the baseline scenario and mitigation scenario restricting the area of application on the most vulnerable soils, September 2006 to August 2009.

Scenario	Year	Baseline	Restricted application on vulnerable soils (%)			
			25 %	50 %	75 %	100 %
90th percentile concentration (µg L⁻¹)	1 (2006/2007)	0.16	0.12	0.08	0.04	< LOQ
	2 (2007/2008)	0.14	0.10	0.07	< LOQ	< LOQ
	3 (2008/2009)	0.06	0.04	< LOQ	< LOQ	< LOQ
Frequency of detections greater than 0.1 µg L⁻¹ (%)	1 (2006/2007)	19 %	7 %	1 %	0 %	0 %
	2 (2007/2008)	14 %	12 %	8 %	2 %	0 %
	3 (2008/2009)	7 %	5 %	4 %	1 %	0 %

7.3.3. Changing crop area and treated crop area

As the area of winter OSR decreases (i.e. the area treated with propyzamide decreases) and the area of spring OSR increases (i.e. the area treated with metazachlor increases), the total frequency of predicted concentrations greater than $0.1 \mu\text{g L}^{-1}$ also decreases in both the Lugg and the Yare catchments in all years considered (Figure 7.3 and Figure 7.4). Generally, as the crop treated area increases so does the total frequency of detections greater than $0.1 \mu\text{g L}^{-1}$, in both the Yare and the Lugg catchments and in all years (Figure 7.3 and Figure 7.4).

In the Lugg catchment in Year 3 (Figure 7.3c), the total frequency of predicted concentrations greater than $0.1 \mu\text{g L}^{-1}$ is lower than in Year 1 (Figure 7.3a) and Year 2 (Figure 7.3b). This is as a result of predicted metazachlor concentrations in Year 3 all being less than $0.1 \mu\text{g L}^{-1}$ as a consequence of lower rainfall from February 2009 to June 2009 (Figure 7.5a), resulting in a larger soil moisture deficit which in turn reduces the amount of pesticide mass displaced from the soil.

In the Yare catchment in Year 2 and Year 3 (Figure 7.4b and Figure 7.4c), the total frequency of concentrations greater than $0.1 \mu\text{g L}^{-1}$ is reduced in comparison to Year 1 (Figure 7.4a). As in the Lugg, this is as a result of metazachlor predictions all being less than $0.1 \mu\text{g L}^{-1}$. The predictions of metazachlor concentrations are larger in Year 1 in both the Lugg and the Yare catchments. Metazachlor is applied in the spring (April – May) and the displacement from the soil to surface water in the model is as a result of the rainfall events and predicted active hydrological pathways in May 2007 and June 2007 after application (Figure 7.5b). As previously discussed (Section 4.5.1.2), this was the wettest summer on record since 1912 (Marsh and Hannaford, 2007).

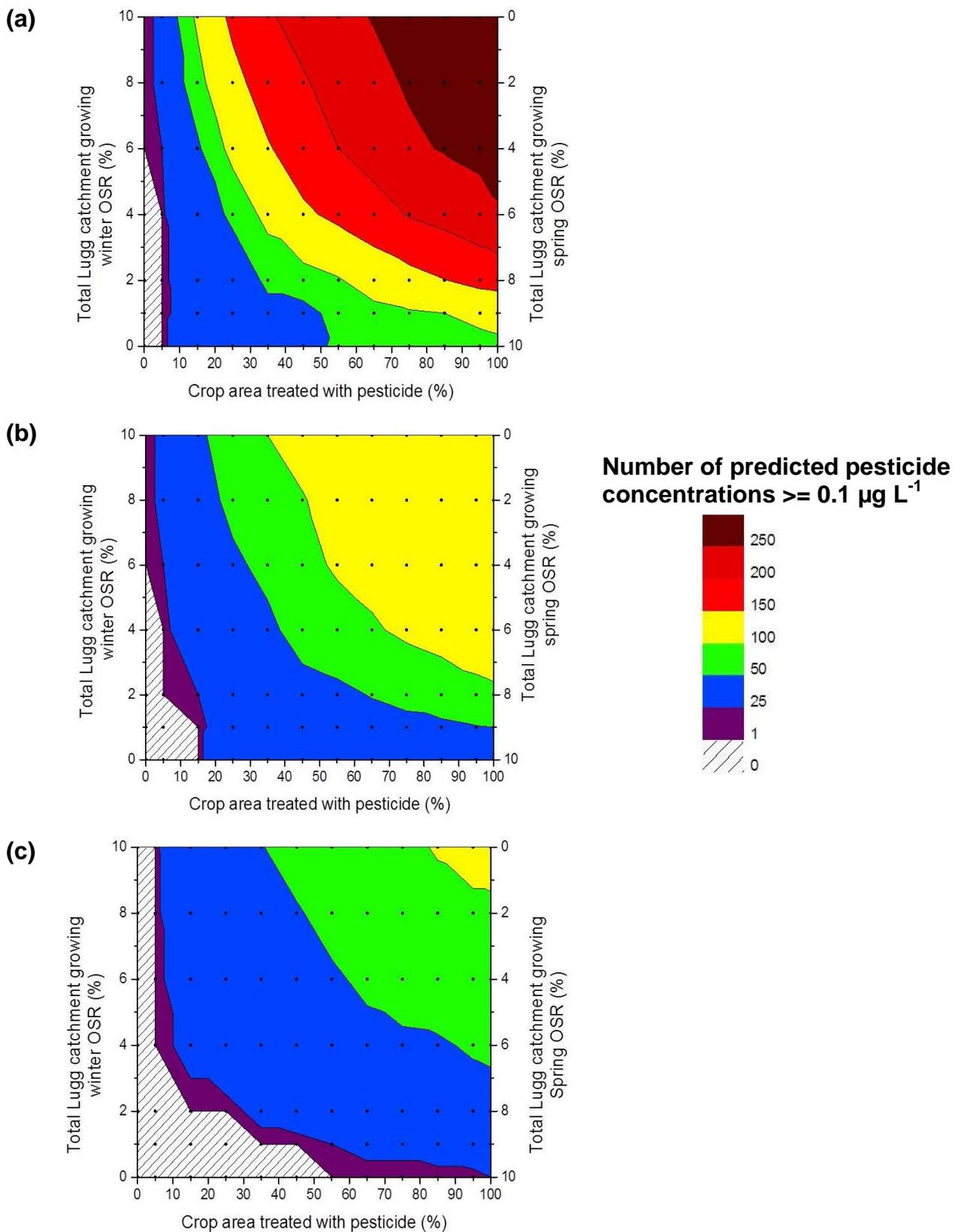


Figure 7.3. Predicted total frequency of propyzamide and metazachlor greater than $0.1 \mu\text{g L}^{-1}$ at the catchment outlet in the Lugg catchment (a) Year 1 (2006/2007), (b) Year 2 (2007/2008) and (c) Year 3 (2008/2009). Black dots represent the data points the model was run for.

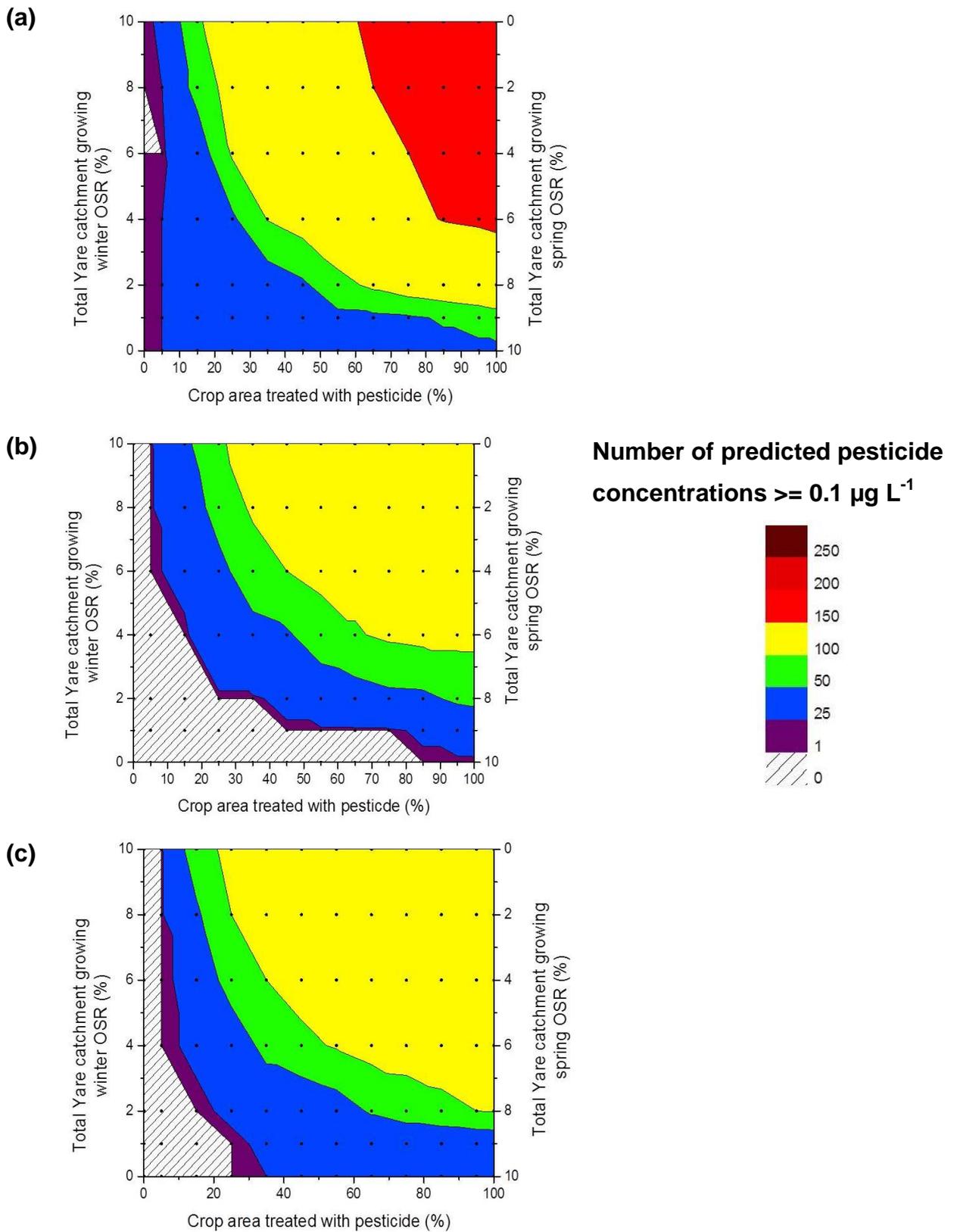


Figure 7.4. Predicted total frequency of propyzamide and metazachlor greater than $0.1 \mu\text{g L}^{-1}$ at the catchment outlet in the Yare catchment (a) Year 1 (2006/2007), (b) Year 2 (2007/2008) and (c) Year 3 (2008/2009).

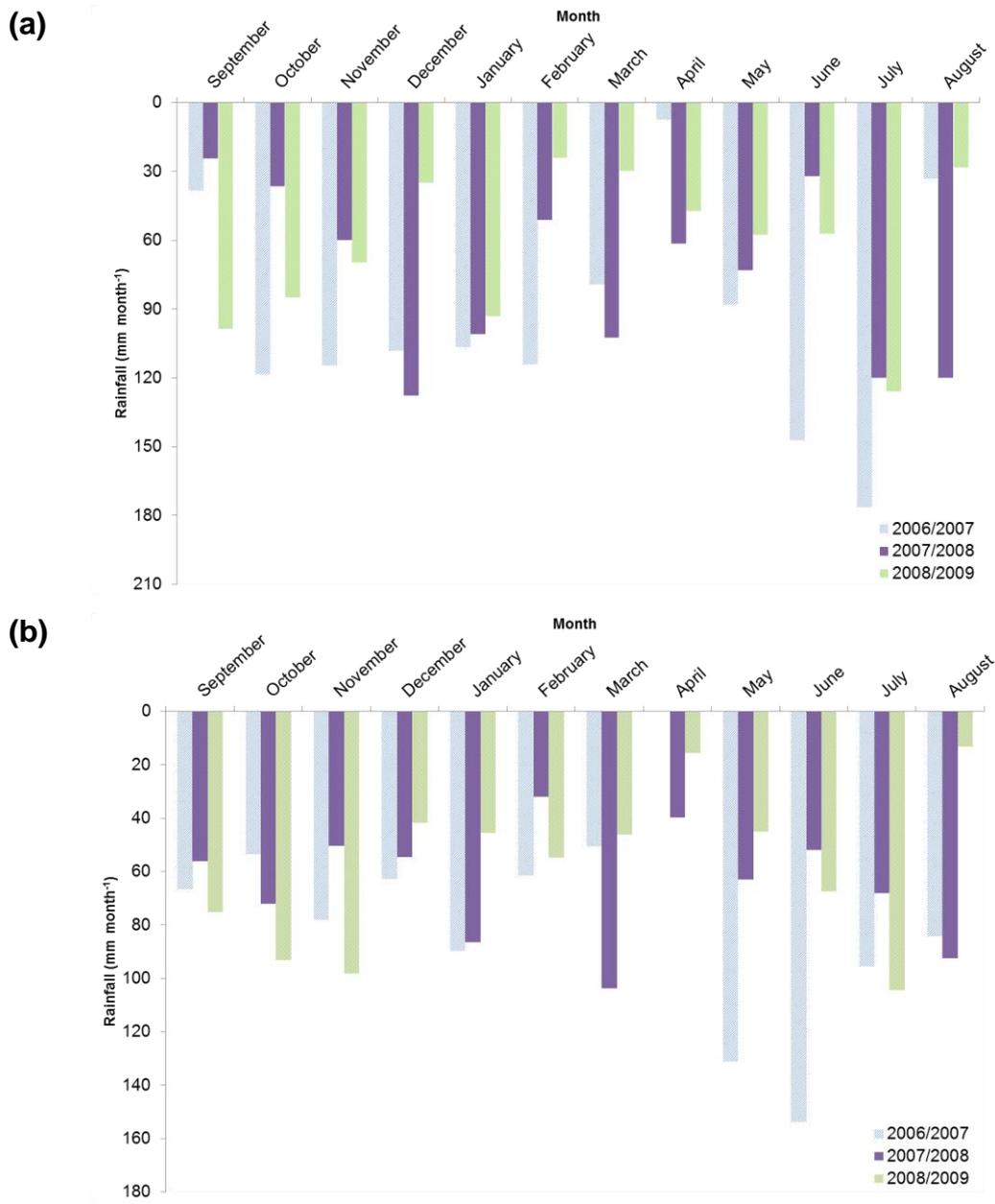


Figure 7.5. Monthly rainfall in (a) the Lugg catchment and (b) the Yare catchment for: Year 1 (2006/2007), Year 2 (2007/2008) and Year 3 (2008/2009).

7.4. Discussion

Four case-study mitigation scenarios were simulated in two catchments, considering changes in predicted propyzamide concentrations at the catchment outlet compared to the baseline. The mitigation scenarios were chosen to explore the utility of the model, more specifically to highlight how temporal and spatial restrictions in pesticide application and changes in land use scenarios might be able to reduce pesticide concentrations below $0.1 \mu\text{g L}^{-1}$.

7.4.1. Temporal restrictions of application

Temporal restrictions of propyzamide application on winter OSR to when drain flow is minimal resulted in a significant reduction in suitable application days. This resulted in a greater application of pesticides on suitable days and as a consequence, a high mass of pesticide was displaced when the drain flow was initiated causing higher concentrations than in the baseline scenario. The success of this scenario is, therefore, weather dependant. In a dry autumn, for example, there may be sufficient delay between application and drain flow events which would provide plenty of opportunity for degradation (Carter, 2000b). In wet years, on the other hand, this type of intervention strategy may be counterproductive.

In the second scenario, a temporal restriction was applied only allowing propyzamide application in September before the typical initiation of drain flow. This did not result in a significant reduction of predicted concentrations to below $0.1 \mu\text{g l}^{-1}$. This is again a consequence of the weather. For example, in 2006 in both the Lugg and the Yare catchment, several large rainfall events occurred within seven days of application.

This was also found by Kanan *et al.* (2006) who used the SWAT model (Neitsch *et al.*, 2005) to look at the leaching in the Colworth catchment in Bedfordshire (UK). They showed that there was an increase in predicted terbuthylazine concentrations when application was delayed, as a result of the new application day coinciding with the occurrence of a significant rainfall event. In a field study

at Brimstone Farm in Oxfordshire, Jones *et al.* (2000) discovered that isoproturon concentrations in drain flow decreased when the time between application and drain flow initiation increased. It could, therefore, be expected that if the initiation of drain flow is delayed (for example because of a warm and dry September and October) then lower concentrations should be expected at the catchment outlet.

It is worth remembering that in the pesticide fate and transport model, pesticide fate and behaviour between application and the start of drain flow will be influenced by the values assumed for DT_{50} and K_{OC} . If a higher K_{OC} and lower DT_{50} are selected the availability of pesticide for displacement when drain flow was initiated would be reduced.

It should be noted that in the case study scenarios presented, the practicability was not considered when restricting the application of propyzamide. For example, farmers will not be able to anticipate the fact that the rest of the winter will be too wet for application, and therefore in reality, it is more likely that application would occur on days when the model assumed that no application will occur. In addition, only allowing a few suitable application days could, for example, have practical constraints for machinery availability (Salmon-Monviola *et al.*, 2011). The agronomic consequence of restricting application has also not been explored. Under some circumstances restricting application could have knock on effects for yield and profitability of winter OSR (Clarke *et al.*, 2009).

7.4.2. Spatial targeting of application on vulnerable soils

Spatial targeting was considered by restricting propyzamide application on vulnerable drained soils and resulted in a reduction in the predicted 90th percentile concentration to less than $0.1 \mu\text{g L}^{-1}$ and a reduction in the frequency of detections at the catchment outlet over $0.1 \mu\text{g L}^{-1}$. Implementations of such measures in the Yare catchment would, however, require considerable catchment cooperation as over 50% of vulnerable soils in the catchment would be affected. There is also a temporal component to the success of this scenario. For example, in 2007/2008 in the Yare catchment a lower spatial targeting was

predicted to be required to reduce the predicted 90th percentile concentration to less than 0.1 µg L⁻¹.

7.4.3. Switching to spring oilseed rape

A switch from growing winter OSR (receiving propyzamide in the autumn/winter) to spring OSR (receiving metazachlor in the spring) resulted in a decrease in the overall frequency of detections greater than 0.1 µg L⁻¹ at the catchment outlet. However, in 2006/2007 a degree of pollution swapping occurred as a significant number of days with metazachlor concentrations at the catchment outlet were predicted to be greater than 0.1 µg L⁻¹. This was as a result of the rainfall events in late spring/early summer 2007. In 2007/2008 and 2008/2009 pollution swapping is minimal in comparison to 2006/2007. Therefore a switch to spring cropping in these years was predicted to reduce propyzamide concentrations at the catchment outlet without increasing the total frequency of pesticide greater than 0.1 µg L⁻¹.

In this scenario, the model has also demonstrated the sensitivity of the predicted concentrations to the assumptions of treated crop area. An under-prediction in treated crop area could lead to unrealistic expectations regarding the success of a scenario or result in pesticides not being considered in the monitoring strategy. On the other hand, an over-prediction in treated area could lead to overly conservative pesticide predictions greater than 0.1 µg L⁻¹.

7.4.4. Drivers and constraints of pesticide application

A pesticide practice survey carried out in the UK found that the decision as to when to apply pesticides was typically made by the farmer (53 %), an agronomist (33 %) or a contractor (12 %; HSE, 2009). If a sprayer operator/contractor is used, the application windows could be restricted by availability of the sprayer. The decision to apply pesticides was based on factors such as wind speed, likelihood of rainfall, crop growth stage and ground conditions (HSE, 2009).

Not applying a pesticide could lead to economic repercussions because of reduced quality and yield. It is worth remembering that crop loss will depend on the level of pest/weed infestation and the timing of the infestation with respect to crop development (Matthews *et al.*, 2014). Applying outside of the application windows could lead to a reduction in the efficacy of the active ingredient on the target organism.

7.4.5. Utility of the pesticide fate and transport model in scenario modelling

The pesticide fate and transport model developed in this thesis has a quick execution time allowing many different management options to be set-up and explored at the catchment scale. The datasets used in the model, such as the national soil map and the EDINA land use map, allow the pesticide fate predictions to be linked to a mapping tool (such as GIS) to give a spatial representation of predictions and thereby highlighting predicted hotspots within a catchment that are contributing a higher proportion of pesticide mass transfer to the catchment outlet. This in turn will identify where risk management scenarios could be explored to determine options that could reduce the pesticide mass flux at the catchment outlet. The model could also be applied by water companies to explore the effect of land use change or a change in use of pesticide active substances on the timing and magnitude of pesticide concentrations in a catchment and thereby consider the medium and long term risk of pesticide exposure to surface or groundwater drinking water resources.

7.5. Conclusions

Overall, of the case study mitigation scenarios considered, the restriction in the spatial targeting performed better than temporal restriction in reducing pesticide concentrations to below $0.1 \mu\text{g L}^{-1}$ at the catchment outlet. The success of temporal restrictions is dependent on weather conditions allowing time for significant degradation between application and the initiation of drain flow. A similar conclusion was drawn by Salmon-Monviola *et al.* (2011) who simulated the effect of technical and environmental constraints, such as machine availability and weather conditions, on pesticide concentrations with the SACADEAU model (Tortrat *et al.*, 2004 IN Salmon-Monviola *et al.*, 2011) in the Férmeur catchment in France.

This chapter has illustrated the potential utility of the pesticide fate and transport model developed by exploring the implications of mitigation scenarios. Four case-study scenarios were considered for propyzamide management in the Lugg and the Yare catchments. The mitigation scenarios considered temporal restrictions to application timing with respect to drain flow, spatial targeting of application with restrictions of application to vulnerable artificially drained soils and a change in crops grown (from winter OSR to spring OSR). The results in both catchments demonstrate that the spatial restrictions to application were more successful in reducing propyzamide concentrations to less than $0.1 \mu\text{g L}^{-1}$ than the temporal restrictions.

[This page is left intentionally blank]

Chapter 8. General Discussion and Conclusions

8.1. Meeting the aim and objectives

The overall aim of this thesis was to develop a broad scale, process-based, pesticide fate and transport model to determine pesticide exposure at the catchment outlet and at the water table in drinking water resources. To achieve this aim the following objectives were completed.

- **Objective 1: To outline a rationale for model development by reviewing catchment-scale pesticide fate and transport models available for pesticide exposure assessment in surface water and groundwater bodies.**

Despite the fact that numerous models of pesticide fate and behaviour in the environment have already been developed, an unoccupied niche still exists for a pesticide fate and transport model that contains enough spatial complexity to be applicable in a wide range of catchments and hydrogeological settings within an integrated hydrological framework and that is computationally undemanding.

- **Objective 2: To develop a pesticide fate and transport model with an integrated hydrological framework that can predict pesticide exposure at the catchment outlet and at the water table for a wide range of catchment types and hydrogeological settings in order to inform the risk assessment and risk management of drinking water resources.**

The new model is composed of a soil water balance model, a pesticide fate and transport model and an unsaturated zone model. It attempts to capture the important processes involved in pesticide transfer to surface and groundwaters (Figure 8.1), although it inevitably makes idealisations and assumptions in order to be applicable at a broad scale.

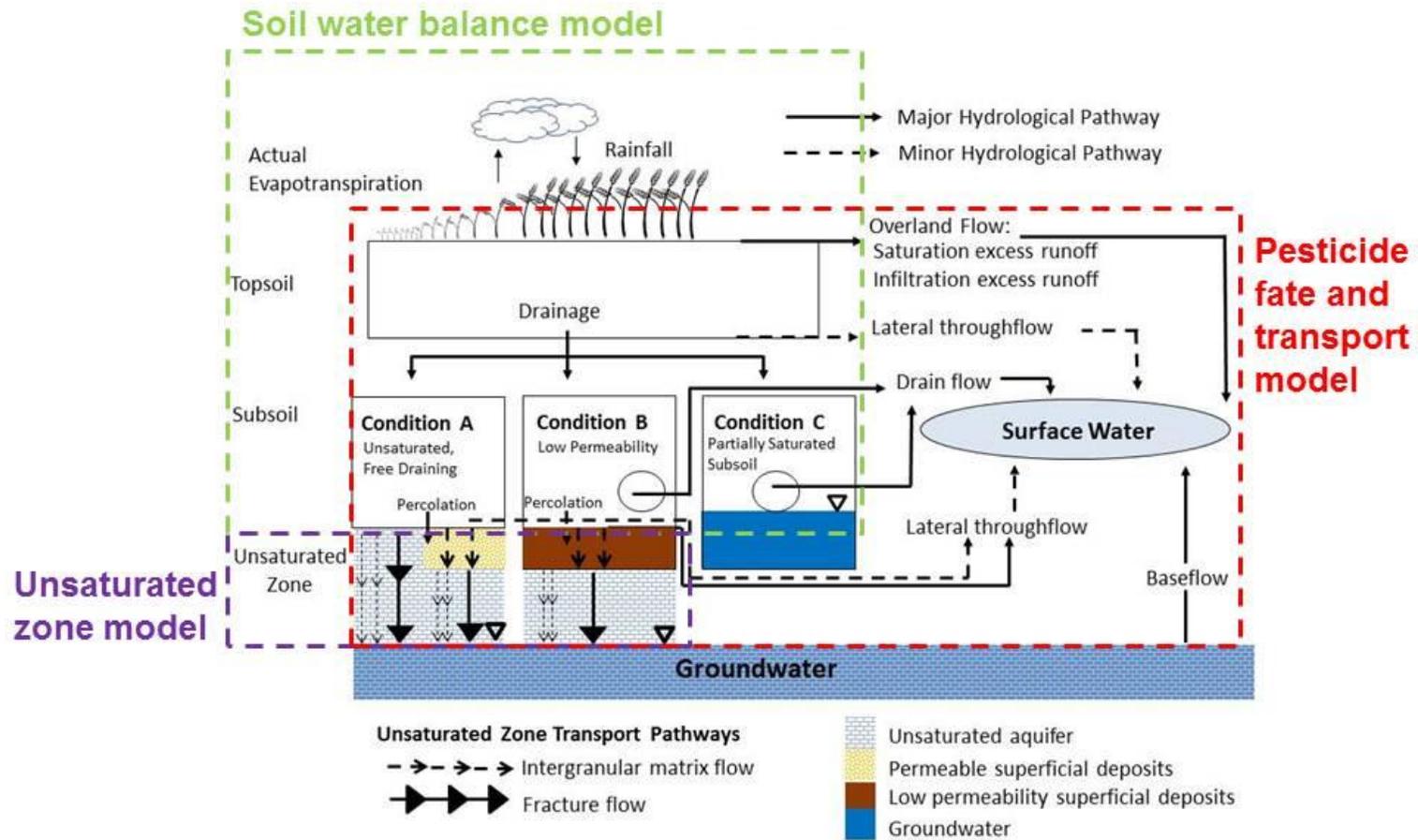


Figure 8.1. Schematic overview of hydrological and hydrogeological pathways included in the soil water balance model and the unsaturated zone model.

The conceptual representation of the key hydrological pathways in the soil water balance model (surface runoff, lateral throughflow, drain flow and/or percolation; Figure 8.1) underpins the pesticide transport pathways to surface and groundwater resources. Soils are assigned to one of three broad, but physically realistic conditions at the subsoil-unsaturated zone boundary (unsaturated and free draining; low permeability with and without drains; and partially saturated subsoil) based on a soil's HOST class (Boorman *et al.*, 1995). The choice of boundary condition determines the dominant hydrological pathways operating.

The fate of pesticides in the soil after application is accounted for in two stages, which are pesticide fate and transport in the soil between application and the first rainfall event and between rainfall event and pesticide fate and transport during a rainfall event. In the pre-rainfall component, pesticides are subject to first-order degradation, linear sorption and advective transport (subject to retardation). During a rainfall event, a hydrological pathway must be active for a pesticide to be displaced out of the mobile water-filled pore space. Water flux-dependant partitioning is used to determine whether pesticides are transported to the catchment outlet or to the top of the unsaturated zone.

The pesticide fate and transport model can be applied in a semi-distributed way for all the soil and land use combinations found in a catchment to make predictions of pesticide concentration and load at the catchment outlet. In order to be applicable in multiple individual catchments in the UK, the model has been designed to run with established national data sets, such as the National Soil Map and CORINE land cover data. As a consequence, it can be easily adapted to new catchments or used predictively to explore potential future catchment conditions (e.g. land use change).

The model was applied to a small headwater sub-catchment in the upper Cherwell and the results demonstrated that, when application timing and treated area are known, the model simulates peak pesticide concentrations that are a good match with measured data, suggesting that pesticide transport pathways

are well simulated. The model also performs well in comparison with the mechanistic MACRO model.

- **Objective 3: To evaluate the ability of the pesticide fate and transport model to reproduce pesticide concentrations at surface water catchment outlets.**

The model was applied to five case-study catchments in England and Wales, which are part of the Catchment Sensitive Farming programme (CSF Evidence Team, 2011), with varying soil-land use and pesticide use combinations. Daily flow and pesticide concentrations at the outlet of each catchment were predicted for eight pesticides over a twenty year period. Seven soil water balance model parameters were calibrated. The NSE and PBIAS were used to evaluate the goodness-of-fit. Performance of the water balance model was generally good. In particular, predictions of the timing and magnitude of peak autumn and winter flow at the catchment outlet were reproduced reasonably well.

Outputs from the pesticide fate model were also reasonable in terms of the frequency of detection greater than $0.1 \mu\text{g L}^{-1}$ and the 90th percentile predicted concentration compared with measured data, although performance was better for some catchment-pesticide combinations than for others. The time-series results demonstrated that the model tended to predict the presence of pesticide at the catchment outlet sooner than observed, however there is uncertainty associated with the measured grab sample data.

The predictions of exposure made by the pesticide fate and transport model developed in comparison with catchment scale pesticide fate models such as SEPTWA (Beernaerts *et al.*, 2005) and SWATCATCH (Hollis and Brown, 1996; Brown *et al.*, 2002) are at a coarser time-step for predicting the time and magnitude of pesticide concentrations at the catchment outlet. Pesticide concentrations are highly temporally variable (Kreuger, 1998; Tediosi *et al.*,

2012) and capturing this variability in a risk assessment is important for water companies.

Comparing the model developed to more complex and mechanistic, daily time-step models such as SWAT (Neitsch *et al.*, 2002) and MACRO (Larsbo and Jarvis, 2003), this model stands out as the number of parameters requiring calibration are smaller (seven compared with over 30 which can require calibration in SWAT and MACRO) and the model run times are much faster (less than 30 minutes to run predicted concentrations at the catchment outlet of a large catchment for eight pesticides over 20 years). The increasing complexity and quantity of parameters often makes physically-based models less suited to exploring the implications of future changes to the system (Binley *et al.*, 1991). The benefits of only a limited number of parameters and quick run times is that the model can be used as a tool to predict pesticide exposure in multiple surface and groundwater resources and to enable scenario modelling thereby allowing many different management options to be set-up and explored by water companies at the catchment scale.

The national datasets used in the model, such as the National Soil Map and the EDINA land use map, allow that pesticide fate predictions to be linked to a mapping tool (such as GIS) to give a spatial representation of predictions and thereby highlighting predicted hotspots within a catchment that are contributing a higher proportion of pesticide mass transfer to the catchment outlet. This in turn will identify where risk management scenarios could be explored to determine options that could reduce the pesticide mass flux at the catchment outlet. The model could also be applied water companies to explore the effect of land use change or a change in use of pesticides active substances on the timing and magnitude of pesticide concentrations in a catchment and thereby consider the medium and long term risk of surface or groundwater drinking water resources.

- **Objective 4: To illustrate the utility of the pesticide fate and transport model with application to mitigation scenarios to reduce pesticide concentrations at the catchment outlet.**

The utility of the pesticide fate and transport model was illustrated with exploration of four case study mitigation scenarios designed to reduce pesticide concentrations (using propyzamide as a representative pesticide) at the catchment outlet in the Lugg and the Yare catchments. The mitigation scenarios considered three strategies: restrictions to application timing with respect to drain flow, spatial targeting with restrictions of application to vulnerable soils and a change in crops grown in a catchment from winter OSR to spring OSR. The results in both catchments demonstrated that spatial restrictions to application were more successful in reducing propyzamide concentrations to less than $0.1 \mu\text{g L}^{-1}$ than temporal restrictions. This is largely due to the fact that temporal restrictions are weather dependant. It is worth noting that the spatial restrictions were also shown to be more successful in some periods than others, as a result of the weather during and after the application period.

- **Objective 5: To explore the importance of the unsaturated zone for determining the timing and magnitude of pesticide transfers to the water table.**

To make predictions of the timing and magnitude of peak pesticide concentrations at the water table in order to explore the potential importance of the unsaturated zone, the soil water balance model and pesticide fate and transport model was run at a point scale and combined with a model of unsaturated zone processes. Note the unsaturated zone model could be run in a semi-distributed framework, as in the surface water catchments. The unsaturated zone model accounts for solute transport through two flow domains (accounting for fracture flow and intergranular matrix flow) in three hydrogeological settings: (i) aquifer at outcrop, (ii) aquifer overlain by permeable superficial deposits, and (iii) aquifer overlain by low permeability deposits

(Figure 8.1). During transport in the intergranular matrix, pesticides are subject to sorption, degradation and dispersion.

The unsaturated zone hydrogeological settings have been parameterised to represent the three principal aquifers found in the UK (chalk, limestone and sandstone). The model was able to demonstrate that representing unsaturated zone processes is often critical for predicting pesticide exposure the water table. Fractures were predicted to cause high concentrations at the water table soon after application, on the other hand, intergranular matrix flow could result in a delay of potentially several years or even decades before pesticides are likely to be observed at the water table.

8.2. Implications of model results of pesticide exposure in surface and groundwater in relation to public water supplies

8.2.1. Implications of model results for surface water drinking water resources

Catchment management is an increasingly important tool for water companies to reduce diffuse pesticide pollution (Dolan *et al.*, 2012). It is promoted under the WFD (EC, 2000) for DrWPAs, and is now recognised by the financial regulator (OFWAT) as a strategy water companies need to invest in (OFWAT, 2011).

In the case-study catchments drain flow is predicted to be the key transport pathway for many soil types for diffuse pesticide transfers to the catchment outlet. This has implications for the management of drinking water quality via catchment management. Traditional catchment management solutions such as grassed buffer strips, which can reduce the impact of surface runoff and soil erosion on water resources and which have been shown to be effective in reducing pesticide transfers from overland flow (Arora *et al.*, 1996) will have

limited effectiveness if field drains by-pass underneath them (Muscutt *et al.*, 1993).

Other mitigation options proposed to reduce pesticide concentrations in surface water bodies include temporal restrictions in the timing of application and spatial restrictions of application to vulnerable soils (FOCUS, 2007; Reichenberger *et al.*, 2007; Brown and van Benium, 2009). The model results suggest that the effectiveness of temporal restrictions is weather dependant and spatial restrictions are more likely to produce consistent reductions in pesticide concentrations.

In the UK, catchment management interventions have largely been voluntary in nature so far. However, it is worth remembering that in a voluntary regime not every farmer will adopt the measures (Garratt and Kennedy, 2006). Even when they are mandatory, there is some uncertainty about the consistent reliability of catchment management measures, which will often be weather dependant, and hence subject to occasional failure under extreme events. For some pesticides, therefore, relying on regulation (restriction or prohibition of use) to reduce concentrations below $0.1 \mu\text{g L}^{-1}$ may be the only viable option.

When pesticide concentrations are predicted over $0.1 \mu\text{g L}^{-1}$ in raw waters this is not the same as $0.1 \mu\text{g L}^{-1}$ at the tap (where the limit is applied) as raw water typically goes through treatment. Some pesticides, however, have a greater “treatability” than others. For example, glyphosate is generally considered to be more treatable than metaldehyde and clopyralid with current technologies, such as granular activated carbon (Dillon *et al.*, 2011). Combining information on pesticide treatability and the treatment technology available at different abstraction points with pesticide predictions in raw water, could lead to more active targeting of problem pesticides in different catchments. The pesticide fate and transport model could be used to explore the effects of pesticides being withdrawn from registration, for example, along with exposure results from alternative available products. This could then be used to generate advice which encourages the selection and use of pesticides with a greater treatability for a water company, with current available technology. This has been

demonstrated in practice with water companies supporting the use of ferric phosphate for slug control over metaldehyde (Water UK, 2013), as the treatability of metaldehyde with current technology is low (Dillon *et al.*, 2011).

8.2.2. Implications of model results for groundwater drinking water resources

Results from the unsaturated zone model have highlighted potential issues resulting from short travel times to the water table as a result of fracture flow. Where travel times are longer, as a result of intergranular matrix flow, pesticides may not appear at the water table for years or even decades after they have been applied. This can result in the appearance of “legacy” pesticides (i.e. those which have been banned but which are still present in the environment as a consequence of their longevity) many years after their use has been curtailed. This has implications for the length of time before the effect that catchment management strategies put in place can be seen, as is recognised in groundwater pollution from nitrate (e.g. Howden *et al.*, 2011).

When assessing the compliance risks posed by pesticide at the water table and when using the model to help select analytical methods for sample analysis, it is important to take these travel time lags into consideration. Without such considerations, leaching assessment based on current use patterns will not be applicable to current risks, monitoring, or management.

8.3. Recommendations for further work

The model’s ability to reproduce the timing of pesticide concentrations is linked to the assumed timing of pesticide application, the application rate and the treated area which, at the individual catchment scale, all have a large degree of uncertainty. Future work is, therefore, required to gain a better understating of pesticide use in individual catchments through for example, more extensive farm surveys or catchment forums. The benefits of more detailed application

data can be seen in the upper Cherwell (Tediosi *et al.*, 2012), where a modified version of the pesticide fate and transport model developed in this thesis was used. The concentration peaks in the drain flow were predicted well at an hourly time-step.

Most measured pesticide monitoring data are infrequent (fortnightly to monthly, at best) in surface water resources. It is recommended that more frequent (daily) observations of pesticide concentrations are made in key catchments in order to gain a better picture of pesticide fluxes and in order to properly assess the performance of the pesticide fate and transport model developed.

The unsaturated zone model presented in this thesis provides a preliminary exploration of the importance of the unsaturated zone in the timing and magnitude of peak transport to the water table. Although this is essentially a point-scale one dimensional model it could be used to integrate leaching losses spatially and temporally to estimate average loads to the water table over time. Further work is recommended to describe pesticide transport in the saturated zone and to expand from the point scale to a groundwater catchment scale (incorporating information on borehole source protection zones). This will allow better predictions of pesticide concentrations in specific boreholes and improved prioritisation of catchment management and pesticide monitoring in groundwater resources.

It is also recommended that further studies should be undertaken to characterise unsaturated zone properties (particularly in superficial deposits), such as saturated intergranular matrix hydraulic conductivity, as well as studies on pesticide sorption, degradation and dispersion behaviour in a range of hydrogeological settings.

In the model conceptualisation there is no accounting for the generation of pesticide metabolites. The $0.1 \mu\text{g L}^{-1}$ limit includes metabolites and degradation products, only if they are pesticidally active. In a borehole in south-east England Lapworth and Goody (2006) identified not only diuron but also its metabolites: dichlorophenylmethyl urea, dichlorophenyl urea and dichloroaniline. Diuron

metabolites are considered to have a greater toxicity than the parent pesticide (Tixier *et al.*, 2000). It is therefore recommended that any future model developments include fate and transport of metabolites.

The modelling framework and conceptual ideas developed in this thesis could be expanded to the rest of Europe with the use of the European Soil Geographic Database (Hollis *et al.*, 2006) which incorporates similar conceptual models to those used in HOST (Boorman *et al.*, 1995). This would require modifications to the model to use European soil properties data and pesticide use information, and consideration of hydrological process (such as snow melt), that are not currently considered. Provided such data could be made available and any new processes were described, there is no reason why a European-wide application would not be possible.

A final recommendation is to explore the effect that climate change might have on pesticide concentrations both in surface and groundwater resources. Climate change could have direct effects on pesticide concentrations by affecting pesticide partitioning and degradation (Steffens, 2013), or cause changes in the importance of hydrological transport pathways with a change in rainfall patterns (Bloomfield *et al.*, 2006b). Climate change could also result in a change in the timing and magnitude of pesticide concentrations as a result of indirect effects, such as a change in pesticide use patterns and crop rotations (Bloomfield *et al.*, 2006b; Gouin *et al.*, 2013).

8.4. Conclusions

The research presented in this thesis has focused on developing a new pesticide fate and transport model to predict pesticide exposure in ground and surface waters used for public water supply. The model contains an integrated hydrological framework for assessing exposure risks in both surface water catchments and in groundwater. The model is computationally undemanding and applicable and broad scale across a range of catchment types and

hydrogeological settings. The model also contains only a few parameters that require calibration and has quick simulation times when compared with other pesticide fate models that predicted pesticide exposure at the catchment outlet at daily time-step. As a consequence, water companies will be able to use the model to assess: risk in order to identify and prioritise pesticide catchment-specific monitoring strategies; target catchment management and highlight potential problems that could arise under future scenarios.

References

- Adams, B., Gale, I., Younger, P., Lerner, D. & Chilton, J. (2000) Groundwater. In: Acreman, M. (ed) *The Hydrology of the UK: a study of change*. Routledge, Abingdon, Oxfordshire, 150 – 179.
- Addiscott, T.M. & Wagenet, R.J. (1985) Concepts of solute leaching in soils: a review of modelling approaches. *Journal of Soil Science*, **36**, 411 – 424.
- Allen, D.J., Brewerton, L.J., Coleby, L.M., Gibbs, B.R., Lewis, M.A., MacDonald, A.M., Wagstaff, S.J. & Williams, A.T. (1997) The physical properties of major aquifers in England and Wales. *British Geological Survey Technical Report* WD/97/34, 312p.
- Allen, R.G., Pereira, L.S., Raes, D. & Smith, M. (1998) *FAO Irrigation and Drainage Paper No. 56 Crop Evapotranspiration*. Food and Agriculture Organization.
- Ander, E.L., Shand, P. & Wood, S. (2006) *Baseline report series: 21. The Chalk and Crag of north Norfolk and the Waveney catchment*. British Geological Survey Commissioned Report No. CR/06/043N, 75p
- Anderson, M.G. & Burt, T.P. (1978) The role of topography in controlling throughflow generation. *Earth Surface Processes*, **3**, 331 – 344.
- Andrews, J.N. & Kay, R.L.F. (1982) $^{234}\text{U}/^{238}\text{U}$ activity ratios of dissolved uranium in groundwaters from a Jurassic Limestone aquifer in England. *Earth and Planetary Science Letters*, **57**, 139 – 151.
- Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J-C. & García-Río, L. (2008) The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agriculture, Ecosystems and Environment*, **123**, 247 – 260.

Armstrong, A., Aden, K., Amraoui, N., Diekkrüger, B., Jarvis, N., Mouvet, C., Nicholls, P. & Wittwer, C. (2000) Comparison of the performance of pesticide-leaching models on a cracking clay soil: results using the Brimstone Farm dataset. *Agricultural Water Management*, **44**, 85-104.

Arnold, J.G., Moriasi, D.N., Gassman, P.W., Abbaspour, K.C., White, M.J., Srinivasan, R., Santhi, C., Harmel, R.D., van Griensven, A., Van Liew, M.W., Kannan, N. & Jha, M.K. (2012) SWAT: Model use, calibration and validation. *Transactions of the ASABE*, **55**, 1491 – 1508.

Arnold, J.G., Srinivasan, R.S., Muttiah, S. & Williams, J.R. (1998) Large-area hydrologic modeling and assessment: part 1 model development. *Journal American Water Resources Association*, **34**, 73 – 89.

Arora, K., Mickelson, S.K., Baker, J.L., Tierney, D.P. & Peters, C.J. (1996) Herbicide retention by vegetative buffer strips from runoff under natural rainfall. *Transactions of the ASAE*, **39**, 2155 – 2162.

Bach, M., Huber, A. & Frede, H.G. (2001) Input pathways and river load of pesticides in Germany--a national scale modeling assessment. *Water Science and Technology*, **43**, 261 – 268.

Barron, J., Rockström, J., Gichuki, F. & Hatibu, N. (2003) Dry spell analysis and maize yields for two semi-arid locations in east Africa. *Agricultural and Forest Meteorology*, **117**, 23 – 27.

Bartram, J., Corrales, L., Davison, A., Deere, D., Dury, D., Gordon, B., Rhinehold, A. & Stevens, M. (2009) *Water safety plan manual: step-by-step risk management for drinking-water supplies*. World Health Organisation, Geneva.

Batu, V (2006) *Applied flow and solute transport modelling in aquifers: fundamental principles and analytical and numerical methods*. Taylor and Francis Group, Boca Raton, Florida.

- Bedos, C., Cellier, P., Calvert, R., Barriuso, E. & Gabrielle, B. (2002) Mass transfer of pesticides into the atmosphere by volatilization from soils and plants: overview. *Agronomie*, **22**, 21 – 33.
- Beernaerts, S., Debongnie, P., Gérard, M., Barthelemy, J.P., Copin, A., Guns, M. & Pussemier, L. (2005) Evaluation of crop-protection-product losses into surface waters with the SEPTWA system. *International Journal of Environmental & Analytical Chemistry*, **85**, 41-50.
- Benaman, J., Shoemaker, C.A. & Haith, D.A. (2005) Calibration and validation of soil and water assessment tool on an agricultural watershed in upstate New York. *Journal of Hydrologic Engineering*, **10**, 363 – 374.
- Beven, K.J (1989) Changing ideas in hydrology – the case of physically-based models. *Journal of Hydrology*, **105**, 157 – 172.
- Beven, K.J. (2006) A manifesto for the equifinality thesis. *Journal of Hydrology*, **320**, 18 – 36.
- Beven, K.J. (2012) *Rainfall-runoff modelling the primer*. Wiley, Hoboken.
- Beven, K.J. & Germann, P. (1982) Macropores and water flow in the soils. *Water Resources Research*, **18**, 1311 – 1325.
- Beven, K.J., Kirkby, M.J., Schofield, N. & Tagg, A.F. (1984) Testing a physically-based flood forecasting model (TOPMODEL) for three UK catchments. *Journal of Hydrology*, **69**, 119 – 143.
- BGS (2013) Digital geology – superficial theme.
http://www.bgs.ac.uk/products/digitalmaps/digmapgb_drift.html. Accessed 01/03/2013.
- Binley, A.M., Beven, K.J., Calver, A. & Watts, L.G. (1991) Changing responses in hydrology: assessing the uncertainty in physically based model predictions. *Water Resources Research*, **27**, 1253 – 1261.

Black, A.D., Lewis, R.T., Grout, M.W. & Witterick, W.R. (2012) Crossing boundaries, the influence of groundwater model boundaries and a method to join and split MODFLOW models. *In: Shepley, M.G., Whiteman, M.I., Hulme, P.J. & Grout, M.W. (eds) Groundwater resources modelling: a case study from the UK.* Geological Society, London, Special Publication, **364**, 155 – 172.

Blanchard, P.E. & Lerch, R.N. (2000) Watershed vulnerability to losses of agricultural chemicals: interactions of chemistry, hydrology, land-use. *Environmental Science and Technology*, **34**, 3315 – 3322.

Blanchoud, H., Farrugia, F. & Mouchel, J.M. (2004) Pesticide uses and transfers in urbanised catchments. *Chemosphere*, **55**, 905 – 913.

Bloomfield, J.P., Brewerton, L.J., & Allen, D.J. (1995) Regional trends in matrix porosity and dry density of the Chalk of England. *Quarterly Journal of Engineering Geology and Hydrogeology*, **28**, 131 – 142.

Bloomfield, J.P., Moreau, M.F. & Newell, A.J. (2006a) Characterization of permeability distributions in six lithofacies from the Helsby and Wilmslow sandstone formations of the Cheshire Basin, UK. *In: Barker, R.D. & Tellam, J.H. (eds) Fluid flow and solute movement in sandstones: the OnShore UK Permo-Triassic Red Bed sequence.* Geological Society, London, Special Publication, **263**, 83 – 101.

Bloomfield, J.P., Williams, R.J., Goody, D.C., Cape, J.N. & Guha, P. (2006b) Impacts of climate change on the fate and behaviour of pesticides in surface and groundwater – a UK perspective. *Science of the Total Environment*, **369**, 163 – 177.

Blöschl, G. & and Sivapalan, M. (1995) Scale issues in hydrological modelling: a review. *Hydrological Processes*, **9**, 251 – 290.

Boesten, J.J.T.I. & and Gottesbüren, B. (2000) Testing PESTLA using two modellers for bentazone and ethoprophos in a sandy soil. *Agricultural Water Management*, **44**, 283 – 305.

- Boivin, A., Cherrier, R. & Schiavon, M. (2005) A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere*, **61**, 668-676.
- Boorman, D.B., Hollis, J.M. & Lilly, A. (1995) *Hydrology of soils: a hydrologically-based classification of soils in the UK*. IH Report No.126.
- Brassington, F.C. & Younger, P.L. (2010) A proposed framework for hydrogeological conceptual modelling. *Water and Environment Journal*, **24**, 261 – 273.
- Brouyère, S., Dassargues, A. & Hallet, V. (2004) Migration of contaminants through the unsaturated zone overlying the Hesbaye chalky aquifer in Belgium: a field investigation. *Journal of Contaminant Hydrology*, **72**, 135 – 164.
- Brown, C.D., Bellamy, P.H. & Dubus, I.G. (2002) Prediction of pesticide concentrations found in rivers in the UK. *Pesticide Management Science*, **58**, 363 – 373.
- Brown, C.D., Carter, A.D. & Hollis, J.M. (1995) Soils and pesticide mobility. *In: Roberts, T.R. & Kearney P.C. (eds), Environmental behaviour of agrochemicals. Environmental behaviour of agrochemicals*. John Wiley & Sons, Chichester, England, 185 – 200.
- Brown, C.D., Dubus, I.G., Fogg, P., Spirlet, M. & Gustin, C. (2004) Exposure to sulfosulfuron in agricultural drainage ditches: field monitoring and scenario-based modelling. *Pest Management Science*, **60**, 765 – 776.
- Brown, C.D., Hodgkinson, R.A., Rose, D.A. Seyers, K. & Wilcockson, S.J. (1995) Movement of pesticides to surface waters from a heavy clay soil. *Pesticide Science*, **43**, 131 – 140.
- Brown, C.D. & Hollis, J.M. (1996) SWAT – a semi-empirical model to predict concentrations of pesticides entering surface waters from agricultural land. *Pesticide Science*, **47**, 41 – 50.

- Brown, C.D. & van Beinum, W. (2009) Pesticide transport via sub-surface drains in Europe. *Environmental Pollution*, **157**, 3314 – 3324.
- Burkhard, N. & Guth, J.A. (1981) Rate of volatilisation of pesticides from soil surfaces; comparison of calculated results with those determined in a laboratory model system. *Pesticide Science*, **12**, 37 – 44.
- Burt, T.P. (2001) Integrated management of sensitive catchment systems. *Catena*, **42**, 275 – 290.
- Butler, A.P. Hughes, A.G., Jackson, C.R., Ireson, A.M., Parker, S.J., Wheeler, H.S. & Peach, D.W. (2012) Advances in modelling groundwater behaviour in Chalk catchments. *In*: Shepley, M.G., Whiteman, M.I., Hulme, P.J. & Grout, M.W. (eds) *Groundwater resources modelling: a case study from the UK*. Geological Society, London, Special Publication, **364**, 155 – 172.
- Capel, P.D., Larson, S.J. & Winterstein, T.A. (2001) The behaviour of 39 pesticides in surface waters as a function of scale. *Hydrological Processes*, **15**, 1251 – 1269.
- Carsel, R.F., Mulkey, L.A., Lorber, M.N. & Baskin, L.B. (1985) The pesticide root zone model (PRZM): a procedure for evaluating pesticide leaching threats to groundwater. *Ecological Modelling*, **30**, 49 – 69.
- Carter, A.D. (2000a) Herbicide movement in soils: principles, pathways and processes. *Weed Research*, **40**, 113 – 122.
- Carter, A.D. (2000b) Herbicide pesticides get into water – and proposed reduction measures. *Pesticide Outlook*, 149 – 156.
- CatchIS (2013) CatchIS. Available at <http://www.catchis.com> from Cranfield University. Accessed 01/01/2011.
- Cavalier, T.C., Lavy, T.L. & Mattice, J.D. (1991) Persistence of selected pesticide in ground-water samples. *Ground Water*, **29**, 225 – 231.

- CEH (2012a) *Station information for the Lugg at Lugwardine*.
<http://www.ceh.ac.uk/data/nrfa/data/station.html?55003>. Accessed 01/10/2012.
- CEH (2012b) *Station information for the Teme at Knightsford Bridge*.
<http://www.ceh.ac.uk/data/nrfa/data/station.html?54029>. Accessed 01/10/2012.
- CEH (2012c) *Station information for the Waveney at Needham Mill*.
<http://www.ceh.ac.uk/data/nrfa/data/station.html?34006>. Accessed 01/10/2012.
- CEH (2012d) *Station information for the Wensum at Costessey Mill*.
<http://www.ceh.ac.uk/data/nrfa/data/station.html?34004>. Accessed 01/10/2012.
- CEH (2012e) *Station information for the Yare at Colney*.
<http://www.ceh.ac.uk/data/nrfa/data/station.html?34001>. Accessed 01/10/2012.
- CEH (2013) *National hydrological monitoring programme – Hydrological Review of the Year*. http://www.ceh.ac.uk/data/nrfa/nhmp/annual_review.html.
Accessed 01/10/2012.
- Chambon, J.C., Binning, P.J., Jørgensen, P.R. & Bjerg, P.L. (2011) A risk assessment tool for contaminated sites in low-permeability fractured media. *Journal of Contaminant Hydrology*, **124**, 82 – 98.
- Chang, M. & Flannery, L.A. (2001) Spherical gauges for improving the accuracy of rainfall measurements. *Hydrological Processes*, **15**, 643 – 654.
- Chave, P. (2001) *The EU Water Framework Directive: an Introduction*. London, IWA Publishing.
- Chilton, P.J., Lawrence, A.R. & Stuart, M.E. (1998) Pesticides in groundwater: some preliminary results from recent research in temperate and tropical environments. In Mather, J., Banks, D., Dumbleton, S. & Fermor, M. (eds) *Groundwater contaminants and their migration*. Geological Society, London, Special Publications, **128**, 333 – 345.

Christiansen, J.S., Thorsen, M., Clausen, T., Hansen, S. & Refsgaard, J.C. (2004) Modelling of macropore flow and transport processes at catchment scale. *Journal of Hydrology*, **299**, 136 – 158.

Clarke, J., Wynn, S., Twining, S., Berry, P., Cook, S., Ellis, S. & Gladders, P. (2009) *Pesticide availability for cereals and oilseeds following revision of Directive 91/414/EEC; effects of losses and new research priorities*. Research Review No.70, ADAS, Boxworth, Cambridge.

Coquet, Y. (2003) Sorption of pesticide atrazine, isoproturon, and metamitron in the vadose zone. *Vadose Zone Journal*, **2**, 40 – 51.

Crommentuijn, T., Sijm, D., de Bruijn, J., van Leeuwen, K. & van de Plassche, E. (2000) Maximum permissible concentrations for some organic substances and pesticides. *Journal of Environmental Management*, **58**, 297 – 312.

Crossland, N.O. (1982) Aquatic toxicology of cypermethrin III fate and biological effects of spray drift deposits in fresh water adjacent to agricultural land. *Aquatic Toxicology*, **2**, 253 – 270.

CSF Evidence Team (2011) *Catchment Sensitive Farming. ECSFDI phase 1 & 2 full evaluation*. Environment Agency.

DEFRA (2005) *Agriculture in the United Kingdom 2006*. The Stationary Office.

DEFRA (2009) *Agriculture in the United Kingdom 2008*. The Stationary Office.

DEFRA (2010) Land use and livestock on agricultural holdings.
<http://archive.defra.gov.uk/evidence/statistics/foodfarm/landuselivestock/junesurvey/results.htm>. Accessed 20/02/2012.

De la Cueva, P. (2006) Identification of agricultural areas in Europe subject to different types of field drainage. *MSc dissertation*. Cranfield University, Silsoe, UK.

De Noyelles, F., Kettle, W., D. & Sinn, D.E. (1982) The responses of plankton communities in experimental ponds to atrazine, the most heavily used pesticide in the United States. *Ecology*, **63**, 1285 – 1293.

Dillon, G., Hall, T., Jönsson, J., Murrell, K., Sheperd, D., Song, J. & Stanger, M. (2011) *Treatment of new and emerging pesticides*. United Kingdom Water Industry Research, London.

Dolan, T., Howsam, P. & Parsons, D.J. (2012) Diffuse pesticide pollution of drinking water resources: impact of legislation and UK responses. *Water Policy*, **14**, 680 – 693.

Dolan, T., Howsam, P., Parsons, D.J. & Whelan, M.J. (2013) Is the EU Drinking Water Directive standard for pesticides in drinking water consistent with the precautionary principal? *Environmental Science and Technology*, **47**, 4999 – 5006.

Dubus, I.G., Beulke, S. & Brown, C.D. (2002) Calibration of pesticide leaching models: critical review and guidance for reporting. *Pest Management Science*, **58**, 745 – 758.

Dubus, I.G., Brown, C.D. & Beulke, S. (2003) Sources of uncertainty in pesticide fate modelling. *The Science of the Total Environment*, **317**, 53 – 72.

Dubus, I.G., Hollis, J.M. & Brown, C.D. (2000) Pesticides in rainfall in Europe. *Environmental Pollution*, **110**, 331 – 344.

Dubus, I.G. & Surdyk, N. (2006) *State-of-the-art review on pesticide fate models and environmental indicators*. Report DL#4 of the FP6 EU-funded FOOTPRINT project [www.eu-footprint.org], 39p.

Duchon, C.E. & Biddle, C.J. (2010) Undercatch of tipping-bucket gauges in high rain rate events. *Advances in Geosciences*, **25**, 11 – 15.

DWI (2009) *Drinking water safety: guidance to health and water professionals*. The Drinking Water Inspectorate, London.

DWI & EA (2012) *The contribution of the water supply (water quality) regulations to the implementation of the Water Framework Directive in England and Wales*. The Drinking Water Inspectorate, London.

EA (2010a) *Managing invasive non-native plants*. Environment Agency, Bristol.

EA (2010b) *River Wensum restoration strategy: implementation river unit 53 Lenwade Mill to Taverham Mill, feasibility & environmental scoping assessment*. Environment Agency, Norwich.

EA (2013) *Anglian river basin district*. <http://www.environment-agency.gov.uk/research/planning/142658.aspx>. Accessed 01/07/2013.

EA (2013b) *New aquifer designations*. <http://www.environment-agency.gov.uk/homeandleisure/117020.aspx>. Accessed 01/10/2013.

EC (1998) *Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption, L330/32 ed*. Official Journal of the European Communities, Brussels.

EC (2000) *Directive 2000/60/EC Establishing a Framework for Community Action in the Field of Water Policy, L 327*. Official Journal of the European Communities, Brussels.

Emerman, S.H. (1995) The tipping bucket equations as a model for macropore flow. *Journal of Hydrology*, **171**, 23 – 47.

European Food Safety Authority (2010) Conclusion on the peer review of the pesticide risk assessment of the active substance carbetamide. *EFSA Journal*, **8**, 1913 – 1970.

Evans, S.P., Mayr, T.R., Hollis, J.M. Brown, C.D. (1999) SWBCM: a soil water balance capacity model for environmental applications in the UK. *Ecological Modelling*, **121**, 17 – 49.

Farlin, J., Gallé, T., Bayerle, M., Pittois, D., Braun, C., El Khabbaz, H., Elsner, M. & Maloszewski, P. (2012) Predicting pesticide attenuation in a fractured aquifer using lumped-parameter models. *Ground Water*, **51**, 276 – 285.

Fausser, P., Thomsen, M., Sørensen, P.B. & Petersen, S. (2008) Predicted concentrations for pesticides in drainage dominated catchments. *Water, Air and Soil Pollution*, **187**, 149 – 156.

FERA (2013) Pesticide usage survey statistics.

<https://secure.fera.defra.gov.uk/pusstats/index.cfm>. Accessed 01/10/2011.

Fetter, C.W. (1993) *Contaminated hydrogeology*. Macmillan Publishing Company, New York.

Finch, J.W. (1998) Estimating direct groundwater recharge using a simple water balance model – sensitivity to land surface parameters. *Journal of Hydrology*, **211**, 112 – 125.

FOCUS (2000) *FOCUS groundwater scenarios in the EU review of active substances*. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference SANCO/321/2000-rev 2, 202p.

FOCUS (2001) *FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC*. Report of the FOCUS Working Group on Surface Water Scenarios. EC Document Reference SANCO/4802/2001-rev 2, 245p.

FOCUS (2007) *Landscape and mitigation factors in aquatic risk assessment. Volume 1. Extended summary and recommendations*. Report of the FOCUS working Group in Landscape Mitigation Factors in Ecological Risk Assessment, EC Document Reference SANCO/10422/2005 v2.0, 169p.

Foster, S.S.D. (1998) Groundwater recharge and pollution vulnerability of British aquifers: a critical review. In: Robins, N.S (ed) *Groundwater pollution, aquifer recharge and vulnerability*. Geological Society, London, Special Publications, **130**, 7 – 22.

Ganzelmeier, I.H., Rautmann, D., Spangenberg, R., Strelake, M., Herrmann, M., Wenzelburger, H.J. & Walter, H.F. (1995) *Studies on the spray drift of plant protection products: results of a test program carried out throughout the Federal Republic of Germany*. Blackwell Wissenschafts-Verlag.

Garratt, J. & Kennedy, A. (2006) Use of models to assess the reduction in contamination of water bodies by agricultural pesticides through the implementation of policy instruments: a case study of the Voluntary Initiative in the UK. *Pest Management Science*, **62**, 1138 – 1149.

Garthwaite, D.G., Thomas, M.R., Anderson, H.M. & Battersby, A. (2006) *Pesticide usage survey report 210: grassland and fodder crops in Great Britain 2005 (including aerial applications 2003 – 2005)*. Department for Environment, Food and Rural Affairs and Scottish Executive Environment & Rural Affairs, Sand Hutton, York, UK.

Garthwaite, D.G., Thomas, M.R., Parrish, G., Smith, L. & Barker, I. (2010) *Pesticide usage survey report 224: arable crops in Great Britain 2008 (including aerial applications 2007 – 2008)*. Department for Environment, Food and Rural Affairs and Scottish Executive Environment & Rural Affairs, Sand Hutton, York, UK.

Gao, J., Liu, L., Liu, X., Lu, J., Zhou, H., Huang, S., Wang, Z. & Spear, P.A. (2008) Occurrence and distribution of organochlorine pesticides – lindane, p,p'-DDT, and heptachlor epoxide – in surface water of China. *Environment International*, **34**, 1097 – 1103.

Ghafoor, A., Jarvis, N.J., Strenström, J. (2013) Modelling pesticide sorption in the surface and subsurface soils of an agricultural catchment. *Pest Management Science*, **69**, 919 – 929.

Grath, J., Ward, R., Scheidleder, A. & Quevauviller, P. (2007) Report on EU guidance on groundwater monitoring developed under the common implementation strategy of the water framework directive. *Journal of Environmental Monitoring*, **9**, 1162 – 1175.

Griffiths, K.J., MacDonald, A.M., Robins, N.S., Merritt, J., Booth, S.J., Johnson, D. & McConvey, P.J. (2011) Improving the characterisation of Quaternary deposits for groundwater vulnerability assessments using maps of recharge and attenuation potential. *Quarterly Journal of Engineering Geology and Hydrogeology*, **44**, 49 – 61.

Goody, D.C., Bloomfield, J.P., Johnson, A.C. & Williams, R.J. (2001) Assessing herbicide concentration in the saturated and unsaturated zone of a chalk aquifer in Southern England. *Ground Water*, **39**, 262 – 271.

Goody, D.C. & Darling, W.G. (2009) Contaminant attenuation through glacial drift overlying the chalk aquifer in southern East Anglia, UK. In: *application of isotopes to the assessment of pollutant behaviour in the unsaturated zone for groundwater protection*. IAEA, 195 – 204, 227p.

Goody, D.C., Stuart, M.E., Lapworth, D.J., Chilton, P.J., Bishop, S., Cachandt, G., Knapp, M. & Pearson, T. (2005) Pesticide pollution of the Triassic Sandstone aquifer of South Yorkshire. *Quarterly Journal of Engineering Geology and Hydrogeology*, **38**, 53 – 63.

Gouin, T., Armitage, J.M., Cousins, I.T., Muir, D.C.G., Ng, C.A., Reid, L. & Tao, S. (2013) Influence of global climate change on chemical fate and bioaccumulation: the role of multimedia models. *Environmental Toxicology and Chemistry*, **32**, 20 – 31.

Grey, D.R.C., Kinniburgh, D.G., Barker, J.A. & Bloomfield, J.P. (1995) *Groundwater in the UK: a strategic study issues and research needs*. Groundwater Forum Report FR/GF 1, Buckinghamshire.

Grimmond, C.S.B. & Oke, T.R. (1999) Evapotranspiration rates in urban areas. *IAHS Publication*, **259**, 235 – 243.

Guo, L., Jury, W.A., Wagenet, R.J. & Flury, M. (2000) Dependence of pesticide degradation on sorption: nonequilibrium model and application to soil reactors. *Journal of Contaminant Hydrology*, **43**, 45 – 62.

- Gustafson, D.I. (1985) Groundwater ubiquity score: a simple method for assessing pesticide leachability. *Environmental Toxicology and Chemistry*, **8**, 339 – 357.
- Gustard, A., Bullock, A. & Dixon, J.M. (1992) *Low flow estimation in the United Kingdom*. Institute of Hydrology, Wallingford, Oxfordshire.
- Haberlandt, U. (2010) From hydrological modelling to decision support. *Advances in Geosciences*, **27**, 11 – 19.
- Hansen, V.E., Israelsen, O.W. & Stringham, G.E. (1979) *Irrigation principles and practices*. Wiley, New York.
- Hargreaves, G.H. & Allen, R.G. (2003) History and evaluation of Hargreaves evapotranspiration equation. *Journal of Irrigation and Drainage Engineering*, **129**, 53 – 63.
- Hargreaves, G.H. & Samani, Z. A. (1985) Reference crop evapotranspiration from temperature. *American Society of Agricultural Engineers*, **1**, 96 – 99.
- Hargreaves, G.L., Hargreaves, G.H. & Riley, J.P. (1985) Irrigation water requirements for Senegal river basin. *Journal of Irrigation and Drainage*, **111**, 265 – 275.
- Haria, A.H., Hodnett, M.G., Johnson, A.C. (2003) Mechanisms for groundwater recharge and pesticide penetration to a chalk aquifer in southern England. *Journal of Hydrology*, **275**, 122 – 137.
- Harris, G.L. & Catt, J.A. (1999) Overview of the studies on the cracking clay soil at Brimstone Farm, UK. *Soil Use and Management*, **15**, 233 – 239.
- Harris, G.L., Nicholls, P.H., Bailey, S.W., Howse, K.R. & Mason, D.J. (1994) Factors influencing the loss of pesticides in drainage from a cracking clay soil. *Journal of Hydrology*, **159**, 235 – 253.

Harvey, C.L., Dixon, H. & Hannaford, J. (2010). Developing best practice for infilling daily river flow data. *In: Kirby, C (ed) role of hydrology in managing consequences of a changing global environment*. Proceedings of the BHS Third International Symposium, British Hydrological Society, Newcastle, UK, 816 – 823.

Heathwaite, A.L., Fraser, A.I., Johnes, P.J., Hutchins, M., Lord, E. & Butterfield, D. (2003) The phosphorus indicators tool: a simple model of diffuse P loss from agriculture land to water. *Soil Use and Management*, **19**, 1 – 11.

Heathwaite, A.L., Quinn, P.F. & Hewett, C.J.M. (2005) Modelling and managing critical source areas of diffuse pollution from agricultural land using flow connectivity simulation. *Journal of Hydrology*, **304**, 446 – 461.

Helling, C.S., Kearney, P.C. & Alexander, M. (1971) Behaviour of pesticides in soils. *Advances in Agronomy*, **23**, 147 – 240.

Henriksen, H.J., Trolborg, L., Nyegaard, P., Sonnenborg, T.O., Refsgaard, J.C. & Madsen, B. (2003) Methodology for construction, calibration, and validation of a national hydrological model for Denmark. *Journal of Hydrology*, **280**, 52 – 71.

Heppell, C.M., Burt, T.P. & Williams, R.J. (2000) Variations in the hydrology of an underdrained clay hillslope. *Journal of Hydrology*, **227**, 236 – 256.

Heppell, C.M., Chapman, A.S., Bidwell, V.J., Forrester, G. & Kilfeather, A.A. (2004a) A lysimeter experiment to investigate the effect of surface sealing on hydrology and pesticide loss from the reconstructed profile of a clay soil.1. Hydrological characteristics. *Soil Use and Management*, **20**, 373 – 383.

Heppell, C.M., Chapman, A.S., Bidwell, V.J., Forrester, G. & Kilfeather, A.A. (2004b) A packed lysimeter experiment to investigate the effect of surface sealing on hydrology and pesticide loss from the reconstructed profile of a clay soil.2. Pesticide loss. *Soil Use and Management*, **20**, 384 – 393.

- Herbst, M., Hardelauf, H., Harms, R., Vanderborght, J. & Vereecken, H. (2005) Pesticide fate at regional scale : development of an integrated model approach and application. *Physics and Chemistry of the Earth*, **30**, 542 – 549.
- Hewitt, A.J., Johnson, D.R., Fish, J.D., Hermansky, C.G. & Valcore, D.L. (2002) Development of the Spray Drift Task force database for aerial applications. *Journal of Environmental Toxicology and Chemistry*, **21**, 648 – 658.
- HGCA (2008) The wheat growth guide: spring 2008, second edition. Agriculture and Horticulture Development Board, 32p.
- Hillel, D. (1998) *Environmental soil physics*. Academic Press, San Diego, California.
- Hiscock, K.M. (1993) The influence of pre-Devensian glacial deposits in the hydrochemistry of the Chalk aquifer system on north Norfolk, UK. *Journal of Hydrology*, **144**, 335 – 369.
- Hiscock, K.M. & Najafi, M.T. (2011) Aquitard characteristics of clay-rich till deposits in East Anglia, Eastern England. *Journal of Hydrology*, **405**, 288 – 306.
- Hodge, C.A.H. (1984) *Soils and their use in Eastern England*. Soil Survey of England and Wales, Harpenden, Hertfordshire.
- Holden, J. & Burt, T.P. (2003) Runoff production in blanket peat covered catchments. *Water Resources Research*, **39**, 1191 – 1200.
- Hollis, J.M. & Brown, C.D. (1996) A catchment-scale model for pesticides in surface water. *The Environmental Fate of Xenobiotics; Proceedings of the X Symposium Pesticide Chemistry*, Piacenza, Italy, 371 – 379.
- Hollis, J.M., Réal, B., Jarvis, N.J., Stenemo, F. & Reichenberger, S. (2006) *Characteristics of European soil hydrochemical scenarios*. Report DL8 of the FP6 EU-funded FOOTPRINT project [ww.eu-footprint.org], 47p.

Holman, I.P., Dubus, I.G., Hollis, J.M. & Brown, C.D. (2004) Using a linked soil model emulator and unsaturated zone leaching model to account for preferential flow when assessing the spatially distributed risk of pesticide leaching to groundwater in England and Wales. *The Science of the Total Environment*, **318**, 73 – 88.

Holman, I.P., Quinn, J.M.A., Konx, J.W. & Hess, T.M. (2005) *National groundwater recharge assessment – crop calendar dataset. R & D Technical Report*. Institute of Water and Environment, Cranfield University and Environment Agency, Bristol.

Holvoet, K., Seuntjens, P. & Vanrolleghem, P.A. (2007) Monitoring and modelling pesticide fate in surface waters at the catchment scale. *Ecological Modelling*, **209**, 53 – 64.

Holvoet, K., van Griensven, A., Gevaert, V., Seuntjens, P. & Vanrolleghem, P.A. (2008) Modifications to the SWAT code for modelling direct pesticide losses. *Environmental Modelling and Software*, **23**, 72 – 81.

Holvoet, K., van Griensven, A., Seuntjens, P. & Vanrolleghem, P.A. (2005) Sensitivity analysis for hydrology and pesticide supply towards the river in SWAT. *Physics and Chemistry of the Earth, Parts A/B/C*, **30**, 518 – 526.

Hornsby, A.G., Wauchope, R.D., & Herner, A.E. (1996) *Pesticide properties in the environment*. Springer-Verlag, New York.

Hough, M.N. & Jones, R.J.A. (1997) The United Kingdom Meteorological Office rainfall and evaporation calculation system: MORECS version 2.0 – an overview. *Hydrology and Earth System Science*, **1**, 227 – 239.

Howden, N.J.K., Burt, T.P., Burt, T.P., Mathias, S.A., Worrall, F. & Whelan, M.J. (2011) Modelling long-term diffuse nitrate pollution at the catchment-scale: data, parameter and epistemic uncertainty. *Journal of Hydrology*, **403**, 337 – 351.

HSE (2009) *HSE Chemicals Regulation Directorate – pesticide practices*. Prepared by ADAS, Wolverhampton, 124p.

- Huang, B. & Fry, J.D. (2000) Turfgrass evapotranspiration. *Journal of Crop Production*, **2**, 317 – 333.
- Hulme, P., Rushton, K. & Fletcher, S. (2001) Estimating recharge in UK catchments. *IAHS Publ.*, 269, pp 33 – 42.
- Hunt, B.W. (1983) *Mathematical analysis of groundwater resources*. Butterworths, London.
- Ireson, A.M., Butler, A.B. & Wheeler, H.S. (2012) Evidence for the onset and persistence with depth of preferential flow in unsaturated fractured porous media. *Hydrology Research*, **43**, 707 – 719.
- Issa, S. & Wood, M. (1999) Degradation of atrazine and isoproturon in the unsaturated zone: a study from Southern England. *Pesticide Science*, **55**, 539 – 545.
- Jackson, D. & Rushton, K.R. (1987) Assessment of recharge compounds for a chalk aquifer unit. *Journal of Hydrology*, **92**, 1 – 15.
- Jakeman, A.J., Letcher, R.A. & Norton, J.P. (2006) Ten iterative steps in development and evaluation of environmental models. *Environmental Modelling and Software*, **21**, 602-614.
- Jarvis, N.J., Hollis, J.M., Nicholls, P.H., Mayr, T. & Evans, S.P. (1997) MACRO-DB: a decision-support tool for assessing pesticide fate and mobility in soils. *Environmental Modelling & Software*, **12**, 251 – 265.
- Jensen, D.T., Hargreaves, G.H., Temesgen, B. & Allen, R.G. (1997) Computation of ETo under nonideal conditions. *Journal of Irrigation and Drainage*, **123**, 394 – 400.
- Jensen, P.K. & Spliid, N.H. (2003) Deposition of spray liquid on the soil below cereal crops after applications during the growing season. *Weed Research*, **43**, 362 – 370.

Johnson, A.C., Batchelor, C.H. & Haria, A.H. (1995) Processes influencing pesticide transport in a drained clay catchment. *IAHS Publications Series of Proceedings and Reports-Intern Associated Hydrological Sciences*, **226**, 39 – 46.

Johnson, A.C., Besien, T.J., Bhardwaj, C.L., Dixon, A., Gooddy, D.C., Haria, A. H. & White, C. (2001) Penetration of herbicides to groundwater in an unconfined chalk aquifer following normal soil applications. *Journal of Contaminant Hydrology*, **53**, 101 – 117.

Jones, H.K. and Cooper, J.D (1998) Water transport through the unsaturated zone of the Middle Chalk: a case study from Fleam Dyke lysimeter. *In* Robins, N.S. (ed) *Groundwater pollution, aquifer recharge and vulnerability*. Geological Society, London, Special Publications, **130**, 117 – 128.

Jones, R.L., Arnold, D.J.S., Harris, G.L., Bailey, S.W., Pepper, T.J., Mason, D.J., Brown, C.D., Leeds-Harrison, P.B., Walker, A., Bromilow, H., Brockie, D., Nicholls, P.H., Craven, A.C.C. & Lythgo, C.M. (2000) Processes affecting movement of pesticides to drainage in cracking clay soils. *Pesticide Outlook*, **11**, 174 – 178.

Jørgensen, P.R., Helstrup, T., Urup, J. & Seifert, D. (2004) Modeling of non-reactive solute transport in fractured clayey till during variable flow rate and time. *Journal of Contaminant Hydrology*, **68**, 193 – 216.

Jørgensen, P.R., McKay, L.D. & Spliid, N.H. (1998) Evaluation of chloride and pesticide transport in a fractured clayey till using large undisturbed soil columns and numerical modelling. *Water Resources Research*, **34**, 539 – 553.

Jury, W.A. & Horton, R. (2004) *Soil physics*. Hoboken, NJ, J. Wiley.

Kah, M., Beulke, S. & Brown, C.D. (2007) Factors influencing degradation of pesticides in soil. *Journal of Agricultural and Food Chemistry*, **55**, 4487 – 4492.

Kah, M. & Brown, C.D. (2007) Prediction of the adsorption in ionizable pesticides in the soil. *Journal of Agricultural Food Chemistry*, **55**, 2312 – 2322.

- Kannan, N., White, S.M., Worrall, F. & Whelan, M.J. (2006) Pesticide modelling for a small catchment using SWAT-2000. *Journal of Environmental Science and Health Part B: Pesticides, Food Contaminates, and Agricultural Wastes*, **41**, 1049 – 1070.
- Kendy, E., Gérard-Marchant, P., Walter, M. T., Zhang, Y., Liu, C. & Steenhuis, T.S. (2003) A soil-water-balance approach to quantify groundwater recharge from irrigated cropland in the North China Plain. *Hydrological Processes*, **17**, 2011 – 2031.
- Klein, M. (1991) *PELMO: pesticide leaching model, version 2.01, users manual*. Fraunhofer-Institut für Umweltchemie und Ökotoxikologie, Schmallenberg, Germany.
- Klinck, B.A., Barker, J.A., Noy, D.J. & Wealthall, G.P. (1996) Mechanisms and rates of recharge through glacial till: experimental and modelling studies from a Norfolk site. Technical Report, British Geological Survey, Keyworth.
- Knapp, M.F. (2005) Diffuse pollution threats to groundwater: a UK water company perspective. *Quarterly Journal of Engineering Geology and Hydrogeology*, **38**, 39 – 51.
- Knox, J., Morris, J., Hess, T. (2010) Identifying future risks to UK agricultural crop production: putting climate change in context. *Outlook on Agriculture*, **39**, 249 – 256.
- Köhne, J.M., Köhne, S. & Šimůnek, J. (2009a) A review of model applications for structured soils: (a) Water flow and tracer transport. *Journal of Contaminant Hydrology*, **104**, 4 – 35.
- Konopka, A. & Turco, R. (1991) Biodegradation of organic compounds in vadose zone and aquifer sediments. *Applied and Environmental Microbiology*, **57**, 2260 – 2268.
- Kördel, W., Egli, H. & Klein, M. (2008) Transport of pesticides via macropores (IUPAC technical report). *Pure and Applied Chemistry*, **80**, 105 – 160.

Krause, P., Boyle, D.P. & Bäse, F. (2005) Comparison of different efficiency criteria for hydrological model assessment. *Advances in Geosciences*, **5**, 89 – 97.

Krause, S. & Bronstert, A. (2007) The impact of groundwater – surface water interactions on the water balance of a mesoscale lowland river catchment in northeastern Germany. *Hydrological Processes*, **21**, 169 – 184.

Kreuger, J. (1998) Pesticides in stream water within an agricultural catchment in southern Sweden, 1990 – 1996. *Science of the Total Environment*, **216**, 227 – 251.

LandIS (2013a) *LandIS soils guide*.

<http://www.landis.org.uk/services/soilsguide/index.cfm>. Accessed 01/08/2011.

LandIS (2013b) *SEISMIC Spatial Environmental Information System for Modelling the Impact of Chemicals*.

<http://www.landis.org.uk/services/seismic.cfm>. Accessed 01/08/2011.

LandIS (2013c) *Soil series properties*. <http://www.landis.org.uk/data/series.cfm>. Accessed 01/08/2011.

Lapworth, D.J. & Goody, D.C. (2006) Source and persistence of pesticides in a semi-confined chalk aquifer of southeast England. *Environmental Pollution*, **144**, 1031 – 1044.

Lapworth, D.J., Baran, N., Stuart, M.E. & Ward, R.S. (2012) Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. *Environmental Pollution*, **163**, 287 – 303.

Lapworth, D.J., Goody, D.C., Stuart, M.E., Chilton, P.J., Cachandt, G., Knapp, M. & Bishop, S. (2006) Pesticides in groundwater: some observations on temporal and spatial trends. *Water and Environment Journal*, **20**, 55 – 64.

Larsbo, M. & Jarvis, N. (2003) *MACRO 5.0. A model of water flow and solute in macroporous soil*. Technical description. Emergo 2003; 6, Studies in the Biogeophysical Environment, SLU, Dept. Soil Sci., Uppsala, 47p.

Larson, I.W. & Peck, E.L. (1974) Accuracy of precipitation measurements for hydrologic modeling. *Water Resources Research*, **10**, 857 – 863.

Lee, L.J.E., Lawrence, D.S.L. & Price, M. (2006) Analysis of water-level response to rainfall and implications for recharge pathways in the Chalk aquifer, SE England. *Journal of Hydrology*, **330**, 604 – 620.

Legates, D.R. & McCabe, G.J. (1999) Evaluating the use of “goodness-of-fit” criteria in hydrologic and hydroclimate model validation. *Water Resources Research*, **35**, 233 – 241.

Leistra, M. & Boesten, J.J.T.I. (1989) Pesticide contamination of groundwater in Western Europe. *Agriculture, Ecosystems and Environment*, **26**, 369 – 389.

Leu, C., Singer, H., Stamm, C., Müller, S.R. & Schwarzenbach, R.P. (2004a) Simultaneous assessment of sources, processes, and factors influencing herbicide losses to surface waters in a small agricultural catchment. *Environmental Science and Technology*, **38**, 3827 – 3834.

Leu, C., Singer, H., Stamm, C., Müller, S.R. & Schwarzenbach, R.P. (2004b) Variability of herbicide losses from 13 fields to surface water within a small catchment after a controlled herbicide application. *Environmental Science & Technology*, **38**, 3835 – 3941.

Liess, M., Schulz, R., Liess, H.-D., Rother, B. & Kreuzig, R. (1999) Determination of insecticide contamination in agricultural headwater streams. *Water Research*, **33**, 239 – 247.

Lindahl, A.M.L., Kreuger, J., Strenström, J., Gärdenäs, A.I., Alavi, G., Roulier, S. & Jarvis, N.J. (2005) Stochastic modeling of diffuse pesticide losses from a small agricultural catchment. *Journal of Environmental Quality*, **34**, 1174 – 1185.

Loague, K. & Green, R.E. (1990) Criteria for evaluating pesticide leaching models. In: Roth, K (ed) *Field-scale water and solute flux in soils*, Birkhäuser Verlag, Basel, 175 – 207.

Logan, T.J., Eckert, D.J. & Beck, D.G. (1994) Tillage, crop and climatic effects on runoff and tile drainage losses of nitrate and four herbicides. *Soil & Tillage Research*, **30**, 75 – 103.

Lu, J., Sun, G., McNulty, S.G., & Amatya, D.M. (2005) A comparison on six potential evapotranspiration methods for regional use in the southeaster United States. *Journal of the American Water Resources Association*, **41**, 621 – 633.

Luo, Y. & Zhang, M. (2009) Management-orientated sensitivity analysis for pesticide transport in watershed-scale water quality modeling using SWAT. *Environmental Pollution*, **157**, 3370 – 3378.

Malek, E. & Bingham, G.E. (1993) Comparison of the Bowen ratio-energy balance and the water balance methods for the measurement of evapotranspiration. *Journal of Hydrology*, **146**, 209 – 220.

Mandal, U.K., Victor, U.S., Srivastava, N.N., Sharma, K.L., Ramesh, V., Vanesa, M., Crower, G.R. & Ramakrishna, Y.S. (2007) Estimating yield of sorghum using root zone water balance model and spectral characteristics of crop in a dry land Alison. *Agricultural Water Management*, **87**, 315 – 327.

Marks, R.J., Lawrence, A.R., Humpage, A.J & Hargreaves, R. (2004a) Recharge through till: developing a methodology for estimating groundwater recharge with examples from two case studies in East Anglia. *British Geological Survey Internal Report*, IR/04/122, 42p.

- Marks, R.J., Lawrence, A.R., Whitehead, E.J., Cobbing, J.E., Mansour, M.M., Darling, W.G. & Hughes, A.G. (2004b) Chalk recharge beneath thick till deposits in East Anglia. *British Geological Survey Internal Report*, IR/04/179, 73p.
- Marsh, T.J. & Hannaford, J. (2007) *The summer 2007 floods in England and Wales – a hydrological appraisal*. Centre for Ecology and Hydrology, 32p.
- Martínez-Cob, A. & Tejero-Juste, M. (2004) A wind-based qualitative calibration of the Hargreaves ET_0 estimation equation in semi-arid regions. *Agricultural Water Management*, **64**, 251 – 264.
- Mathias, S.A., Butler, A.P., Jackson, B.M. & Wheeler, H.S. (2006) Transient simulations of flow and transport in the Chalk unsaturated zone. *Journal of Hydrology*, **330**, 10 – 28.
- Mathews, G., Bateman, R. & Miller, P. (2014) *Pesticide application methods, 4th Edition*. John Wiley and Sons, Chichester, West Sussex.
- McCuen, R.H., Knight, Z. & Cutter, A.G. (2006) Evaluation of the Nash-Sutcliffe Efficiency index. *Journal of Hydrologic Engineering*, **11**, 597 – 602.
- McKay, L.D. & Spliid, N.H. (1998) Evaluation of chloride and pesticide transport in a fractured clayey till using large undisturbed soil columns and numerical modelling. *Water Resources Research*, **34**, 539 – 553.
- McQueen, D.A.R., Farenhorst, A., Allaire, S. & Cessna, A.J. (2007) Automation and evaluation of three pesticide fate models for a national analysis of leaching risk in Canada. *Canadian Journal of Soil Science*, **87**, 20 – 212.
- Mermoud, A. & Meiwirth, K. (2004) Herbicide transport and vulnerability of a shallow groundwater: local and regional scale study. In: *2nd International Workshop on Integrated Soil and Water Protection: Risks from Diffuse Pollution (SOWA)*, 73 – 78.

Middelkoop, H., Daamen, K., Gellens, D., Grabs, W., Kwadjik, J.C.J., Lang, H., Parmet, W.A.H., Schädler, B., Schulla, J. & Wilke, K. (2001) Impact of climate change on hydrological regimes and water resources management in the Rhine basin. *Climatic Change*, **49**, 105 – 128.

Mitchell, C., Brodie, J. & White, I. (2005) Sediments, nutrients and pesticide residues in event flow conditions of the Mackay Whitsunday Region, Australia. *Marine Pollution Bulletin*, **51**, 23 – 26.

Moriasi, D.N., Arnold, J.G., Van Liew, M.W., Binger, R.L., Harmel, R.D. & Veith, T.L. (2007) Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. *Transactions of the ASABE*, **50**, 885 – 900.

Müller, K., Deurer, M., Hartmann, H., Bach, M., Spiteller, M. & Frede, H.-G. (2003) Hydrological characterisation of pesticide loads using hydrograph separation at different scales in a German catchment. *Journal of Hydrology*, **273**, 1 – 17.

Mullins, J.A., Carsel, R.F., Scarborough, J.E. & Ivery, A.M. (1993) *PRZM-2, a model for predicting pesticide fate in the crop root and the unsaturated soil zones: user's manual for release 2.0*. Athens GA Environmental Research Laboratory Office of Research and Development, US Environmental Protection Agency.

Muscatt, A.D., Harris, G.L., Bailey, S.W. & Davies, D.B. (1993) Buffer zones to improve water quality: a review of their potential use in UK agriculture. *Agriculture, Ecosystems and Environment*, **45**, 59 – 77.

Nash, J. & Sutcliffe, J.V. (1970) River flow forecasting through conceptual models part I – a discussion of principals. *Journal of Hydrology*, **10**, 282 – 290.

Neitsch, S.L., Arnold, J.G., Kiniry, J.R., Srinivasan, R. & Williams, J.R. (2002) *Soil and water assessment tool user's manual version 2000*. GSWRL report, 202 (02-06).

Niehoff, D., Fritsch, U. & Bronstert, A. (2002) Land-use impacts of storm-runoff generation: scenarios of land use change and simulation of hydrological response in a meso-scale catchment in SW-Germany. *Journal of Hydrology*, **267**, 80 – 93.

Nimmo, J.R. (2012) Preferential flow occurs in unsaturated conditions. *Hydrological Processes*, **26**, 786 – 789.

OFWAT (2011) *From catchment to customer. Can upstream catchment management deliver a better deal for water customers and the environment*. OFWAT, Birmingham.

Palmer, R.C. & Lewis, M.A. (1998) Assessment of groundwater vulnerability in England and Wales. In Robins, N.S. (ed) *Groundwater pollution, aquifer recharge and vulnerability*. Geological Society, London, Special Publications, **130**, 191-198.

Pang, L. & Hunt, B. (2001) Solutions and verification of a scale-dependant dispersion model. *Journal of Contaminant Hydrology*, **53**, 21 – 39.

Pesticide Forum (2011) *Pesticides in the UK: The 2011 report on the impacts and sustainable use of pesticides*. A report of the Pesticide Forum, Chemicals Regulation Directorate, York, 72p.

Petersen, C.T., Holm, J., Koch, C.B., Jensen, H.E. & Hansen, S. (2002) Movement of pendimethalin, ioxynil and soil particles to field drainage tiles. *Pesticide Management Science*, **59**, 85 – 96.

Petit, V., Cabridenc, R., Swannell, R.P.J. & Sokhi, R.S. (1995) Review of strategies for modelling the environmental fate of pesticides discharged into riverine systems. *Environment International*, **21**, 167 – 176.

Pirastru, M. & Niedda, M. (2013) Evaluation of the soil water balance in an alluvial flood with a shallow groundwater table. *Hydrological Sciences*, **58**, 898 – 811.

Ponce, V.M. & Hawkins, R.H. (1996) Runoff curve number: has it reached maturity? *Journal of Hydrologic Engineering*, **1**, 11 – 19.

Pretty, J.N., Brett, C., Gee, D., Hine, R.E., Mason, C.F., Morison, J.I.L., Raven, H., Rayment, M.D. & van der Bijl, G. (2000) An assessment of the total external costs of UK agriculture. *Agricultural Systems*, **65**, 113 – 136.

Price, M., Downing, R.A. & Edmunds, W.M. (1993) The chalk as an aquifer. In Downing, R.A., Price, M. & Jones, G.P (eds) *The hydrogeology of the Chalk of north-west Europe*. Clarendon, Oxford, 35 – 58.

Quilbé, R., Rousseau, A.N. & Lafrance, P. (2006) Selecting a Pesticide Fate Model at the Watershed Scale Using a Multi-criteria Analysis. *Water Quality Resources Journal Canada*, **41**, 283 – 295.

Quinn, P. (2004) Scale appropriate modelling: representing cause-and-effect relationships in nitrate pollution at the catchment scale for the purpose of catchment scale planning. *Journal of Hydrology*, **291**, 197 – 217.

Rabiet, M., Margoum, C., Gouy, V., Carluer, N. & Coquery, M. (2010) Assessing pesticide concentrations and fluxes in the stream of a small vineyard catchment – effect of sampling frequency. *Environmental Pollution*, **158**, 737 – 748.

Ragab, R., Finch, J. & Harding, R. (1997) Estimation of groundwater recharge to chalk and sandstone aquifers using simple soil models. *Journal of Hydrology*, **190**, 19 – 41.

Ramwell, C.T., Heather, A.I.J. & Shepherd, A.J. (2002) Herbicide loss following application to a roadside. *Pest Management Science*, **58**, 695 – 701.

Ramwell, C.T., Heather, A.I.J. & Shepherd, A.J. (2004) Herbicide loss following application to a railway. *Pest Management Science*, **60**, 556 – 564.

Ranatunga, K., Nation, E.R. & Barratt, D.G. (2008) Review of soil water models and their applications in Australia. *Environmental Modelling & Software*, **23**, 1182 – 1206.

- Reeves, M.J. (1979) Recharge and pollution of the English chalk: some possible mechanisms. *Engineering Geology*, **14**, 231 – 240.
- Refshaard, J.C., Storm, B. & Singh, V.P. (1995) MIKE SHE. *In: Singh, V.P (ed) Computer models of watershed hydrology*. Water Resources Publications, Highlands Ranch, Colorado, 809 – 846.
- Reichenberger, S., Bach, M., Skitschak, A. & Frede, H-G. (2007) Mitigation strategies to reduce pesticide inputs into ground-and surface water and their effectiveness; a review. *Science of the Total Environment*, **384**, 1 – 35.
- Renaud, F.G., Bellamy, P.H. & Brown, C.D. (2008) Simulating pesticides in ditches to assess ecological risk (SPIDER): I. Model description. *Science of the Total Environment*, **394**, 112 – 123.
- Ritchie, J. T. (1974) Atmospheric and soil water influences on the plant water balance. *Agricultural Meteorology*, **14**, 183 – 198.
- Robinson, M. (1990) *Impact of improved land drainage on river flows*. Report 113, Institute of Hydrology.
- Rodda, J.C. (1967) The rainfall measurement problem. *Proceedings IAHS General Assembly, Bern*, IAHS Publication, **78**, 215 – 231.
- Rodvang, S.J. & Simpkins, W.W. (2000) Agricultural contaminants in Quaternary aquitards: A review of occurrence and fate in North America. *Hydrogeology Journal*, **9**, 44 – 59.
- Röpke, B., Bach, M. & Frede, H. (2004) DRIPS—a DSS for estimating the input quantity of pesticides for German river basins. *Environmental Modelling & Software*, **19**, 1021 – 1028.
- Rose, S.C., Mason, P.J., Foster, I.D.L., Walker, A. & Carter, A.D. (2001) The design of a pesticide handling and washdown facility. *In: Pesticide behaviour in soils and water*. Proceedings of a Symposium organized by the British Crop Protection Council, Brighton, UK, 13-15 November 2001, 379 – 384.

- Rüdel, H. (1997) Volatilisation of pesticides from soil and plant surfaces. *Chemosphere*, **35**, 143 – 152.
- Rushton, K.R. (2003) *Groundwater hydrology conceptual models and computational models*. Wiley, Chichester, West Sussex.
- Rushton, K.R. (2005) Estimating recharge for British aquifers. *Water and Environment Journal*, **19**, 115 – 124.
- Russell, R.W., Hecnar, S.J. & Haffner, G.D. (1995) Organochlorine pesticide residues in southern Ontario spring peepers. *Environmental Toxicology and Chemistry*, **14**, 815 – 817.
- Salmon-Monviola, J., Gascul-Odoux, C., Garcia, F., Tortrat, F., Cordier, M-O., Masson, V. & Trépos. (2011) Simulating the effect of technical and environmental constraints on the spatio-temporal distribution of herbicide applications and stream losses. *Agriculture, Ecosystems and Environment*, **140**, 382 – 394.
- Samani, Z.A. & Pessarakli, M. (1986) Estimating potential crop evapotranspiration with minimum data in Arizona. *Transactions of American Society of Agricultural Engineers*, **29**, 522 – 524.
- Schulz, R. (2001) Comparison of spray drift- and runoff-related input of azinphos-methyl and endosulfan from fruit orchards into the Lourens River, South Africa. *Chemosphere*, **45**, 543 – 551.
- Shahidian, S., Serralherio, R.P., Serrano, J. & Teixeira, J.L. (2012) Parametric calibration of the Hargreaves-Samani equation for use at new locations. *Hydrological Processes*, **27**, 605 – 616.
- Shipitalo, M.J., Nuutinen, V. & Butt, K.R. (2004) Interaction of earthworm burrow and cracks in a clayey, subsurface-drained soil. *Applied Soil Ecology*, **26**, 209 – 217.

Singhal, B.B.S., & Gupta, R.P. (1999) *Applied hydrogeology of fractured rocks*. Springer, Netherlands.

Skark, C., Zullei – Seibert, N., Wilme, U., Gatzemann, U. & Schlett, C. (2004) Contribution of non-agricultural pesticides to pesticide load in surface water. *Pest Management Science*, **60**, 525 – 530.

Smakhtin, V.U. (2001) Low flow hydrology: a review. *Journal of Hydrology*, **240**, 147 – 186.

Smith, M. (1992) *CROPWAT: A computer program for irrigation planning and management*. Vol 46, FAO, Rome.

SNIFFER (2006) *An approach to hydrogeological assessment in Quaternary deposits in the UK. Part 1 background*. Project WFD 34, Final Report, BGS, Wallingford, Oxfordshire, 41p.

Soley, R.W.N. & Heathcote, J.A. (1998) Recharge through drift: a case study of contrasting Chalk catchments near Redgrave Fen, UK. *In: Robins, N.S (ed) Groundwater pollution, aquifer recharge and vulnerability*. Geological Society, London, Special Publications, **130**, 129 – 141.

Southwick, L.M., Grigg, B.C., Fouss, J.L. & Kornecki, T.S. (2003) Atrazine and metolachlor in surface runoff under typical rainfall conditions in southern Louisiana. *Journal of Agricultural and Food Chemistry*, **51**, 5355 – 5361.

Spark, K.M. & Swift, R.S. (2002) Effect of soil composition and dissolved organic matter on pesticide sorption. *The Science of the Total Environment*, **298**, 147 – 161.

Spitz, K. & Moreno, J. (1996) *A practical guide to groundwater and solute transport modelling*. John Wiley & Sons, New York.

- Steffens, K., Larsbo, M., Moeys, J., Jarvis, N. & Lewan, E. (2013) Predicting pesticide leaching under climate change: importance of model structure and parameter uncertainty. *Agriculture, Ecosystems, and Environment*, **172**, 24 – 34.
- Stehr, A., Debels, P., Romero, F. & Alcayaga, H. (2008) Hydrological modelling with SWAT under conditions of limited data availability: evaluation of results from a Chilean case study. *Hydrological Sciences*, **53**, 588 – 601.
- Stevens, C.J. & Quinton, J.N. (2009) Policy implications of pollution swapping. *Physics and Chemistry of the Earth*, **34**, 589 – 594.
- Su, G.W., Nimmo, J.R. & Dragila, M.I. (2003) Effect of isolated fractures on accelerated flow in the unsaturated porous rock. *Water Resources Research*, **39**, 1326 – 1337.
- Syversen, N. & Bechmann, M. (2004) Vegetative buffer strips as pesticide filters for simulated surface runoff. *Ecological engineering*, **22**, 175 – 184.
- Taghavi, L., Merlina, G. Probst, J-L. (2011) The role of storm flows in concentration of pesticides associated with particulate and dissolved fractions as a threat to aquatic ecosystems case study: the agricultural watershed of the Save river (Southwest of France). *Knowledge and Management of Aquatic Ecosystems*, **6**, 1-11.
- Taghavi, L., Probst, J-L., Merlina, G., Marchand, A-L., Durbe, G. & Probst, A. (2010) Flood event impact on pesticide transfer in a small agricultural catchment (Montousse at Aurade, south west France). *International Journal of Environmental and Analytical Chemistry*, **90**, 390 – 405.
- Tang, Z., Zhu, B. & Katou, H. (2012) A review of rapid transport of pesticides from sloping farmland to surface waters: processes and mitigation strategies. *Journal of Environmental Sciences*, **24**, 351 – 361.

Tediosi, A., Whelan, M.J., Rushton, K.R. & Gandolfi, C. (2013) Predicting rapid herbicide leaching to surface waters from an artificially drained headwater catchment using a one dimensional two-domain model coupled with a simple groundwater model. *Journal of Contaminant Hydrology*, **145**, 67 – 81.

Tediosi, A., Whelan, M.J., Rushton, K.R., Thompson, T.R.E., Gandolfi, C. & Pullan, S.P. (2012). Measurements and conceptual modelling of herbicide transport to field drains in a heavy clay soil with implications for catchment-scale water quality management. *Science of the Total Environment*, **438**, 103 – 112.

Tiktak, A., van der Berg, F., Boesten, J.J.T.I., van Kraalingen, D., Leistra, M. & van der Linden, A.M.A. (2000) *Manual of FOCUS PEARL version 1.1.1*. Alterra Green World Research, RIVM report 711401 008, Wageningen, Netherlands, Alterra.

Tiktak, A., van der Linden, A.M.A., & Boesten, J.J.T.I. (2003) *The GeoPEARL model: model description, applications and manual*. Wageningen, Netherlands.

Tixier, C., Bogaerts, P., Sancelme, M., Bonnemoy, F., Twagilimana, L., Cuer, A., Bohatier, J. & Veschambre, H. (2000) Fungal biodegradation of a phenylurea herbicide, diuron: structure and toxicity of metabolites. *Pest Management Science*, **56**, 455 – 462.

Todd, D.K. & Mays, L.W. (2005) *Groundwater hydrology*. Wiley, Hoboken, New Jersey.

University of Hertfordshire (2013) *The Pesticide Properties DataBase (PPDB)* developed by the Agricultural & Environment Research Unit (AERU), University of Hertfordshire, 2006 – 2013.

Uusitalo, R., Turtola, E., Kauppila, T. & Lilja, T. (2001) Particulate phosphorus and sediment runoff and drainflow from clayey soils. *Journal of Environmental Quality*, **30**, 589 – 595.

- van Beinum, W. & Beulke, S. (2010) *Collection and evaluation of relevant information on crop interception for the revision of the guidance document on persistence in the soil*. EFSA external report CFT/EFSA/PPR/2009/02, 41p.
- van Dam, J.C. (2000) *Field-scale water flow and solute transport: SWAP model concepts, parameter estimation and case studies*. PhD Thesis, Wageningen University.
- Van den Daele, G.F.A., Barker, J.A., Connell, L.D., Atkinson, T.C., Darling, W.G. & Cooper, J.D. (2007) Unsaturated flow and solute transport through the Chalk: Tracer test and dual permeability modelling. *Journal of Hydrology*, **342**, 157 – 172.
- van Genuchten, M.T. (1980) A closed-form equation for predicting the hydraulic conductivity of unsaturated soil. *Soil Science Society of America Journal*, **44**, 892 – 898.
- Vanclooster, M., Ducheyne, S., Dust, M. & Vereecken, H. (2000) Evaluation of pesticide dynamics of the WAVE-model. *Agricultural Water Management*, **44**, 371 – 388.
- Warren, N., Allan, I.J., Carter, J.E., House, W.A. & Parker, A. (2003) Pesticides and other micro-organic contaminants in freshwater sedimentary environments—a review. *Applied Geochemistry*, **18**, 159 – 194.
- Walker, A., Jurado-Exposito, Bending, G.D. & Smith, V.J.R. (2001) Spatial variability in the degradation rate of isoproturon in soil. *Environmental Pollution*, **111**, 407 – 415.
- Wang, L., Butcher, A.S., Stuart, M.E., Goody, D.C. Bloomfield, J.P. (2013) The nitrate time bomb: a numerical way to investigate nitrate storage and lag time in the unsaturated zone. *Environmental Geochemistry and Health*, **35**, 667 – 681.
- Water UK (2013) Briefing paper on metaldehyde.
<http://www.water.org.uk/home/policy/positions/metaldehyde-briefing/water-uk-policy-briefing-metaldehyde-13-aug-2013.pdf>. Accessed 01/11/2013.

Wauchope, R.D., Yeh, S., Linders, J.B.H.J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kördel, W., Gerstl, Z., Lane, M. & Unsworth, J.B. (2002) Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. *Pesticide Management Science*, **58**, 419 – 445.

Wei, M. & Menzel, L. (2008) A global comparison of four potential evapotranspiration equations and their relevance to stream flow modelling in semi-arid environments. *Advances in Geosciences*, **18**, 15 – 23.

Wellings, S. R. (1984) Recharge of the Upper Chalk aquifer at a site in Hampshire, England: 1. Water balance and unsaturated flow. *Journal of Hydrology*, **69**, 259 – 273.

Whelan, M.J. & Gandolfi, C. (2002) Modelling of spatial controls on denitrification at the landscape scale. *Hydrological Processes*, **16**, 1437 – 1450.

Whelan, M.J., Hope, E.G., Fox, K. (2002) Stochastic modelling of phosphorus transfers from agricultural land to aquatic ecosystems. *Water Science and Technology*, **45**, 167 – 176.

Whitehead, R. (2006) *The UK pesticide guide 2006*. CABI Publishing, Wallingford, Oxfordshire.

Whitehead, R. (2008) *The UK pesticide guide 2008*. CABI Publishing, Wallingford, Oxfordshire.

Williams, R.J., Brooke, D.N., Clare, R.W., Matthiessen, P. & Mitchell, R.D.J. (1996) *Rosemaund pesticide transport study 1987 – 1993*. Report 129, Institute for Hydrology, Wallingford, Oxfordshire.

Wilson, K.B., Hanson, P.J., Mulholland, P.J., Baldocchi, D.B. & Wullschlegel, S.D. (2001) A comparison of methods for determining forest evapotranspiration and its components: sap-flow, soil water budget, eddy covariance and catchment water balance. *Agriculture and Forest Meteorology*, **106**, 153 – 168.

Wittmer, I.K., Bader, H.P., Scheidegger, R., Singer, H., Lück, A., Hanke, I., Carlsson, C. & Stamm, C. (2010) Significance of urban and agricultural land use for biocide and pesticide dynamics in surface waters. *Water Research*, **44**, 2850 – 2862.

Wu, Q., Riise, G., Lundekvam, H., Mulder, J. & Haugen, L.E. (2004) Influences of suspended particles on the runoff of pesticides from an agricultural field at Askim, SE-Norway. *Environmental Geochemistry and Health*, **26**, 295 – 302.

Yoder, R.E., Odhiambo, L.O. & Wright, W.C. (2005) Evaluation of methods for estimating daily reference crop evapotranspiration at a site in the humid southeast United States. *Applied Engineering in Agriculture*, **21**, 197 – 202.

Zheng, C., & Bennett, G.D. (2002) *Applied contaminant transport modeling*. Wiley-Interscience, New York.

Appendix A. Model Symbols

Table A.1. List of model symbols.

Symbol	Explanation	Units
A	Catchment area	m^2
AF	First-order attenuation factor	-
BF	Baseflow constant	-
C_{ADE}	Intergranular matrix concentration calculated with the advection-dispersion equation	$\mu g m^{-3}$
$C_{ADE, peak}$	Peak intergranular matrix calculated by the advection-dispersion equation	$\mu g L^{-1}$
C_{AO}	Intergranular matrix concentration calculated with the advection only equation	$\mu g L^{-1}$
C_d	Maximum drain flow constant	$mm day^{-1}$
C_f	Fracture concentration	$\mu g L^{-1}$
C_g	Groundwater constant	$mm day^{-1}$
C_{int}	Concentration of pesticide in the interactive soil water	$\mu g L^{-1}$
C_{lat}	Sub-lateral flow parameter	-
C_m	Drain flow parameter that controls the rate of the recession curve	-
$C_{outlet(t)}$	Pesticide concentration at the surface water catchment outlet	$\mu g L^{-1}$
D	Dispersion coefficient	$m^2 day^{-1}$
DT_{50}	Degradation half-life	days
$DT_{50(UZ)}$	Degradation half-life in the unsaturated zone	days

E	Emission (on application) to the soil	$\mu\text{g m}^{-2}$
ES	Evaporation from bare soil	mm day^{-1}
ET_a	Actual evapotranspiration	mm day^{-1}
ET_c	Potential crop evapotranspiration	mm day^{-1}
ET_o	Reference evapotranspiration	mm day^{-1}
f_d	Fraction of chemical in dissolved phase	-
f_{matrix}	Fraction of flow via the intergranular matrix	-
$f_{fracture}$	Fraction of flow via the fracture	-
f_{OC}	Fraction of organic carbon	-
f_t	Fraction of actual evapotranspiration from topsoil	-
$fractR$	Fraction of rainfall that becomes infiltration excess overland flow	-
FW	Pore water velocity	m day^{-1}
GW_t	Water in the groundwater store	mm
I_{eOF}	Infiltration excess overland flow	mm day^{-1}
J	Mass flux of pesticides	$\mu\text{g m}^{-2} \text{day}^{-1}$
J_{sw}	Pesticide mass flux from drain flow	$\mu\text{g m}^{-2} \text{day}^{-1}$
$J_{outlet(t)}$	Weighted sum of the mass of pesticide from each soil type and crop combination	$\mu\text{g m}^{-2} \text{day}^{-1}$
J_{sw}	Pesticide mass flux to surface water	$\mu\text{g m}^{-2} \text{day}^{-1}$
J_{uz}	Pesticide mass flux entering the top of the unsaturated zone	$\mu\text{g m}^{-2} \text{day}^{-1}$
k	First-order degradation coefficient	day^{-1}
$K(\theta_t)$	Unsaturated hydraulic conductivity	mm day^{-1}
K_{BC}	Maximum hydraulic conductivity of the bottom boundary	mm day^{-1}

K_c	Evapotranspiration crop coefficient	-
K_d	Pesticide partition coefficient	L kg ⁻¹
K_e	Bare evaporation coefficient	-
K_f	Hydraulic conductivity of the fracture in the unsaturated zone	m day ⁻¹
K_{lat}	Saturated lateral hydraulic conductivity	mm day ⁻¹
K_{matrix}	Hydraulic conductivity of the matrix in the unsaturated zone	m day ⁻¹
K_{OC}	Soil organic carbon to water partition coefficient	L kg ⁻¹
K_s	Water stress coefficient	-
K_{sat}	Saturated hydraulic conductivity	mm day ⁻¹
K_T	Hargreaves equation empirical coefficient	-
m	van Genuchten curve parameter	-
$M_{soil(t)}$	Mass of pesticide in the soil	µg m ⁻²
$M_{soilwater}$	Mass of pesticide in the soil water phase	µg m ⁻²
$MSRV$	Minimum Standard Rainfall Volume	mm
N	Total number of land use and soil combinations	-
NSE	Nash Sutcliffe Efficiency	-
OC_{soil}	Organic carbon content of the topsoil	%
OC_{soil}	Organic carbon content of the unsaturated zone	%
p	fraction of Total Available Water that can be depleted before the crop suffers water stress	-
p_2	Proportional constant for calculating infiltration excess overland flow	-
$PBIAS$	Percentage bias	%

R	Rainfall	mm day^{-1}
R_a	Extra-terrestrial radiation	mm day^{-1}
RAW	Readily Available Water	mm
REW	Readily Evaporable Water	mm
$RF_{(t)}$	Retardation factor	-
RF_{UZ}	Retardation factor unsaturated zone	-
R_{mob}	Volume of daily rainfall required to mobilise pesticides	mm day^{-1}
R_s	Solar radiation	mm day^{-1}
R_{WB}	Rainfall entering the soil water balance	mm day^{-1}
SE_{OF}	Saturation excess overland flow	mm day^{-1}
SMS_t	Soil moisture deficit in the subsoil	mm
SMT_t	Soil moisture deficit in the topsoil	mm
t	Time	days
TAW	Total Available Water	mm
TC	Daily average temperature	$^{\circ}\text{C}$
TEW	Total Evaporable Water	mm
t_f	Travel time through the fracture	days
t_m	Travel time through the intergranular matrix	days
T_{max}	Maximum temperature	$^{\circ}\text{C}$
T_{min}	Minimum temperature	$^{\circ}\text{C}$
t_{uz}	Time from the mass being added to the hydrogeological unit	days
Q	Total flow	L day^{-1}
q	Drainage from the topsoil to subsoil	mm day^{-1}

$q_{baseflow}$	Baseflow from the groundwater store	L day ⁻¹
qBF	Baseflow from the groundwater store	mm day ⁻¹
q_{drain}	Flow from sub-surface artificial field drains	mm day ⁻¹
qL_{top}	Sub- lateral throughflow from the topsoil	mm day ⁻¹
qL_{sub}	Sub- lateral throughflow from the subsoil	mm day ⁻¹
Q_{mob}	Volume of water required in the active hydrological pathway to transport pesticides	mm day ⁻¹
Q_o	Observed flow	mm day ⁻¹
$Q_{o,t}$	Observed flow on day t	mm day ⁻¹
$Q_{s,t}$	Simulated flow on day t	mm day ⁻¹
qSF	Surface runoff	mm day ⁻¹
qP	Percolation	mm day ⁻¹
q_{quick}	Water flux from the hydrologically active pathways that will reach surface water resources	mm day ⁻¹
Q_{quick}	Quick flow from each land use and crop combination	L day ⁻¹
q_{tot}	Total flux of water displaced from the soil	mm day ⁻¹
W_i	Fraction of the total catchment area which is under land use and soil combination	-
V_{mob}	Volume of water of displaced water from the most mobile pores	L m ⁻² day ⁻¹
$Z_{(t)}$	Depth penetrated	mm
Z_e	Depth of evaporable water in bare soil	mm
Z_r	Root depth	mm
Z_{sub}	Subsoil depth	mm
Z_{top}	Topsoil depth	mm

Z_{uz}	Thickness of the hydrogeological unit	m
α_L	Longitudinal dispersivity	m
Δt	time increment in numerical solution	days
Φ	Total porosity of the hydrogeological unit	-
θ_5	Water content at -5 kPa tension	$\text{cm}^3 \text{cm}^{-3}$
θ_{200}	Water content at -200 kPa tension	$\text{cm}^3 \text{cm}^{-3}$
θ_{1500}	Water content at -1500 kPa tension	$\text{cm}^3 \text{cm}^{-3}$
θ_*	Dimensionless water content	-
θ_{int}	Interactive water content	$\text{cm}^3 \text{cm}^{-3}$
θ_{mob}	Mobile water content	$\text{cm}^3 \text{cm}^{-3}$
θ_{sat}	Saturated water content	$\text{cm}^3 \text{cm}^{-3}$
θ_{top}	Water content of the subsoil	$\text{cm}^3 \text{cm}^{-3}$
θ_t	Water content at time t	$\text{cm}^3 \text{cm}^{-3}$
θ_{top}	Water content of the topsoil	$\text{cm}^3 \text{cm}^{-3}$
ρ_b	Soil bulk density	g cm^{-3}
$\rho_{b,uz}$	Unsaturated zone bulk density	g cm^{-3}

Appendix B. Catchment Maps

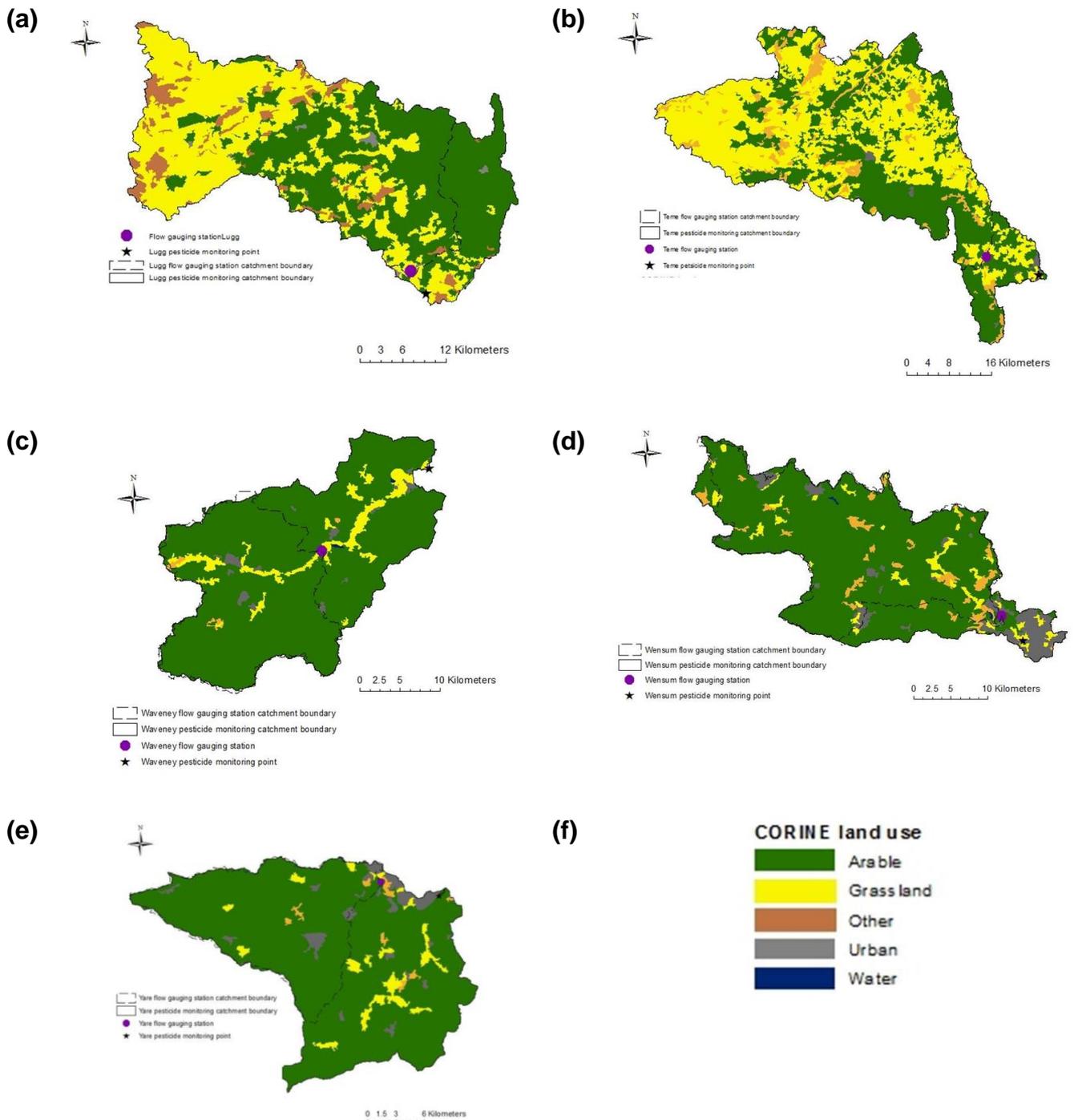


Figure B.1. CORINE land cover maps for the five case-study catchments:(a) Lugg, (b) Teme, (c) Waveney, (d) Wensum, (e) Yare and (f) land cover legend. Data from CORINE (CLC, 2000).

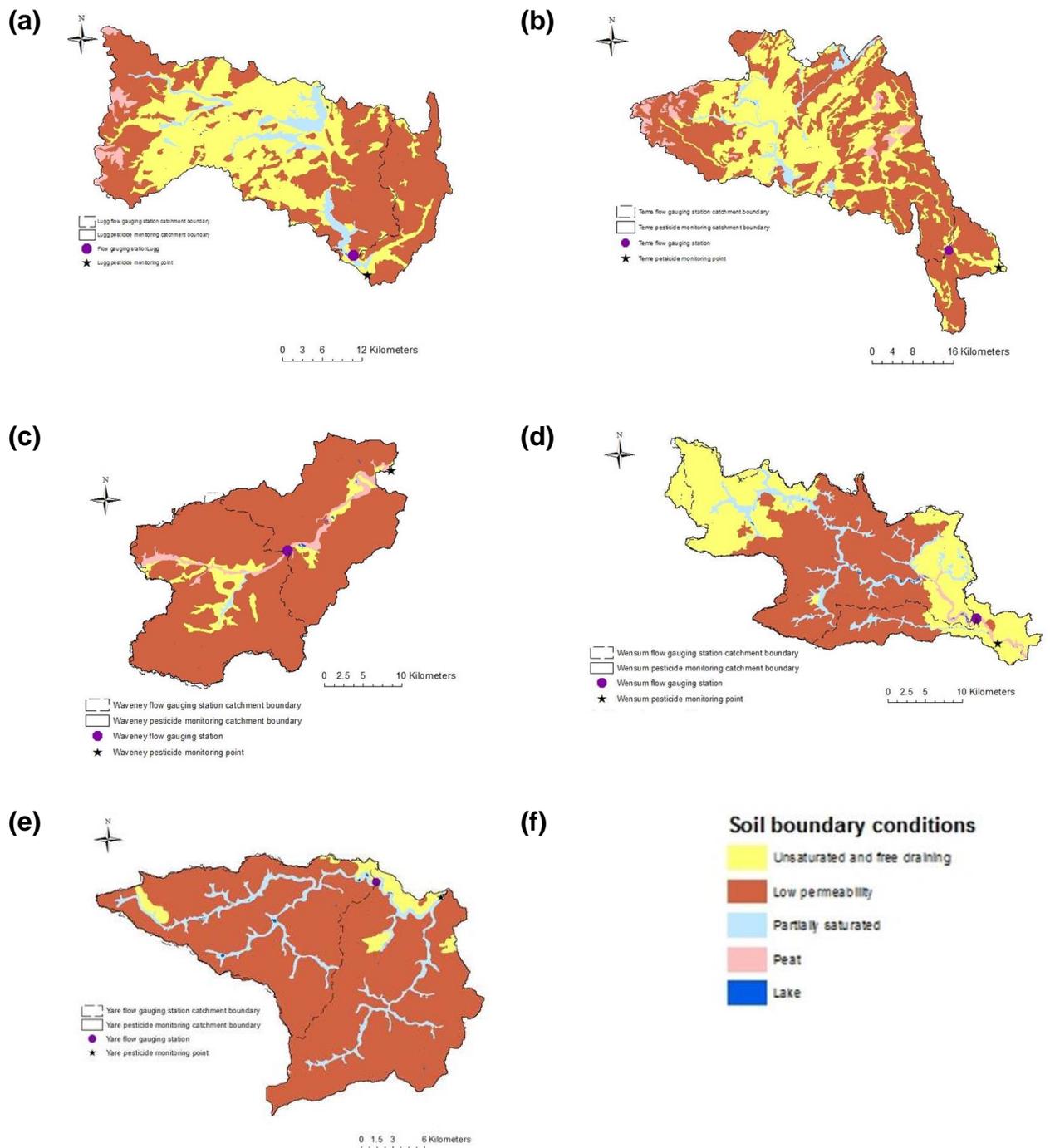


Figure B.2. Soil boundary condition maps for the five case-study catchments:(a) Lugg, (b) Teme, (c) Waveney, (d) Wensum, (e) Yare and (f) soil boundary condition legend. Base data from the National Soil Map (NSRI).

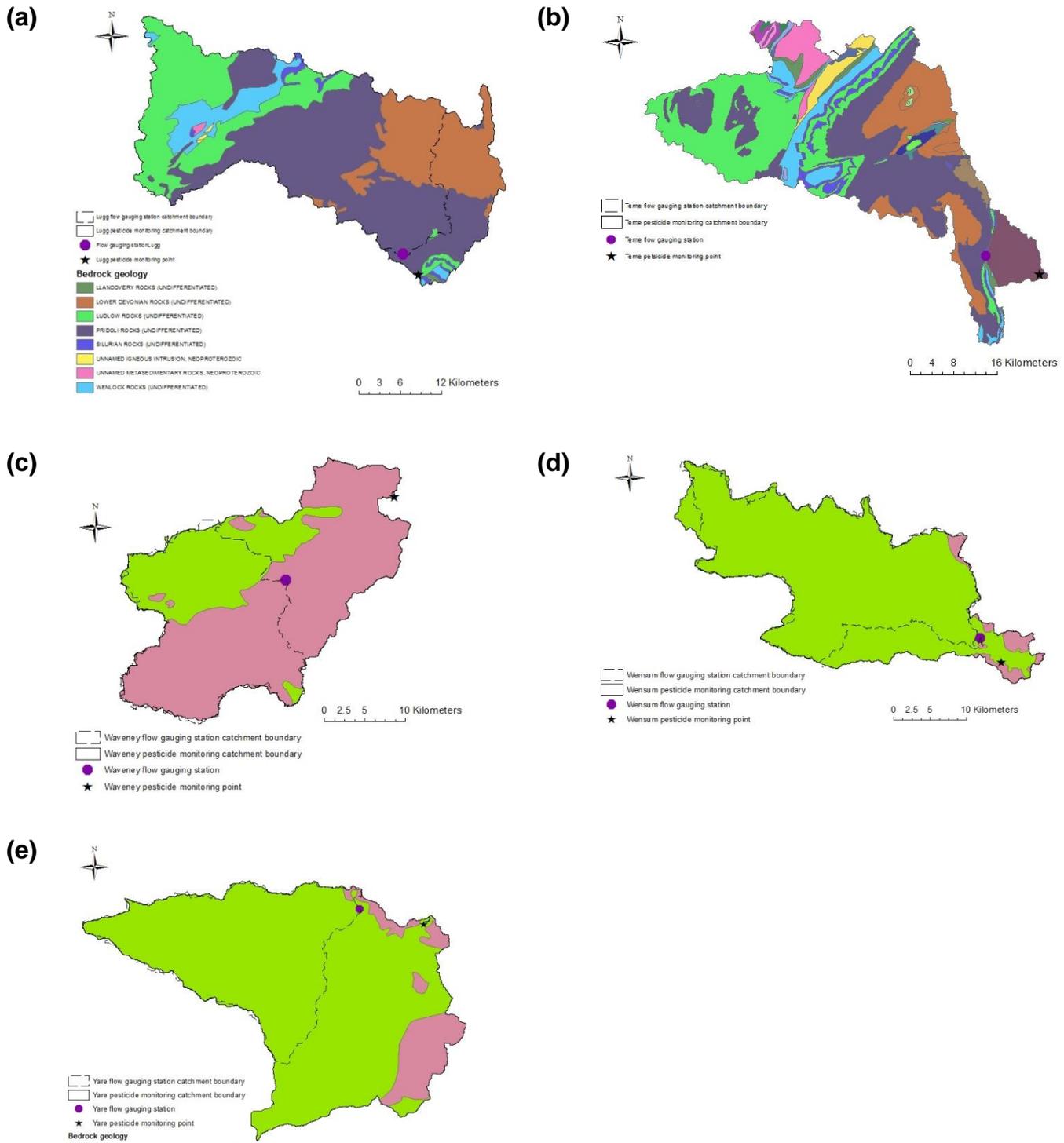


Figure B.3. Geology maps for the five case-study catchments:(a) Lugg, (b) Teme, (c) Waveney, (d) Wensum and (e) Yare. The legend is provided in Figure B.4. Data from EDINA Digimap.



Figure B.4. Legend for Geology Maps

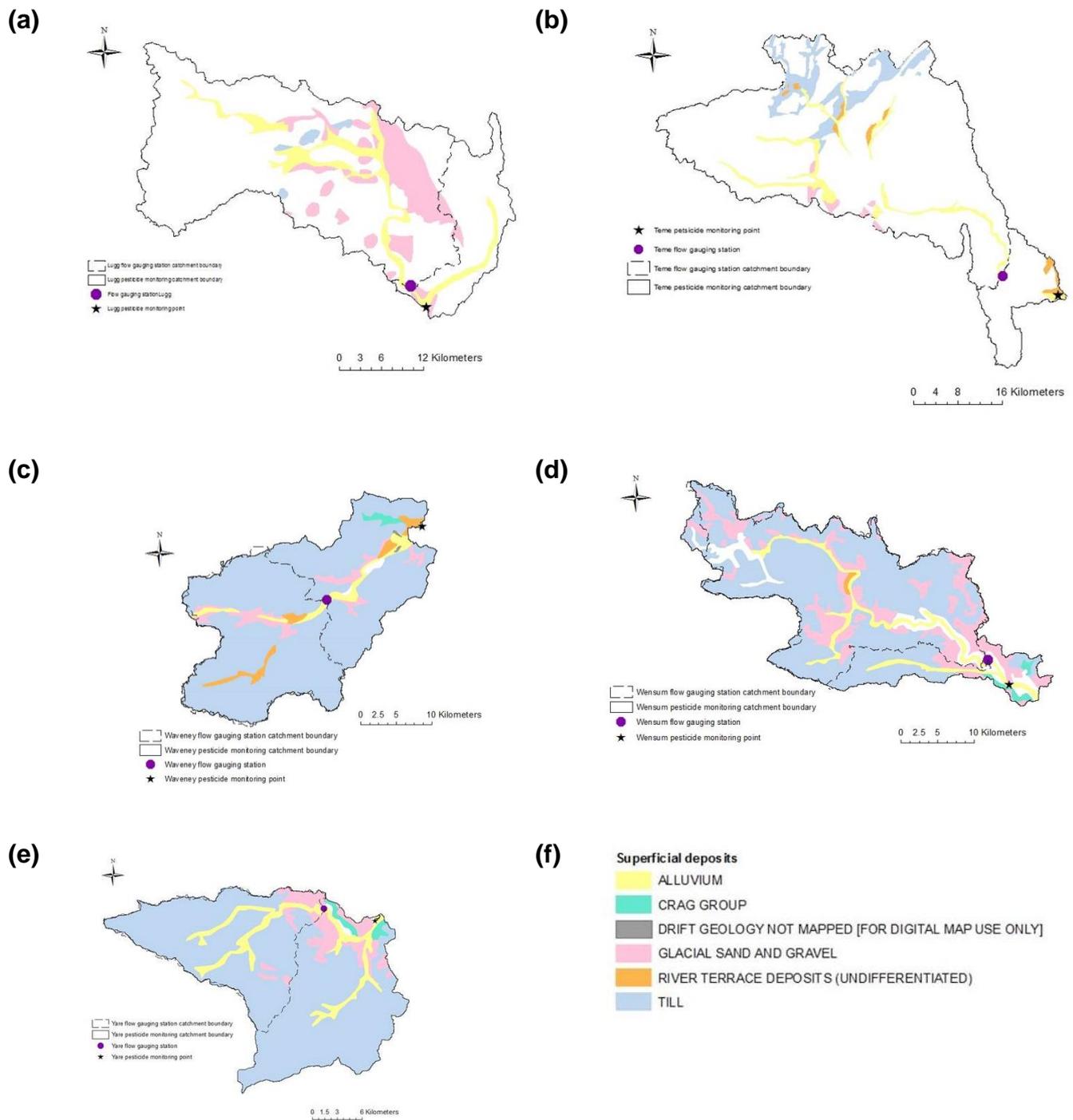


Figure B.5. Superficial geology maps for the five case-study catchments:(a) Lugg, (b) Teme, (c) Waveney, (d) Wensum (e) Yare, (f) legend for superficial geology. Data from EDINA Digimap.

Appendix C. Rainfall and Temperature Regression Graphs

For gaps in measured rainfall and temperature data (Section 4.3.1), values from neighbouring stations (which were not used typically due to lack of data during the model run period) were analysed for suitability as replacements. To assess the suitability of the replacement weather station a regression model was constructed to describe the relationship between the replacement station (x) and the main chosen station (y). If R^2 was greater than 0.7 and m (from the regression equation $y = mx + c$) was between 0.7 and 1.3, then the replacement station is considered suitable (Allen *et al.*, 1996), in all other situations the substitute was rejected. The main weather stations chosen and the replacement weather stations for each catchment are shown in Table 4.6. In the Lugg catchment two Newport weather stations were used as one was operational from 1992 to 2007 (Figure C.1a) and the second from 2008 to 2010 (Figure C.1b). The regression graphs are shown in order for rainfall and maximum and minimum temperature in the Lugg, Waveney, Wensum and Yare catchments. The Teme catchment is not shown as there was a full data set at Pennerley.

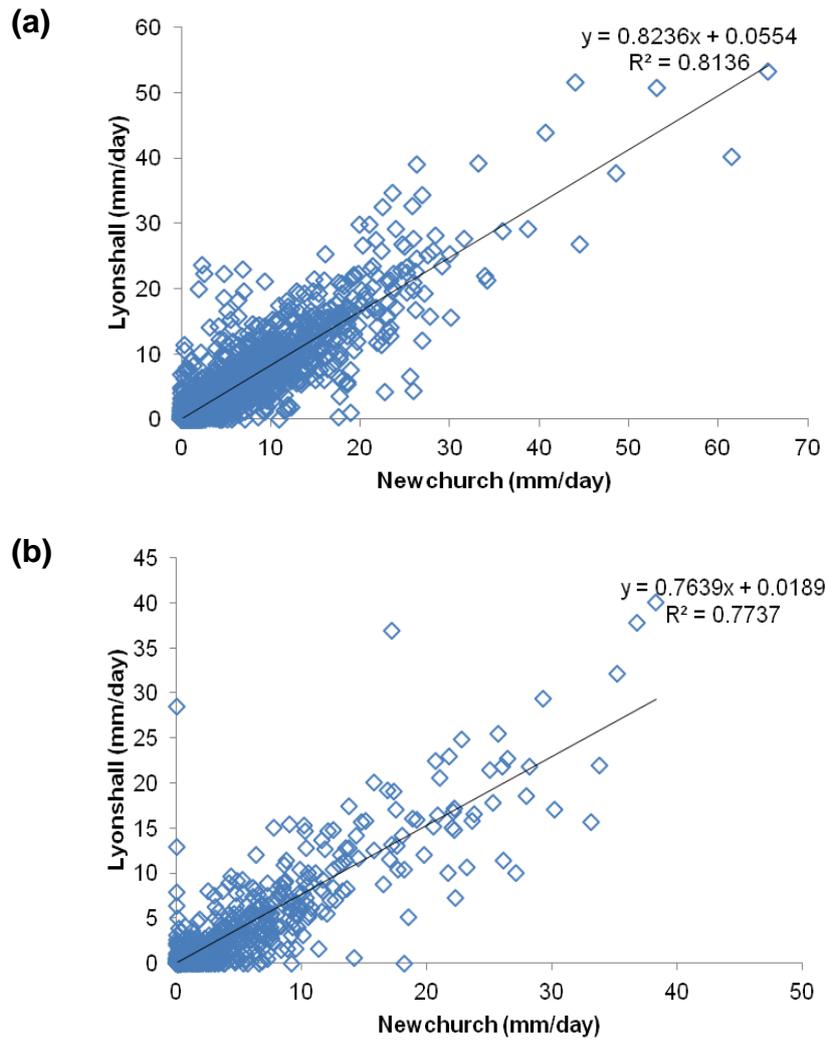


Figure C.1. Regression of daily rainfall with data from (a) Newchurch (1992 to 2007) and Lyonshall (b) and Newchurch (2008 to 2010) and Lyonshall, in the Lugg catchment.

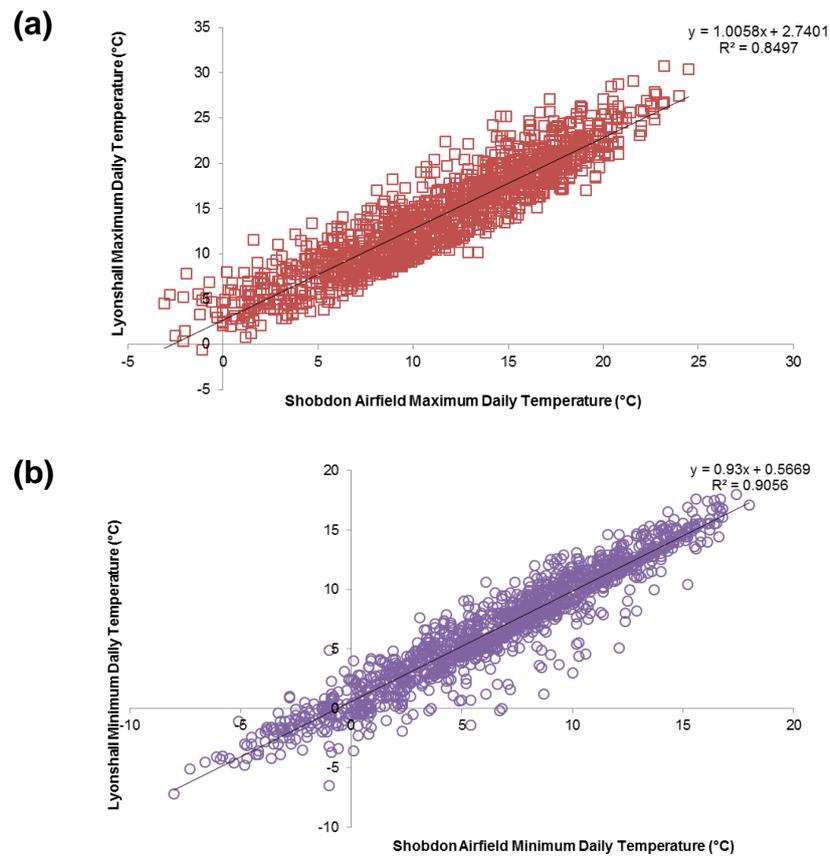


Figure C.2. Regression of (a) maximum daily temperature and (b) minimum daily temperature with data from Shobdun Airfield and Lyonshall between 1989 and 2010 in the Lugg catchment.

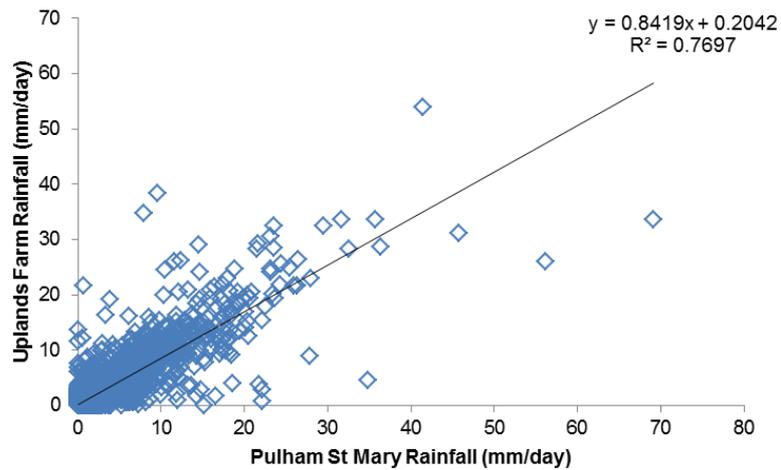


Figure C.3. Regression of daily rainfall with data from Pulham St Mary and Uplands Farm between 1989 and 2010 in the Waveney catchment.

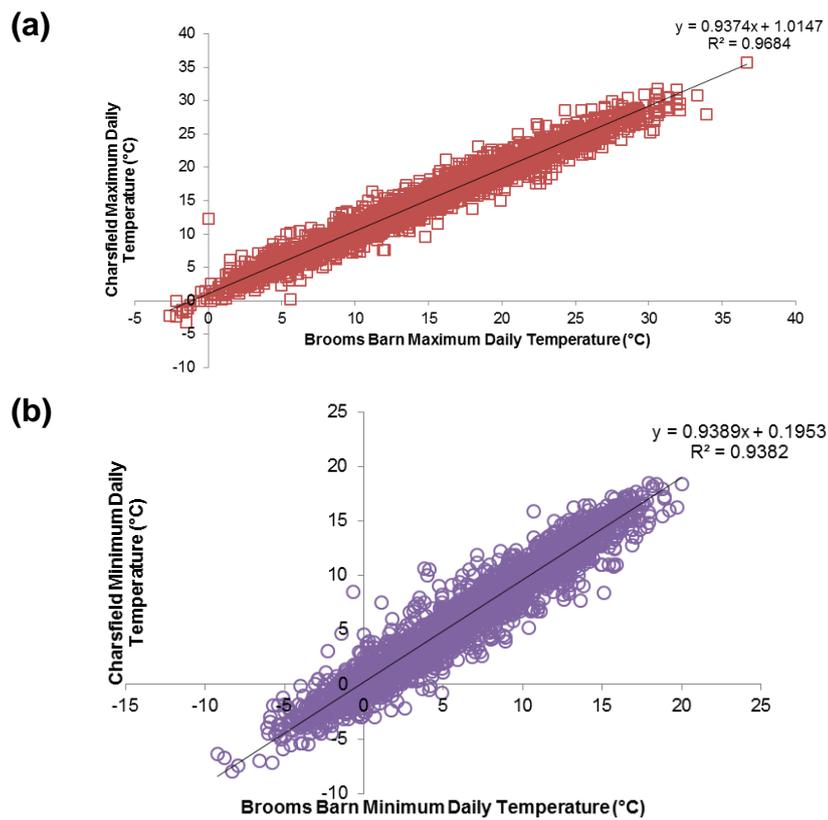


Figure C.4. Regression of (a) maximum daily temperature and (b) minimum daily temperature with data from Brooms Barn and Charsfield between 1992 and 2010 in the Waveney catchment.

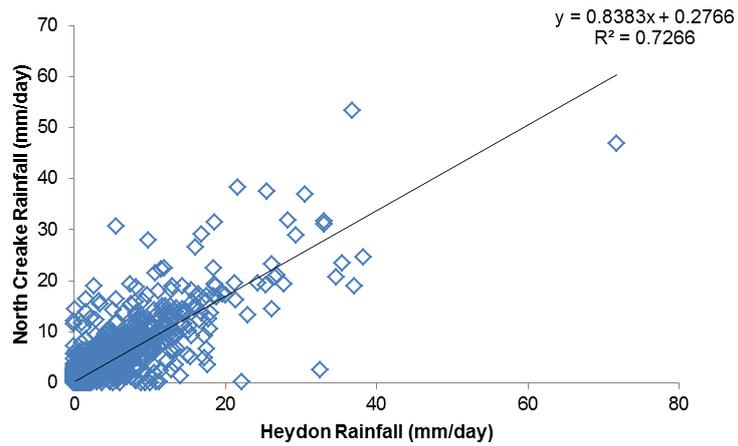


Figure C.5. Regression of daily rainfall with data from Heydon and North Creake between 1989 and 2010 in the river Wensum catchment.

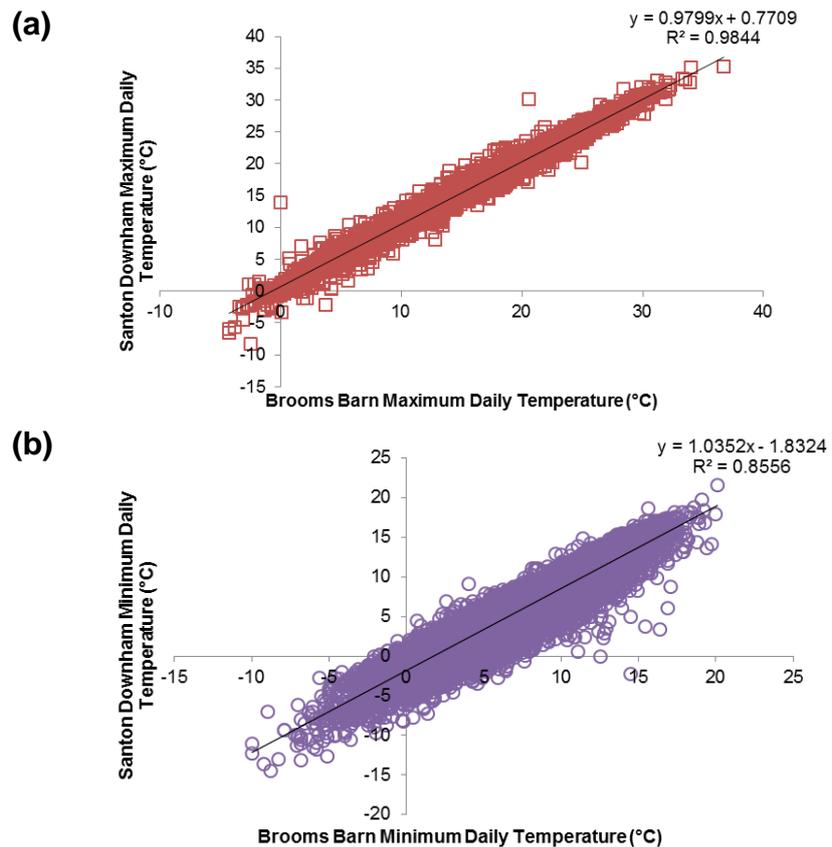


Figure C.6. Regression of (a) maximum daily temperature and (b) minimum daily temperature with data from Brooms Barn and Santon Downham between 1989 and 2010 for the river Yare and Wensum catchments.

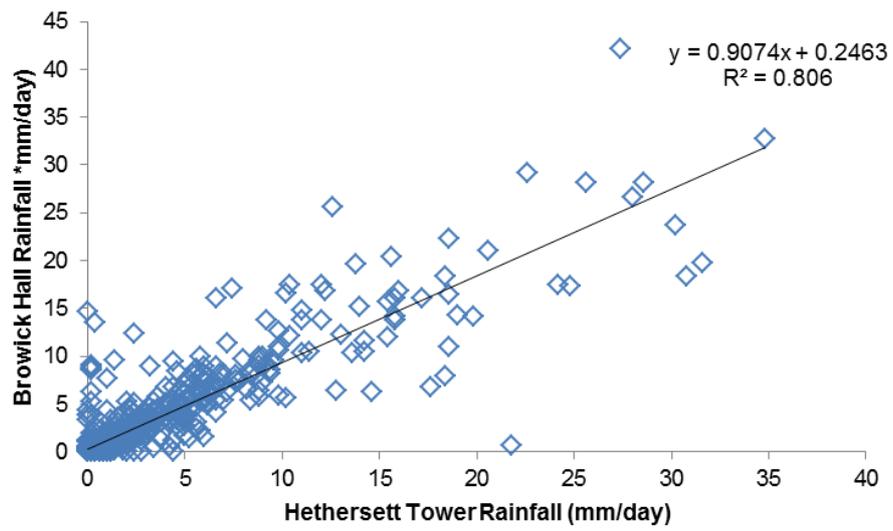


Figure C7. Regression of daily rainfall with data from Hethersett Tower and Browick Hall for between 1989 and 2010 in the Yare catchment.

Appendix D. CORINE Land Cover Classes

The land use in each catchment was determined using the CORINE land cover map 2000 (CLC, 2000). CORINE considers 44 land cover classes, listed in Table D.1. These classes were grouped to form broader categories: arable, grassland and urban and other as shown in Table D.1.

Table D.1. Land cover classes in CORINE grouped into boarder land cover categories.

Broad land cover category	Land cover category CORINE (3 rd tier)	Broad land cover category	Land cover category CORINE (3 rd tier)	Broad land cover category	Land cover category CORINE (3 rd tier)	Broad land cover category	Land cover category CORINE (3 rd tier)
Urban	Continuous urban fabric Discontinuous urban fabric Industrial or commercial units Road and rail networks and associated land Port areas Airports Mineral extraction sites Dump sites Construction sites	Arable	Non-irrigated arable land Permanently irrigated arable land Rice fields Annual crops associated with permanent crops Complex cultivation areas Land use principally occupied by agriculture, with significant areas of natural vegetation. Vineyards Fruit trees and berry plantations Olive groves	Grass	Green urban areas Sport and leisure facilities Pastures Natural Grassland	Other	Agro-forestry areas Broad-leaved forest Coniferous forest Mixed forest Transitional woodland shrub Moors and Heathland Beaches, dunes and sands Bare rocks Sparsely vegetated areas Burnt areas Glaciers and perpetual snow Inland Marshes Peat bogs Salt marshes Saline intertidal flats Water courses Water bodies Costal lagoons Estuaries Sea and Ocean

Appendix E. Pesticide Application Rate and Timing

E.1. Crop growth stages for use in pesticide application

The information regarding pesticide application rate and timing came from product labels, Environmental Information Sheets (EIS) from the Voluntary Initiative¹ and the UK Pesticide Guide (Whitehead, 2008). On product labels last application date is typically provided or a reference to the Zadoks crop growth stage. When referring to pesticide application rate and timing, only the crops in the thesis, grass, winter wheat and winter oilseed rape will be considered.

E.1.1. Winter wheat growth stages

The Winter Growth Guide (HGCA, 2008) provides approximate dates for growth stages, summarised in Table D.1. The timing of the crop development is linked to thermal time from sowing in °C days above 0°C. In warmer years it could therefore be expected the approximate dates in Table E.1 are earlier, and in colder years later.

Table E.1. Approximate dates of winter wheat growth stages. Adapted from HGCA (2008).

Growth stages	Approximate date
1 st leaf stage (GS10)	15 th October
Fully tillered (GS29)	25 th March
Leaf-sheath erect (GS30)	31 st March
1 st Node detectable (GS31)	10 th April
2 nd Node detectable (GS32)	20 th April

*Note, GS refers to the Zadoks growth stage.

¹ <http://www.voluntaryinitiative.org.uk/content/eis.aspx>. Accessed 01/03/2012.

E.1.2. Winter oilseed rape growth stages

For winter oilseed rape the crop dates in Table 4.9 detailing: planting date, emergence, 10 % cover, 100 % cover, senescence and harvest from Holman *et al.* (2005) were used.

E.2. Maximum application rate and timing window

E.2.1. 2,4-D maximum application rate and timing window

2,4-D is used on cereals and grass. In winter cereals it is recommended by Whitehead (2008) to spray in the spring between leaf-sheath erect (GS30) but before 1st node detectable (GS31). Assuming maximum label dose rate of 2.5 l ha⁻¹ with 500 g l⁻¹ of 2,4-D active ingredient², gives an application rate of 1.25 kg ha⁻¹.

In grass the latest time of application is before it is 25cm high². In the pesticide fate and transport model grass is not assumed to be harvested, the roots are at a constant depth and the crop evapotranspiration parameters (K_c) are fixed at 1. For pesticide application the growing season for grass is assumed to start on 15th of March and end on the 30th of October (Holman *et al.*, 2005). Assuming maximum label dose rate of 3.3 l ha⁻¹, with 500 g l⁻¹ of 2,4-D active ingredient, gives an application rate of 1.65 kg ha⁻¹.

E.2.2. Carbetamide maximum application rate and timing window

Carbetamide is used on winter oilseed rape. Application is assumed to be between the middle of October and end of February (Figure E.1). The maximum application rate from the product label³ is assumed to be 3.5 kg ha⁻¹.

² http://technical.nufarm.co.uk/documents/herbicide/label/depitox_labelinfo.pdf. Accessed 01/10/2012

CROP SPECIFIC INFORMATION		
Application Timing		
Crop: Winter oilseed rape, fodder rape seed and kale seed.	Seasonal Timing: Mid-October to the end of February.	Crop Growth Stage: Crop to have at least 3-4 true leaves. Do not treat when growing away in the spring.
Seed crops of cabbage, turnip, swede and sugar beet.	November to end of February.	Crop to have 3-4 true leaves.
Winter field beans.	November to end of February.	Pre- or post-crop emergence.
Lucerne and sainfoin.	November to end of February.	After crop establishment.

Figure E.1. Information from Carbetamide product label for Crawler manufactured by Makhteshim³

E.2.3. Chlorotoluron maximum application rate and timing window

Chlorotoluron is used on winter wheat and for best results Whitehead (2008) recommends used soon after drilling and before leaf sheath erect (GS30). From the EIS⁴ the maximum label dose rate is 3.5 kg ha⁻¹.

E.2.4. Clopyralid maximum application rate and timing window

Clopyralid is a spring applied herbicide in oilseed rape, applied between the two full extended leaf stage and when flower buds are visible above the canopy⁵. The latest application is assumed to be at 100% crop cover 243 days after planting (Table 4.9). The maximum application rate, from the EIA⁶ is 0.2 kg ha⁻¹.

E.2.5. Isoproturon maximum application rate and timing window

Isoproturon was a post-emergence herbicide used on winter wheat (Whitehead, 2008); it has been banned from use since June 2009. The measured data has been collected between 2006 and 2009 and isoproturon was therefore still in use. The latest timing of application is before second node detectable (GS32) and the maximum application rate is 1.5 kg ha⁻¹ ⁷.

³ <http://www.mauk.co.uk/pdfs/labels/Crawler%2010kg%20label.pdf>. Accessed 0/12/2012

⁴ http://www.voluntaryinitiative.org.uk/_Attachments/resources/526_s4.pdf. Accessed 0/12/2012

⁵ http://msdssearch.dow.com/PublishedLiteratureDAS/dh_0890/0901b80380890020.pdf?filepath=/uk/pdfs/noreg/011-01126.pdf&fromPage=GetDoc. Accessed 0/12/2012

⁶ http://www.voluntaryinitiative.org.uk/_Attachments/resources/295_s4.pdf. Accessed 0/12/2012

⁷ http://www.dhm.ie/products/herb/Arelon%20500%20IRL_12Apr10.pdf. Accessed 0/12/2012

E.2.6. MCPA maximum application rate and timing window

MCPA is used in both wheat and grass. In winter wheat application is between the crop being fully tillered (GS29) to 1st node detectable (GS31) Whitehead (2008). The maximum application rate is 1.6 kg ha⁻¹ ⁸. In grass the application is typically dictated by the species of weed (Whitehead, 2008) and, therefore, a board application window has been assumed between spring and mid-summer. Maximum application rate is 1.6 kg ha⁻¹ ⁷.

E.2.7. Mecoprop maximum application rate and timing window

Mecoprop is applied to winter wheat and grass. The application window for mecoprop on winter wheat is between GS10 and GS32 (Whitehead, 2008). Maximum application rate is 1.3 kg ha⁻¹ ⁹. An example product label for mecoprop used in grass¹⁰ is shown in Figure E.2, and highlights that application in spring will provide the best efficacy.

Grassland

Dose

5.5 l/ha.

Maximum number of applications

Two per year.

Water volume

Apply in 200–400 litres of water per hectare.

Spray in the spring when weed growth is vigorous. This is usually in April, but can be earlier if conditions are suitable. A second application can be made in the following autumn, where weed growth is vigorous and there is at least one month of growing weather following treatment. Best results are from two applications made in the spring of succeeding years.

Timing

Where grassland has been grazed or cut for conservation allow at least 14 days or when the weeds have re-grown before treatment. Weed growth and control is usually enhanced by an application of nitrogen fertilizer two or three weeks before treatment.

Do not apply to grass or turf established for less than 18 months.

Figure E.2. Information from mecoprop product label for Pierce manufactured by NuFarm¹⁰.

⁸ <http://www.headland-ag.co.uk/product-download.asp?id=144>. Accessed 01/10/2012

⁹ http://technical.nufarm.co.uk/documents/Herbicide/Label/Compitox_Plus_labelinfo.pdf. Accessed 01/10/2012

¹⁰ http://technical.nufarm.co.uk/documents/Herbicide/Label/Pierce_labelinfo.pdf. Accessed 01/10/2012

E.2.8. Propyzamide maximum application rate and timing window

Propyzamide is used on winter oilseed rape, application is between 1st of October and the 31st of January (Figure E.3) and maximum label dose rate is 0.8 kg ha⁻¹ ¹¹.

Crop	Rate of Use	Weed Species	Stage of Weed Growth			Time of Year	Timing Stage of Crop	Soil Type (Soil Texture (85 System))
			Germinating	Up to 2 leaf	Established			
Winter oilseed rape	1.75 litres/ha	Annual meadow-grass, barren brome, volunteer cereals, wild-oat	S	S	S	1 st October to 31 st January	As soon as possible after 3rd true leaf stage. Crop selectivity is by depth	All soils with less than 10% organic matter
		Common chickweed	S	S	S ¹			
		Blackgrass	S	S	MS ²			
		Black-bindweed, black nightshade, fat-hen, knotgrass, redshank, small nettle, speedwells	S	S	MR			
		Field forget-me-not	MS	MS	R			
		Cleavers	MS	MR	R			

Figure E.3. Information from propyzamide product label for Kerb Flo manufactured by Dow AgroSciences¹¹.

E.2.9. Metazachlor maximum application rate and timing window

Metazachlor is a post-emergence herbicide applied to spring oilseed rape. Metazachlor is only used in the pesticide fate and transport model in the scenario modelling chapter, Chapter 7. The application is assumed to be between emergence (24th of April) and before the 10th true leaf stage in spring oilseed rape, assuming 100 % crop cover (14th of May). The maximum application rate is 0.75 kg ha⁻¹ ¹².

¹¹

http://msdssearch.dow.com/PublishedLiteratureDAS/dh_0831/0901b80380831d1e.pdf?filepath=/uk/pdfs/noreg/011-01346.pdf&fromPage=GetDoc. Accessed 01/10/2012

¹² http://www.agricentre.basf.co.uk/agroportal/uk/media/product_files_uk/labels/Butisan_S.pdf. Accessed 01/10/2012

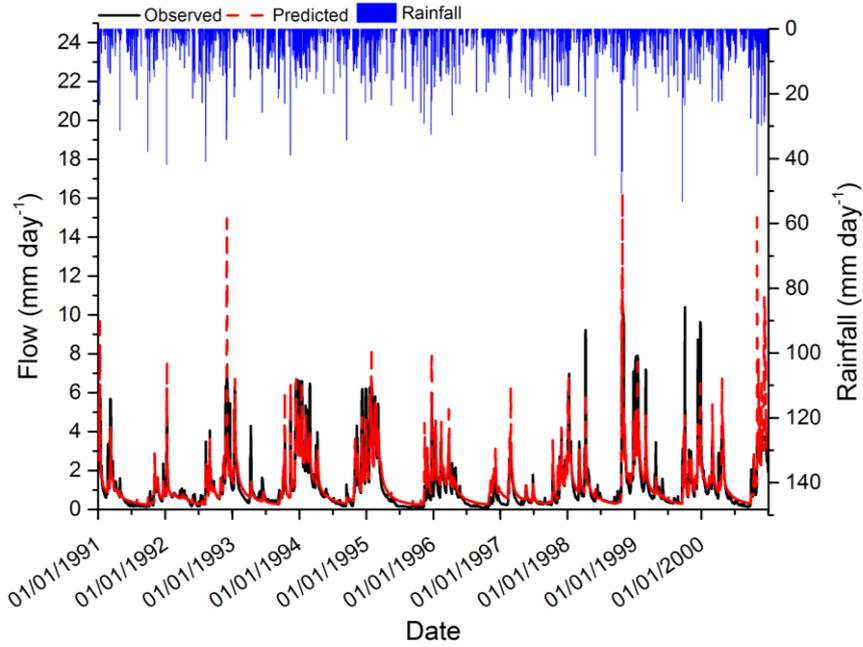
Appendix F. Hydrographs for Calibration and Validation Period and Sensitivity Analysis.

F.1. Hydrograph results

F.1.1. Lugg hydrograph results

The hydrographs shown in Figure F.1 in the Lugg catchment show a good degree of similarity between observed and predicted daily river flow in both the calibration and validation period. There is some over prediction of peak flow events, particularly in the validation period.

(a)



(b)

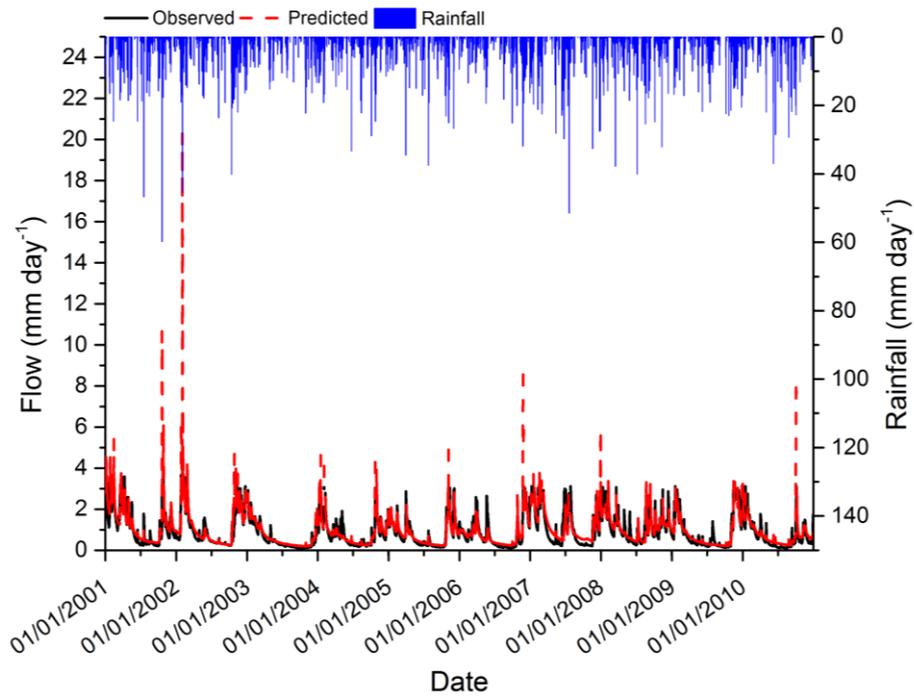


Figure F.1. River Lugg at Lugwardine observed and predicted daily river flow and daily rainfall in (a) calibration period (1991 – 2000) and (b) validation period (2001 – 2010).

F.1.2. Teme hydrograph results

The hydrographs shown in Figure F.2 in the Teme catchment show a good degree of similarity between observed and predicted daily river flow in both the calibration and validation period. There is some under-prediction of peak flow events, particularly in the validation period.

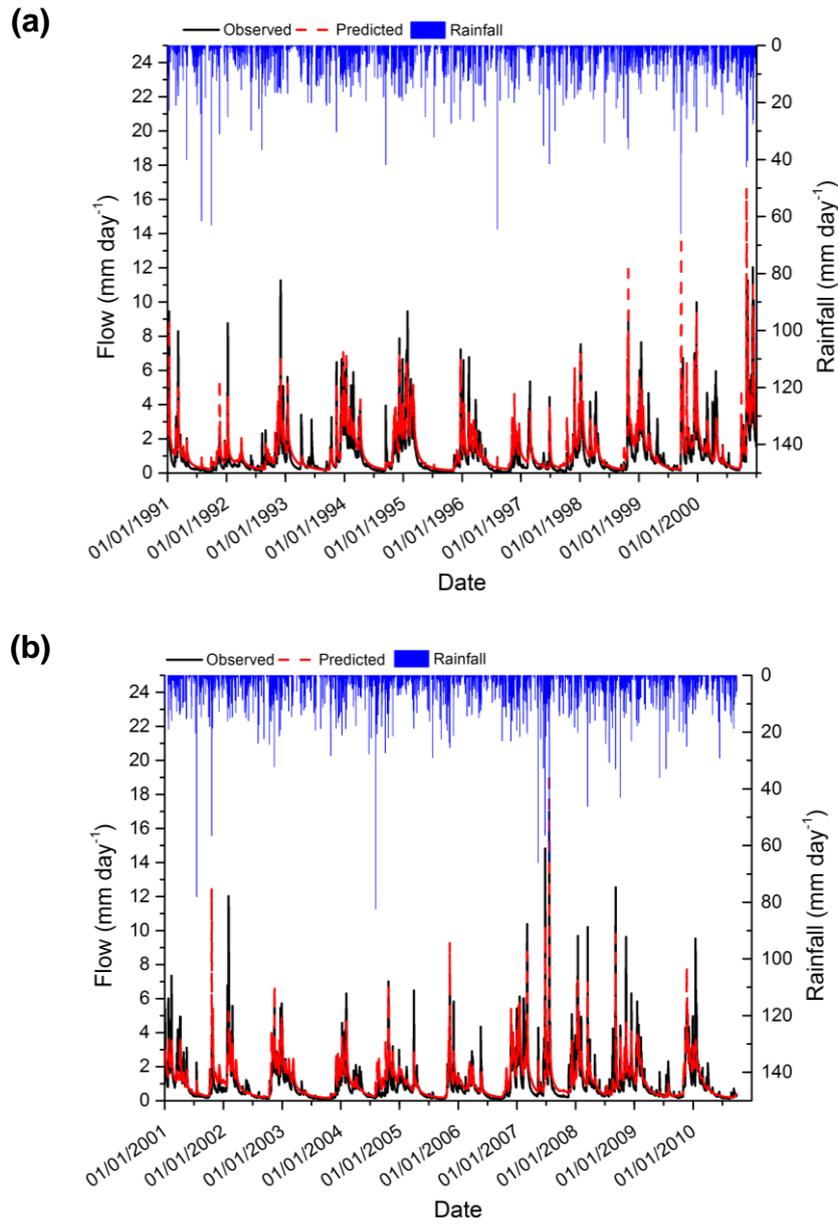


Figure F.2. River Teme at Knightsford Bridge observed and predicted daily river flow and daily rainfall at the catchment outlet in (a) calibration period (1991 – 2000) and (b) validation period (2001 – 2010).

F.1.3. Waveney hydrograph results

The hydrograph results in Figure F.3 in the Waveney catchment demonstrate that there is good agreement between the observed and predicted daily flow. In both the calibration period and the validation period it can be seen that in the summer months the model does not pick up on the peak flow events seen in the measured data

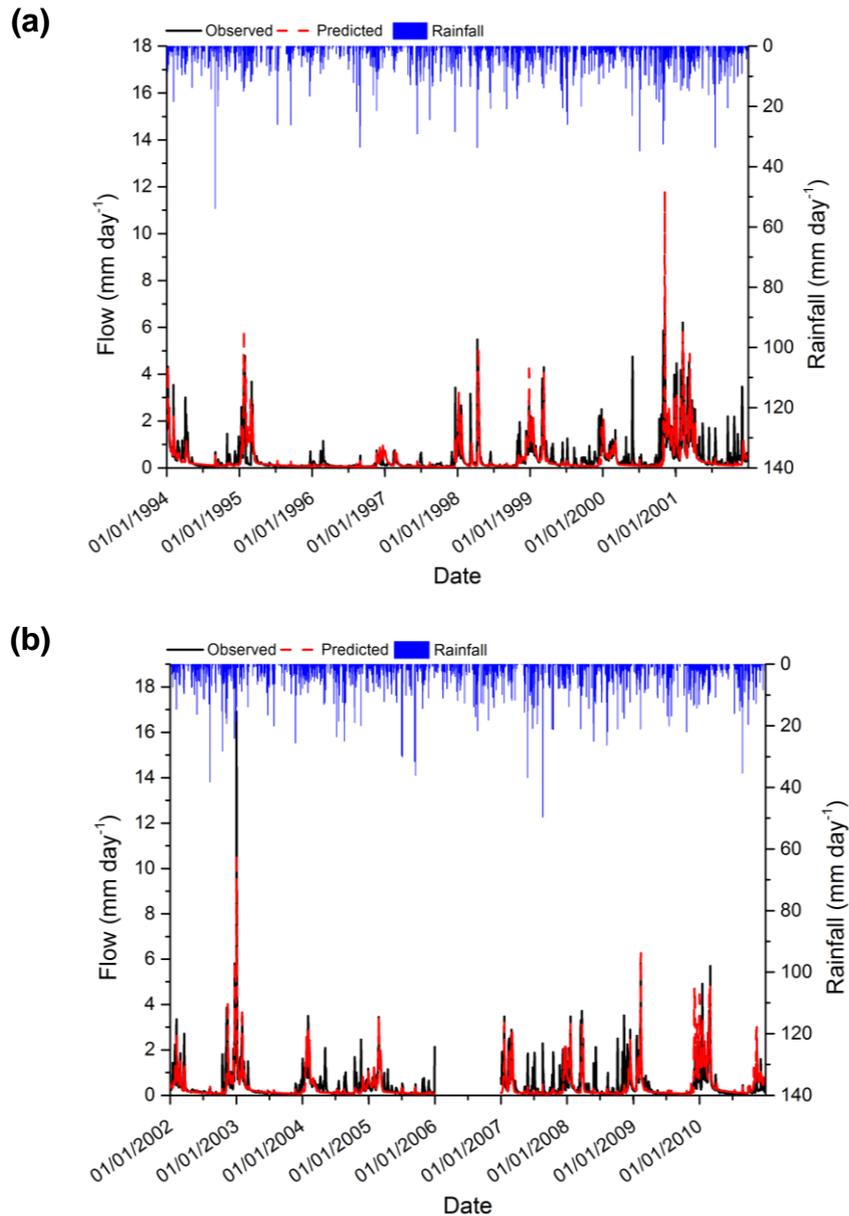


Figure F.3. River Waveney at Needham Mill observed and predicted daily river flow and daily rainfall at the catchment outlet in (a) calibration period (1994 – 2001) and (b) validation period (2002 – 2010).

F.1.4. Wensum hydrograph results

The hydrograph results in the Wensum, Figure F.4, generally display a poor agreement between observed and predicted flow. The model does pick up on large peak flow events in the calibration and validation period; however, the model tends to over-predict these events. The prediction of baseflow in the validation period does not show a good agreement to measured data, Figure F.7b, and it can be seen that the modelled baseflow recession is occurring for too long.

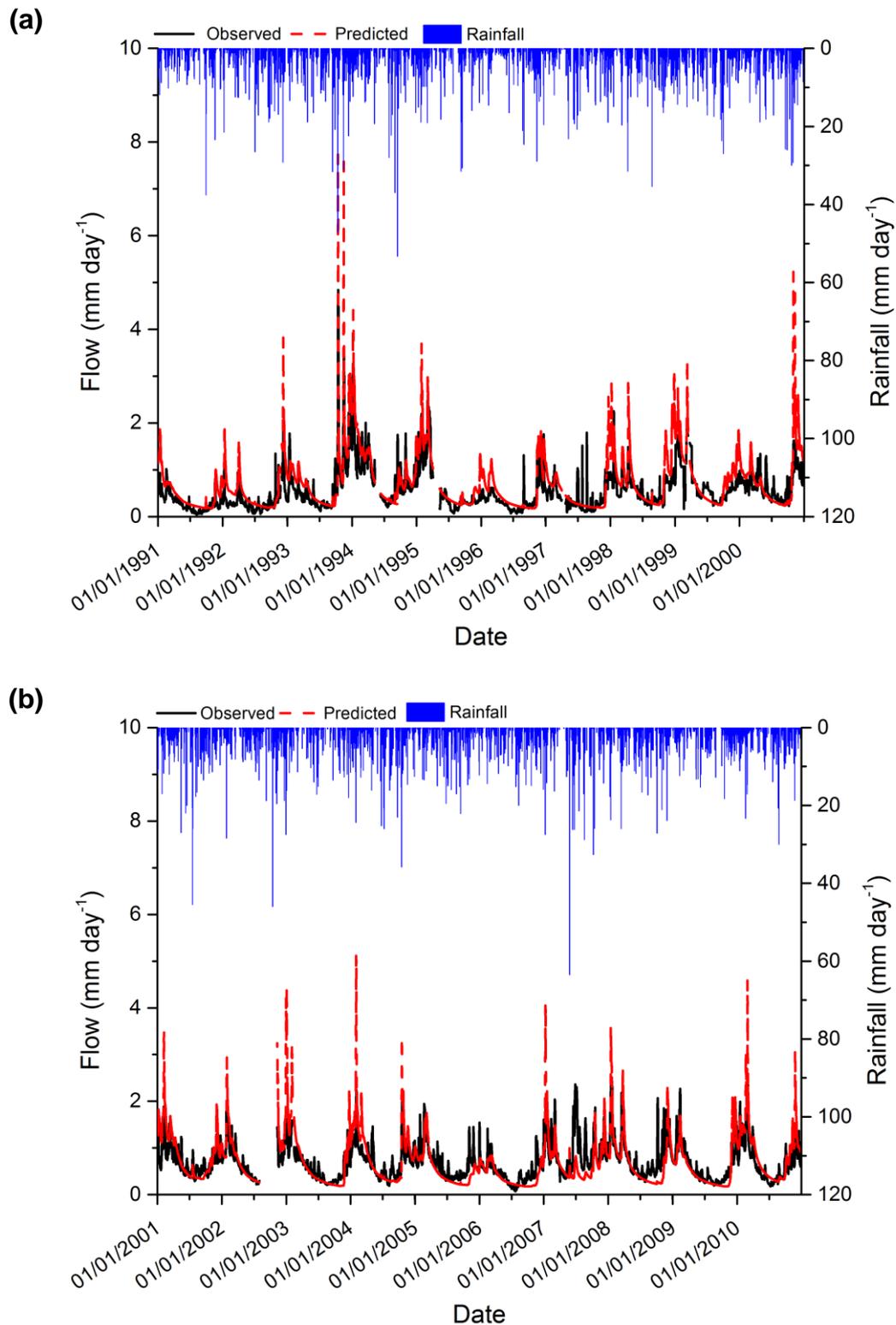


Figure F.4. River Wensum at Costessey Mill observed and predicted daily river flow and daily rainfall at the catchment outlet in (a) calibration period (1991 – 2000) and (b) validation period (2001 – 2010).

F.1.5. Yare hydrograph results

In the Yare catchment the agreement between observed and predicted flow in the calibration and validation period is generally quite good (Figure F.5). The model tends to over-predict peak flow events; this is particularly evident at the end of December 2000 in the calibration period (Figure F.5a) when there is a large modelled flow response to several days of heavy rainfall, which is not displayed in the measured hydrograph. As in the Waveney catchment, there is some under-prediction of peak flow events in the summer.

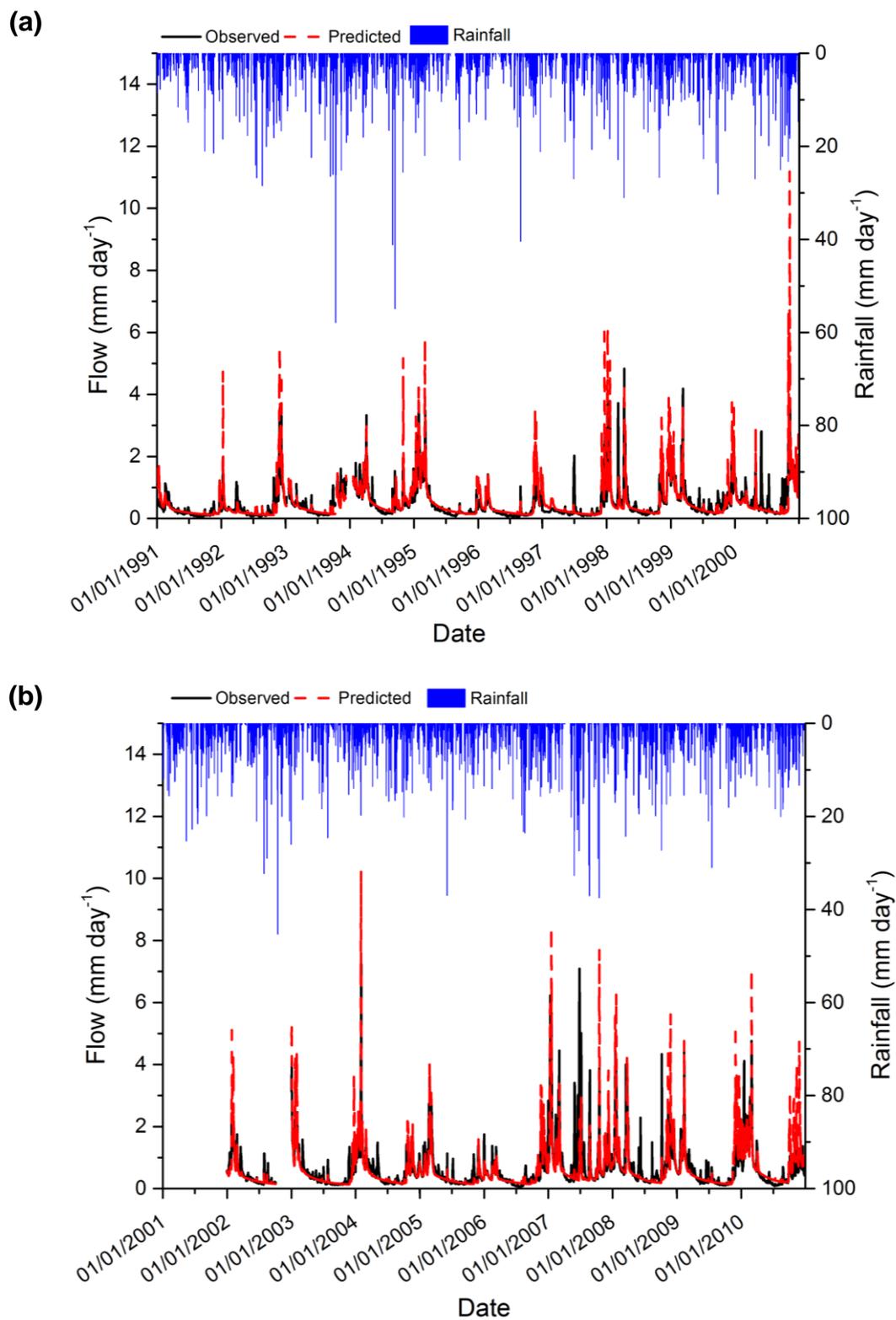


Figure F.5. River Yare at Colney observed and predicted daily river flow and daily rainfall at the catchment outlet in (a) calibration period (1991 – 2000) and (b) validation period (2002 – 2010).

Appendix G. Pesticide Cumulative Frequency

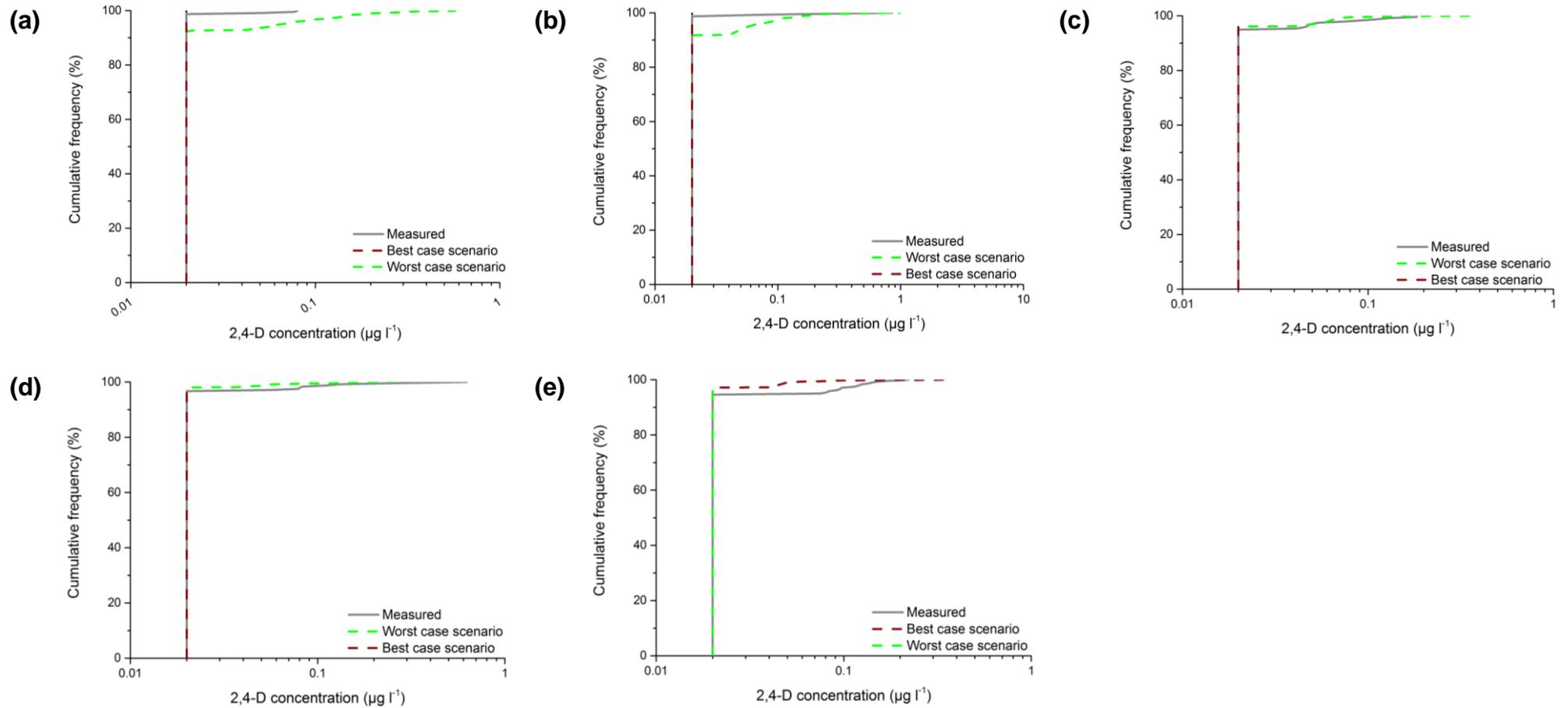


Figure G.1. Cumulative frequency distributions for measured 2,4-D concentrations with predicted best case and worst case concentrations at the catchment outlet in the (a) Lugg, (b) Teme, (c) Waveney, (d) Wensum, (e) Yare.

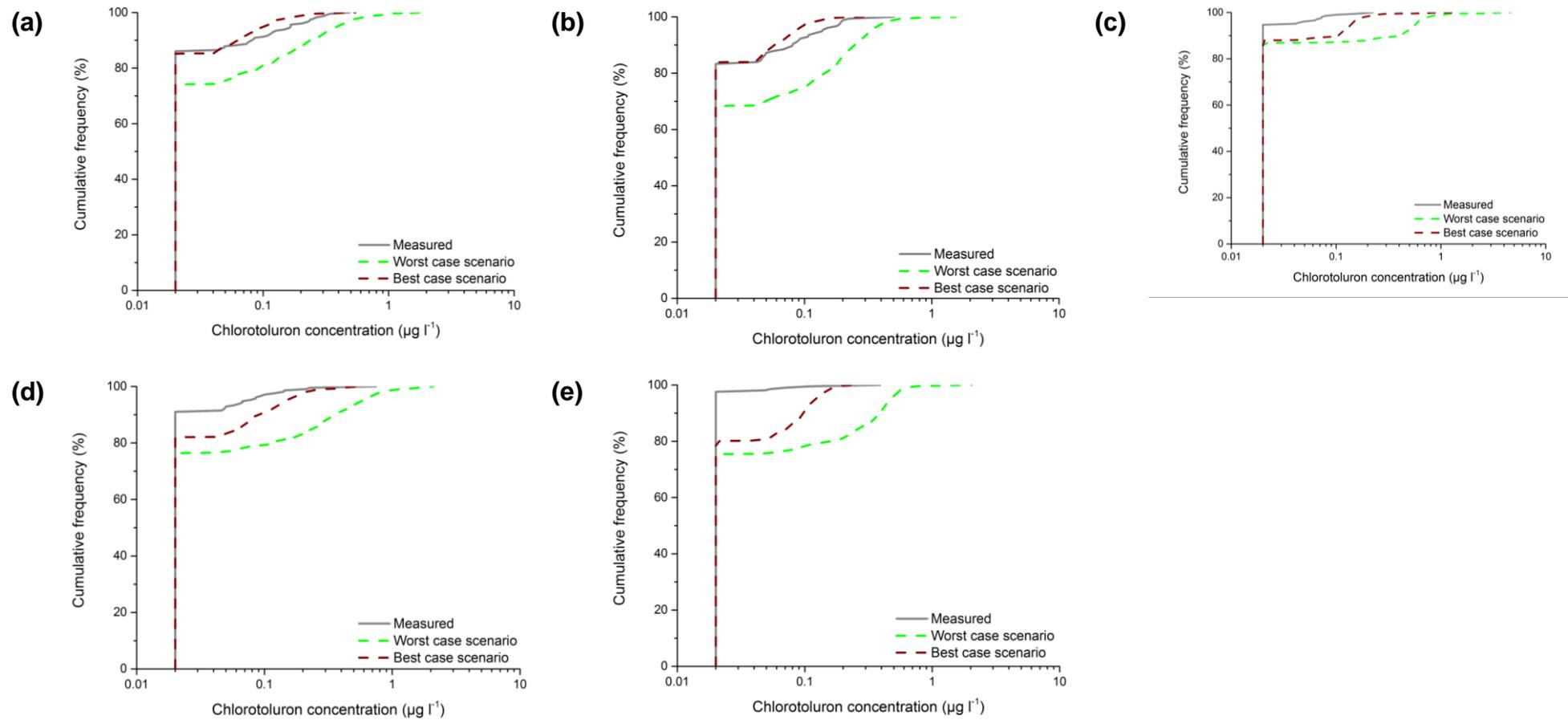


Figure G.2. Cumulative frequency distributions for measured chlorotoluron concentrations with predicted best case and worst case concentrations at the catchment outlet in the (a) Lugg, (b) Teme, (c), Waveney, (d) Wensum, (e) Yare.

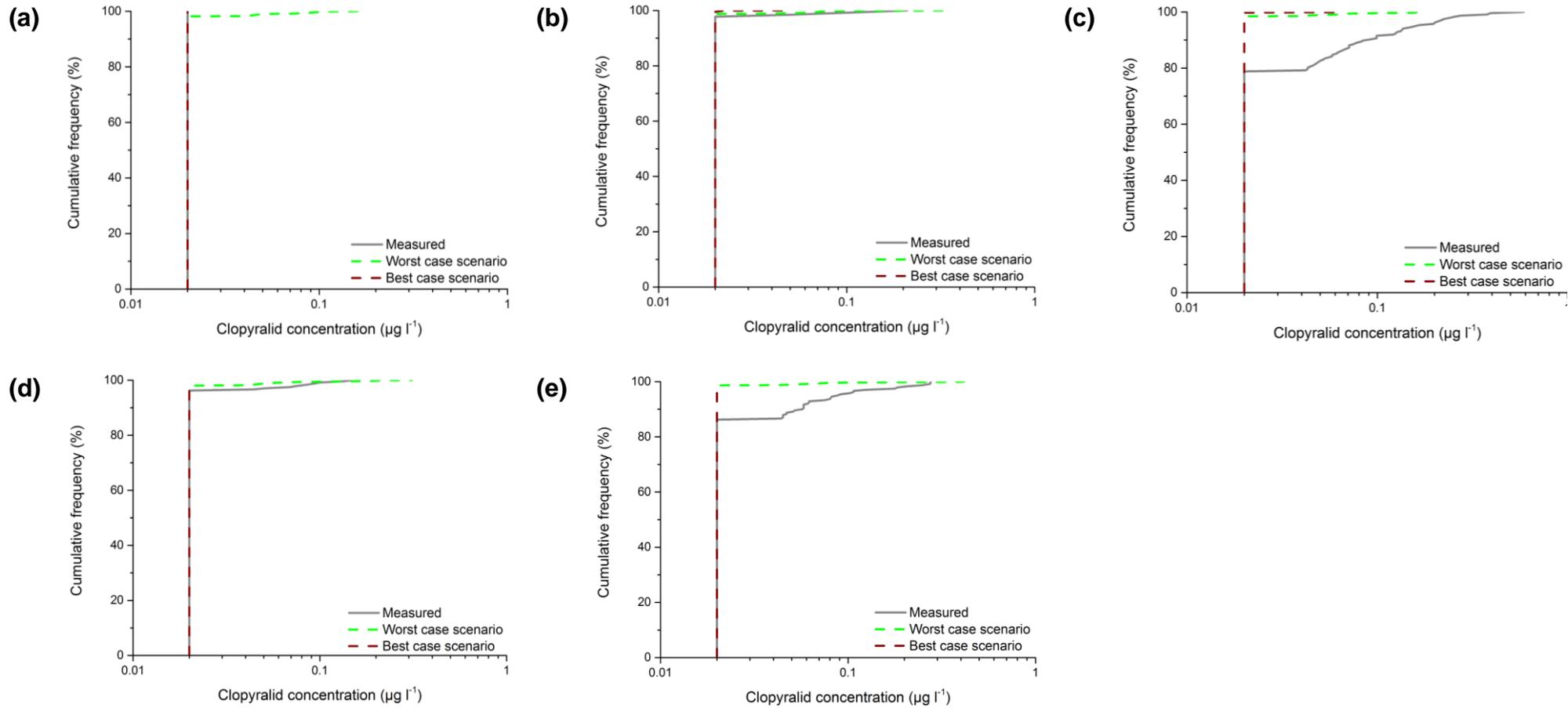


Figure G.3. Cumulative frequency distributions for measured clopyralid concentrations with predicted best case and worst case concentrations at the catchment outlet in the (a) Lugg, (b) Teme, (c), Waveney, (d) Wensum, (e) Yare.

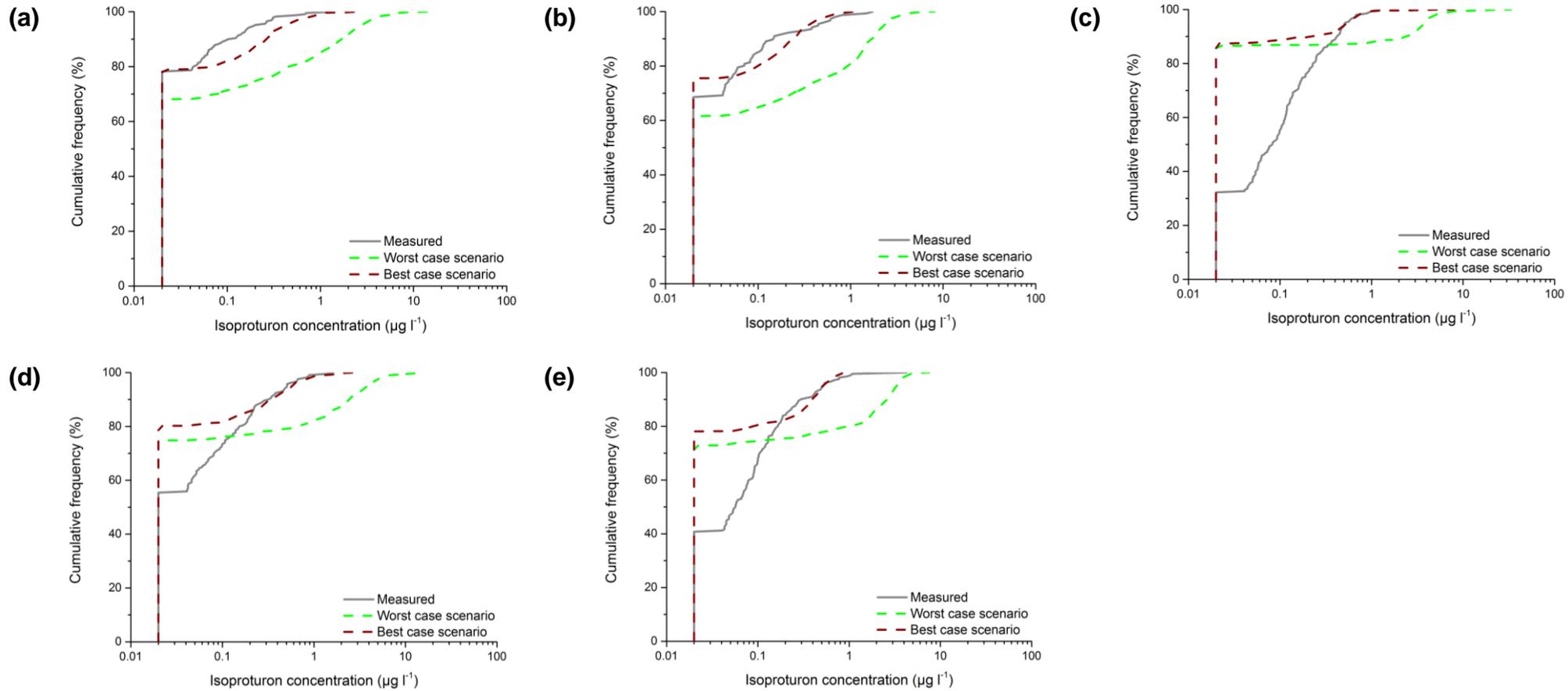


Figure G.4. Cumulative frequency distributions for measured isotoputuron with predicted best case and worst case concentrations at the catchment outlet in the (a) Lugg, (b) Teme, (c), Waveney, (d) Wensum, (e) Yare.

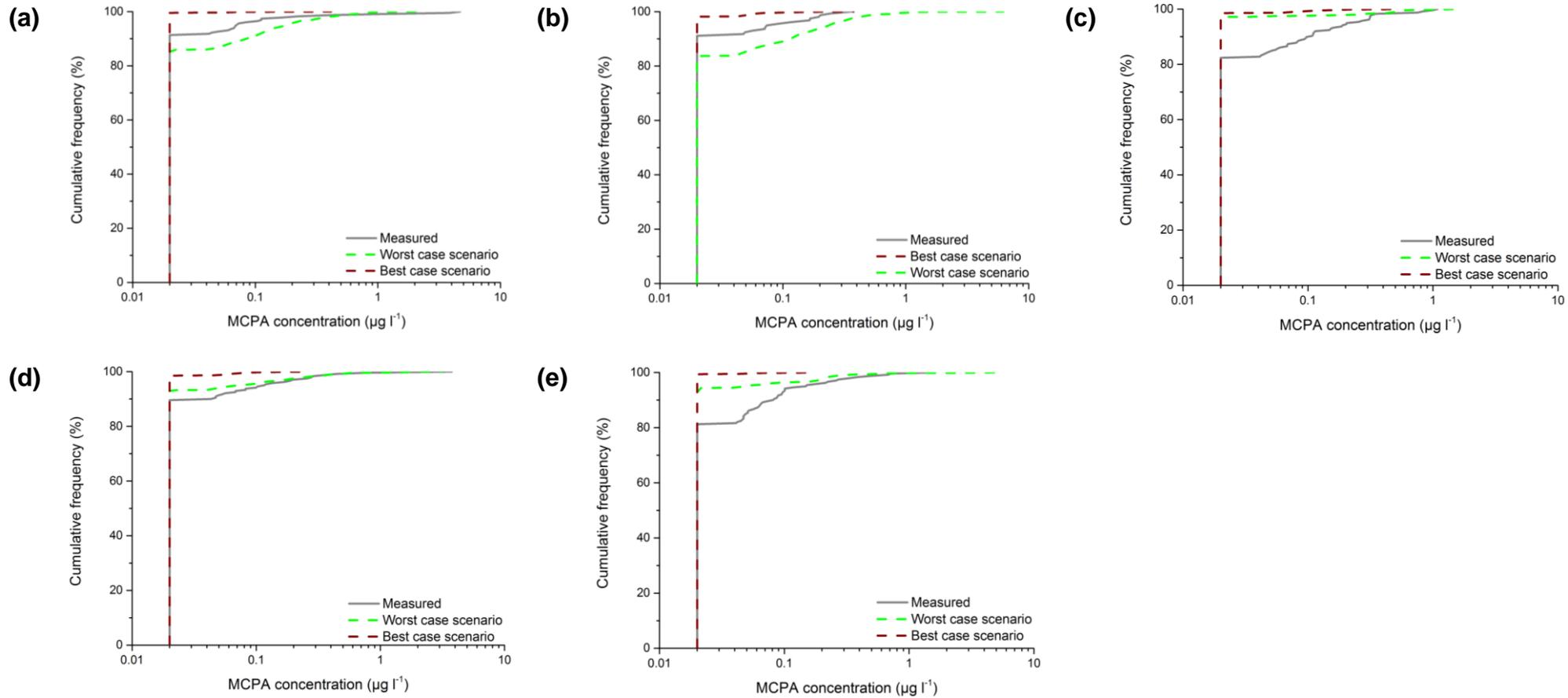


Figure G.5. Cumulative frequency distributions for measured MCPA concentrations with predicted best case and worst case concentrations at the catchment outlet in the (a) Lugg, (b) Teme, (c), Waveney, (d) Wensum, (e) Yare.

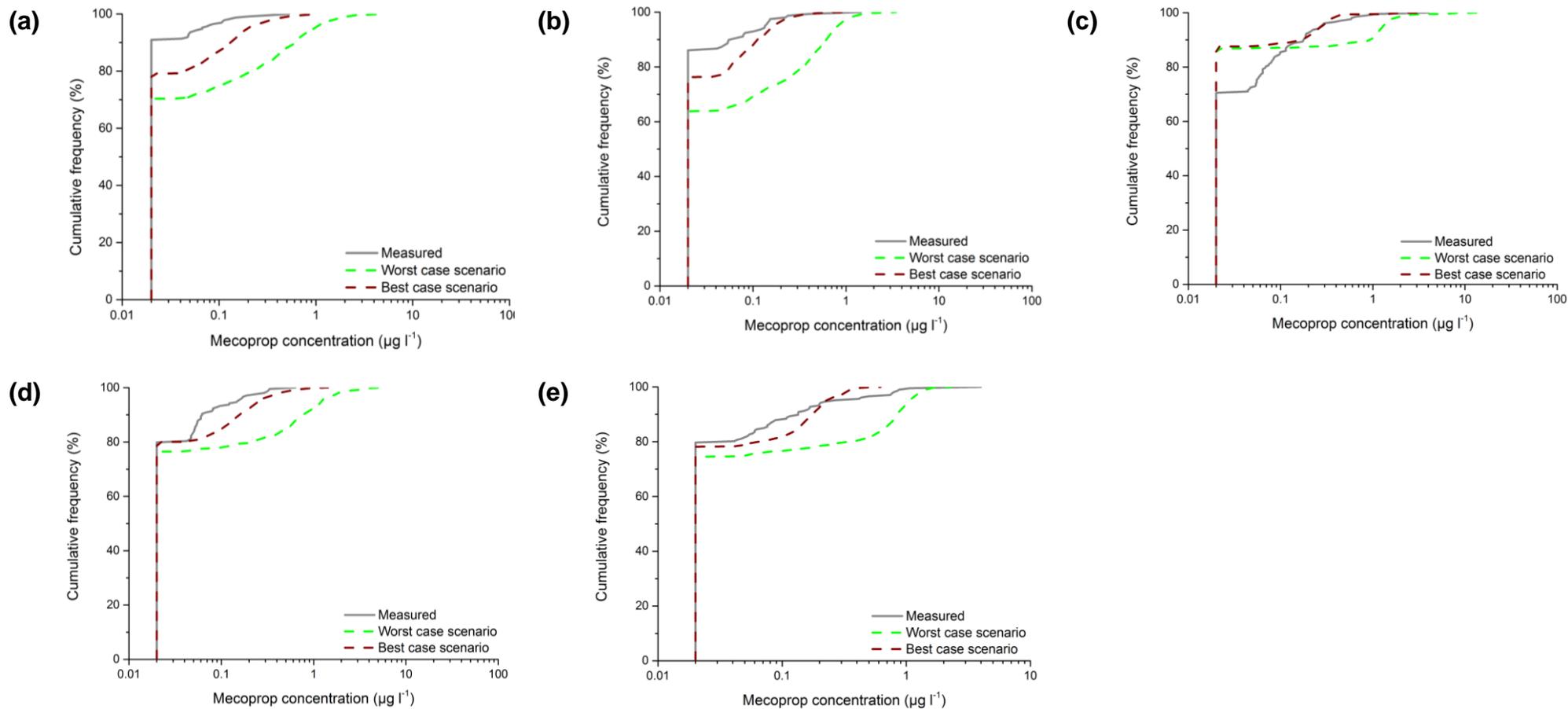


Figure G.6. Cumulative frequency distributions for measured mecoprop concentrations with predicted best case and worst case concentrations at the catchment outlet in the (a) Lugg, (b) Teme, (c), Waveney, (d) Wensum, (e) Yare.

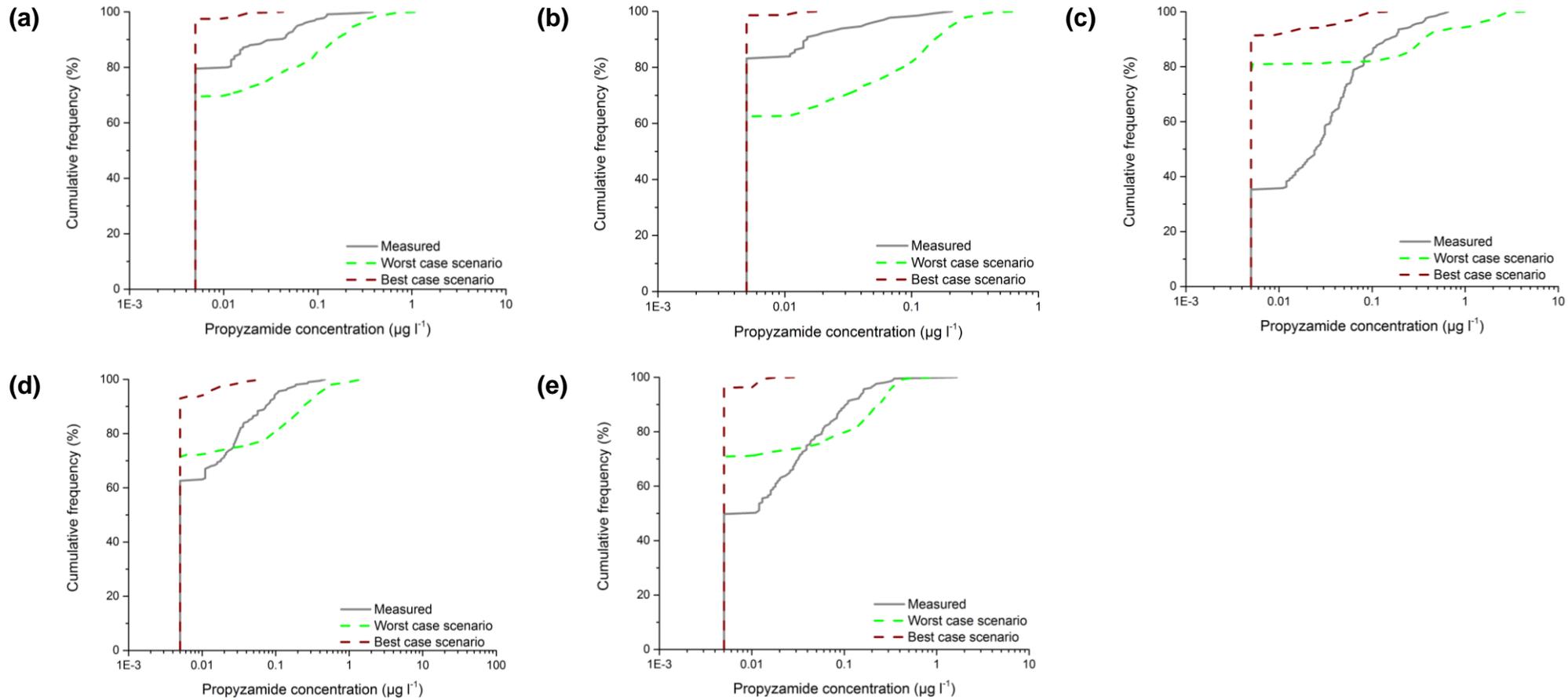


Figure G.7. Cumulative frequency distributions for measured propyzamide concentrations with predicted best case and worst case concentrations at the catchment outlet in the (a) Lugg, (b) Teme, (c), Waveney, (d) Wensum, (e) Yare.

Appendix H. Pesticide Time Series Results

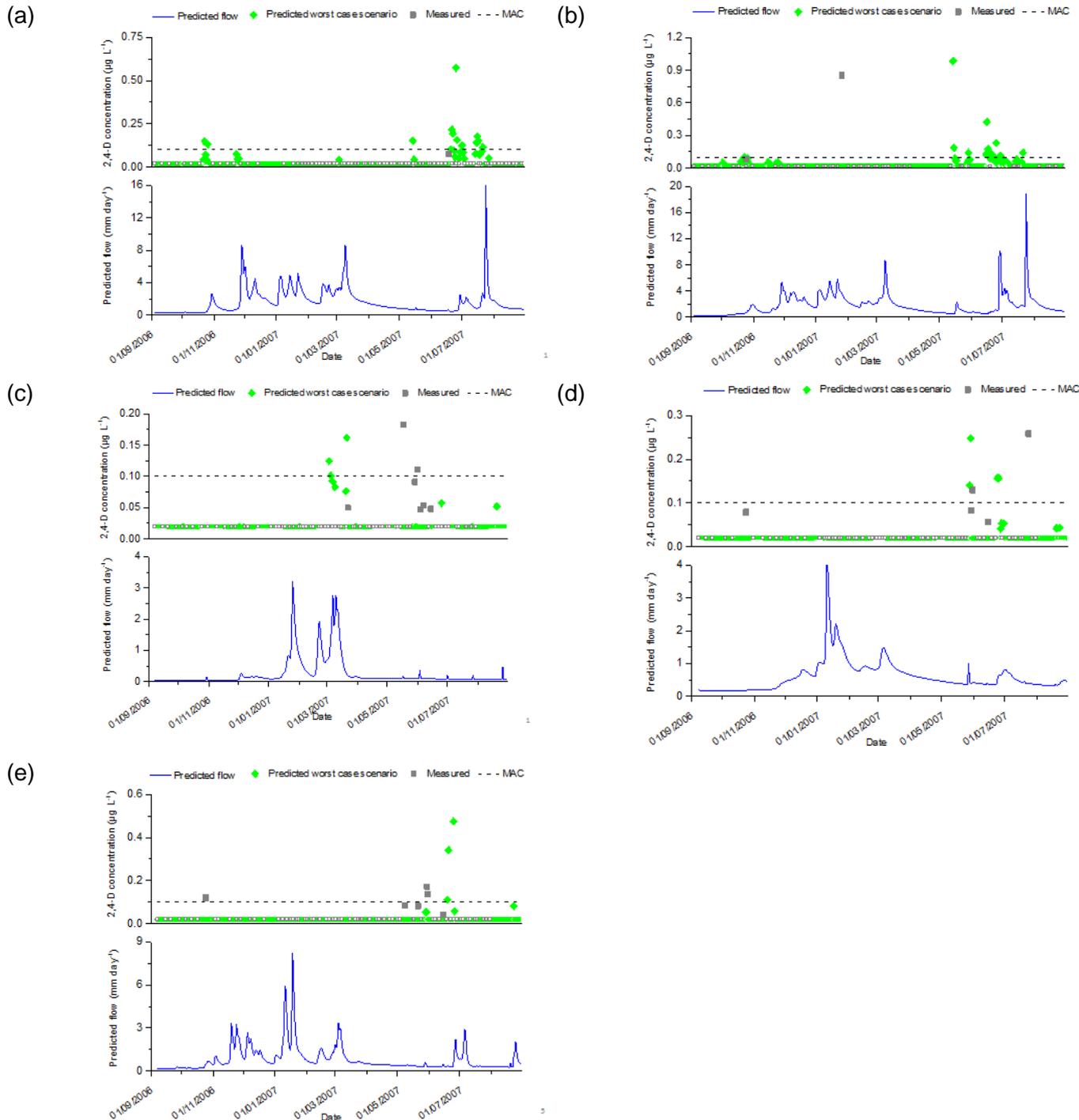


Figure H.1. Comparison of predicted and measured 2,4-D concentrations and predicted flow between September 2006 and September 2007 in the (a) Lugg (b) Teme (c) Waveney (d) Wensum and (e) Yare catchments. Note the difference in scales between the catchments.

The timing of predicted 2,4-D concentrations compares well with the measured data (Figure H.1). In the Teme, Wensum and Yare there are measured points that are not predicted by the model, this is as a result of the assumed application window. In the Lugg and the Teme catchments there are predicted concentrations of 2,4-D in the autumn, despite the fact that the last assumed application is in April. This is because the results shown are for the worst case scenario, which assumes a slow degradation rate. Therefore when the soils reaches wet's up at the beginning of autumn, and the field drains start flow as a result of a rainfall event any remaining pesticide is transported from the soil to the catchment outlet.

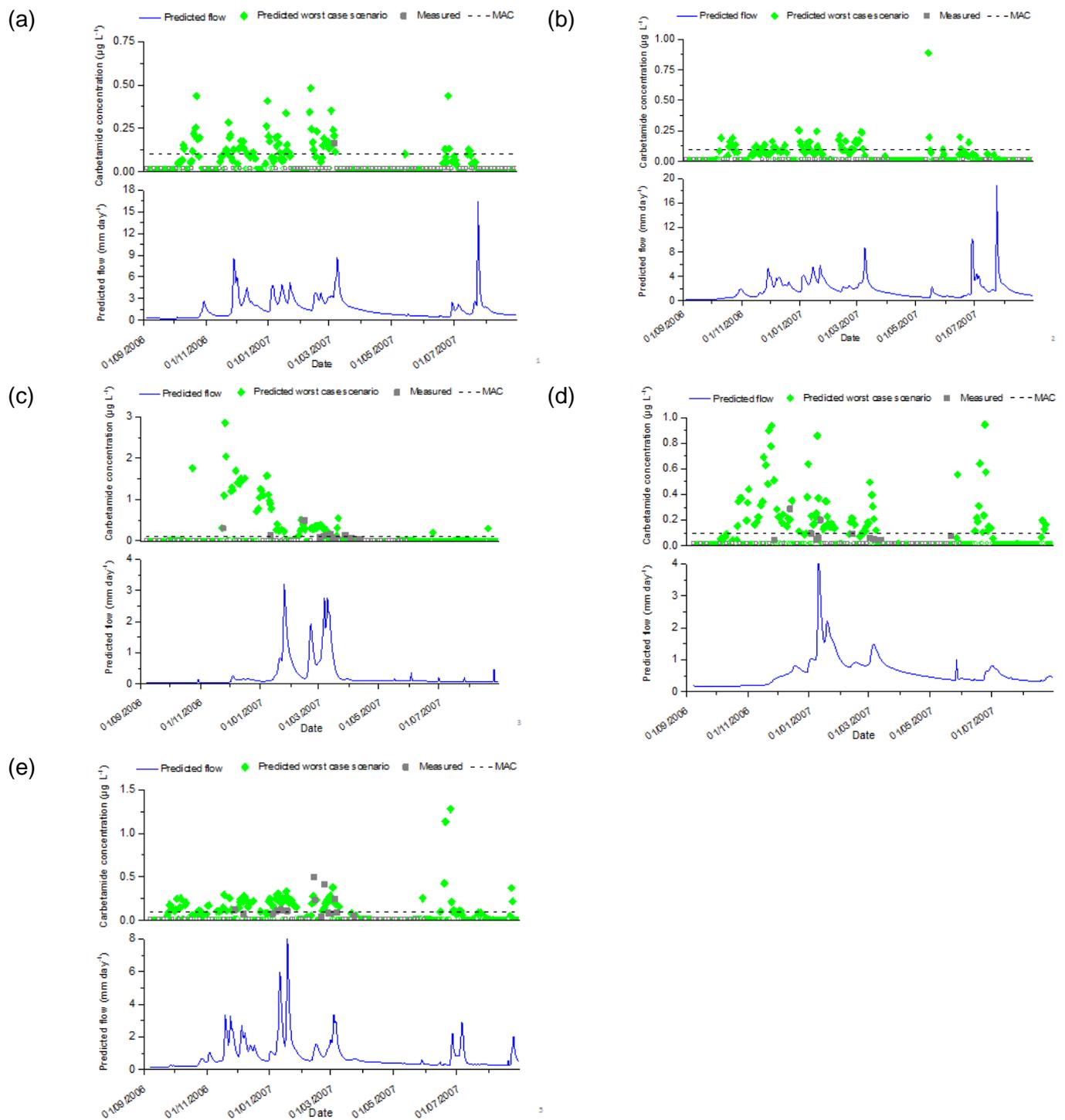


Figure H.2. Comparison of predicted and measured carbetamide concentrations and predicted flow between September 2006 and September 2007 in the (a) Lugg (b) Teme (c) Waveney (d) Wensum and (e) Yare catchments. Note the difference in scale between the catchments.

Predicted concentrations of carbetamide in all the catchments occur before the measured concentrations (Figure H.2), this is seen in the propyzamide results presented in Section 4.6. As in the propyzamide results, there are carbetamide concentrations predicted to occur in May and June 2007.

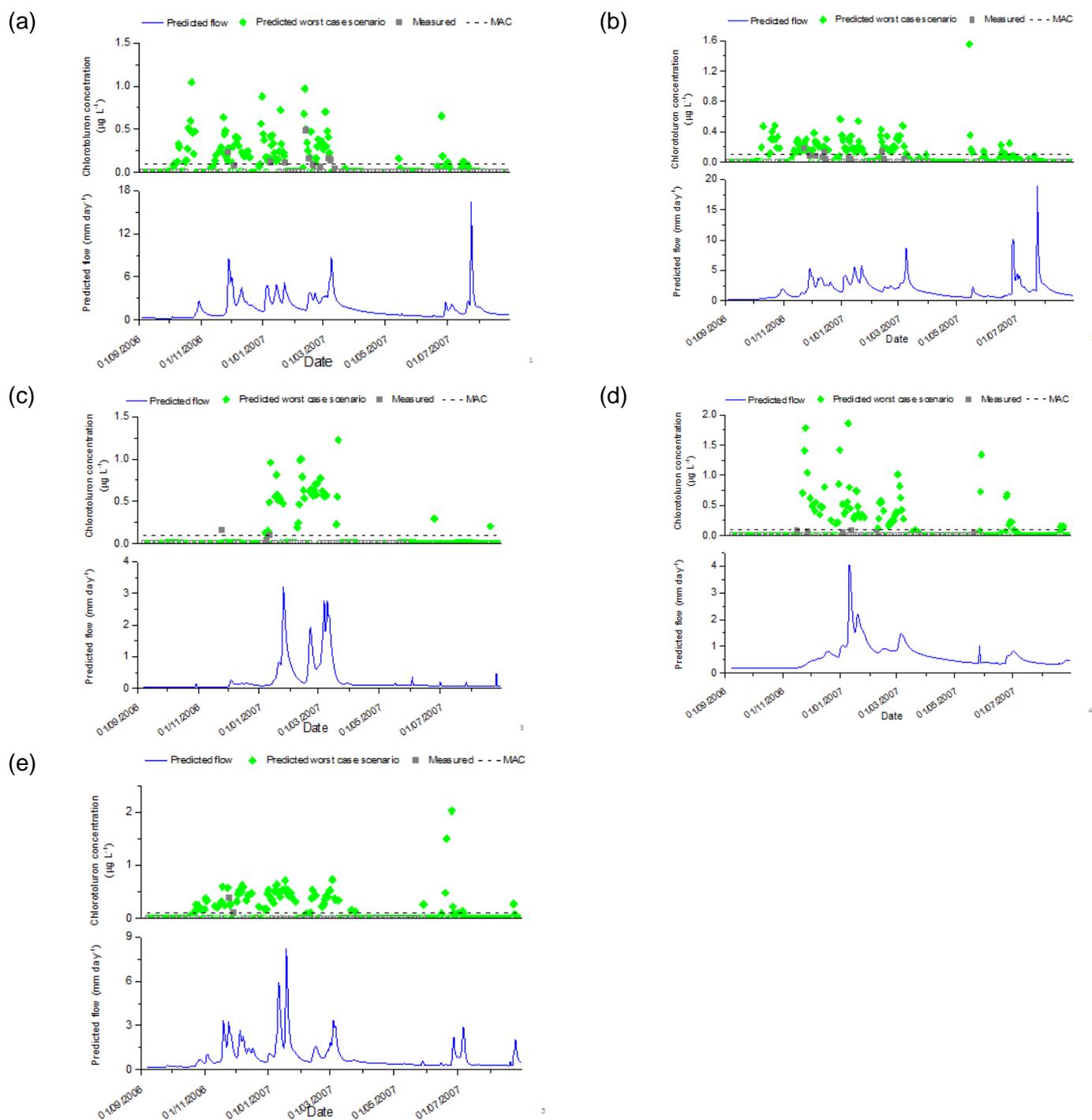


Figure H3. Comparison of predicted and measured chlorotoluron concentrations and predicted flow between September 2006 and September 2007 in the (a) Lugg (b) Teme (c) Waveney (d) Wensum and (e) Yare catchments. Note the difference in scale between the catchments.

Predicted concentrations of chlorotoluron in all catchments occur before the measured concentrations (Figure H.3), this is seen in the propyzamide results presented in Section 4.6. As in the propyzamide results, there are chlorotoluron concentrations predicted to occur in May and June 2007.

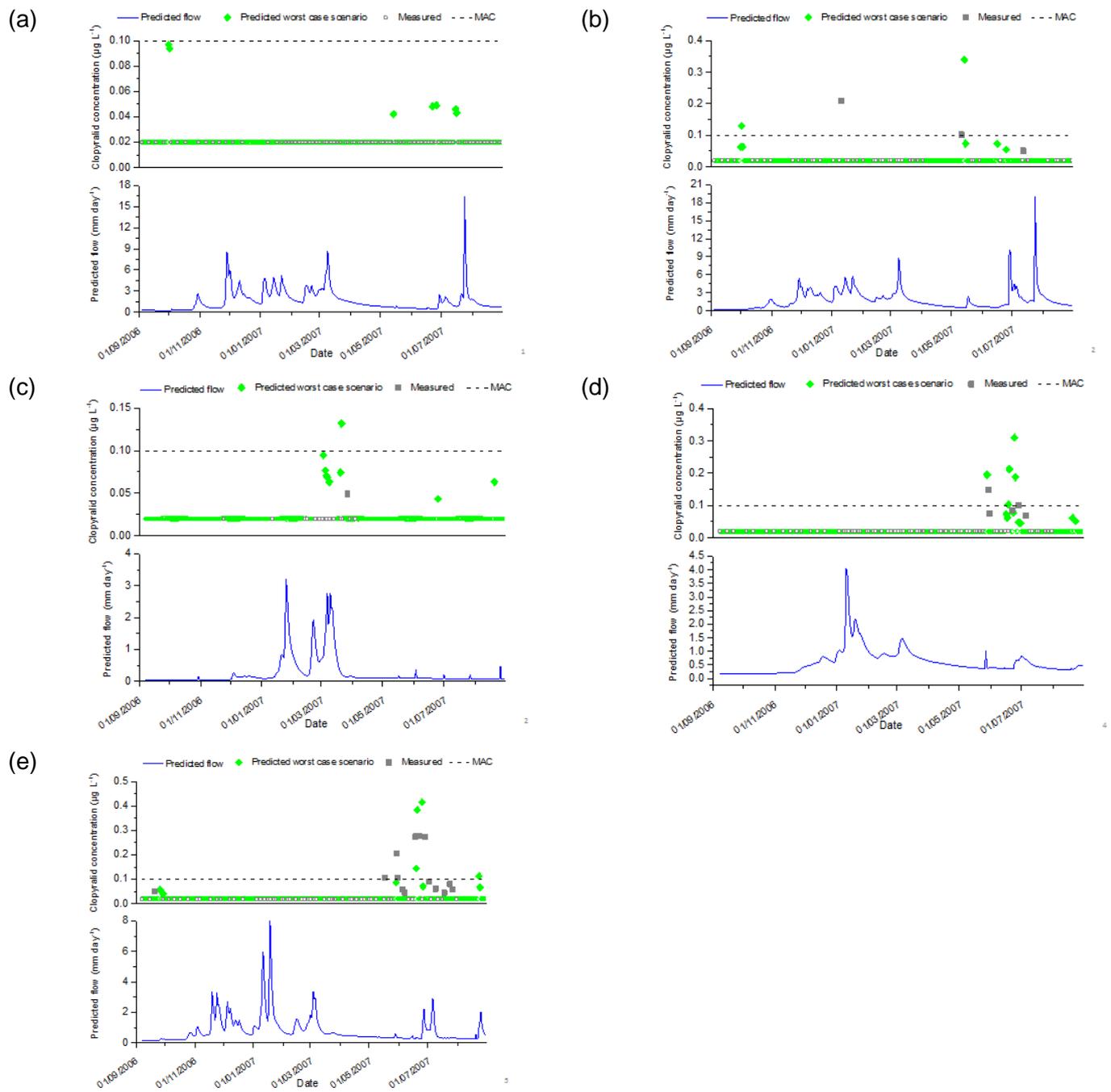


Figure H.4. Comparison of predicted and measured clopyralid concentrations and predicted flow between September 2006 and September 2007 in the (a) Lugg (b) Teme (c) Waveney (d) Wensum and (e) Yare catchments. Note the difference in scale between the catchments.

The timing and magnitude of predicted concentrations of clopyralid corresponds well to the measured concentrations (Figure H.4). In the Teme catchment there is a measured concentration of clopyralid that is not captured by the model.

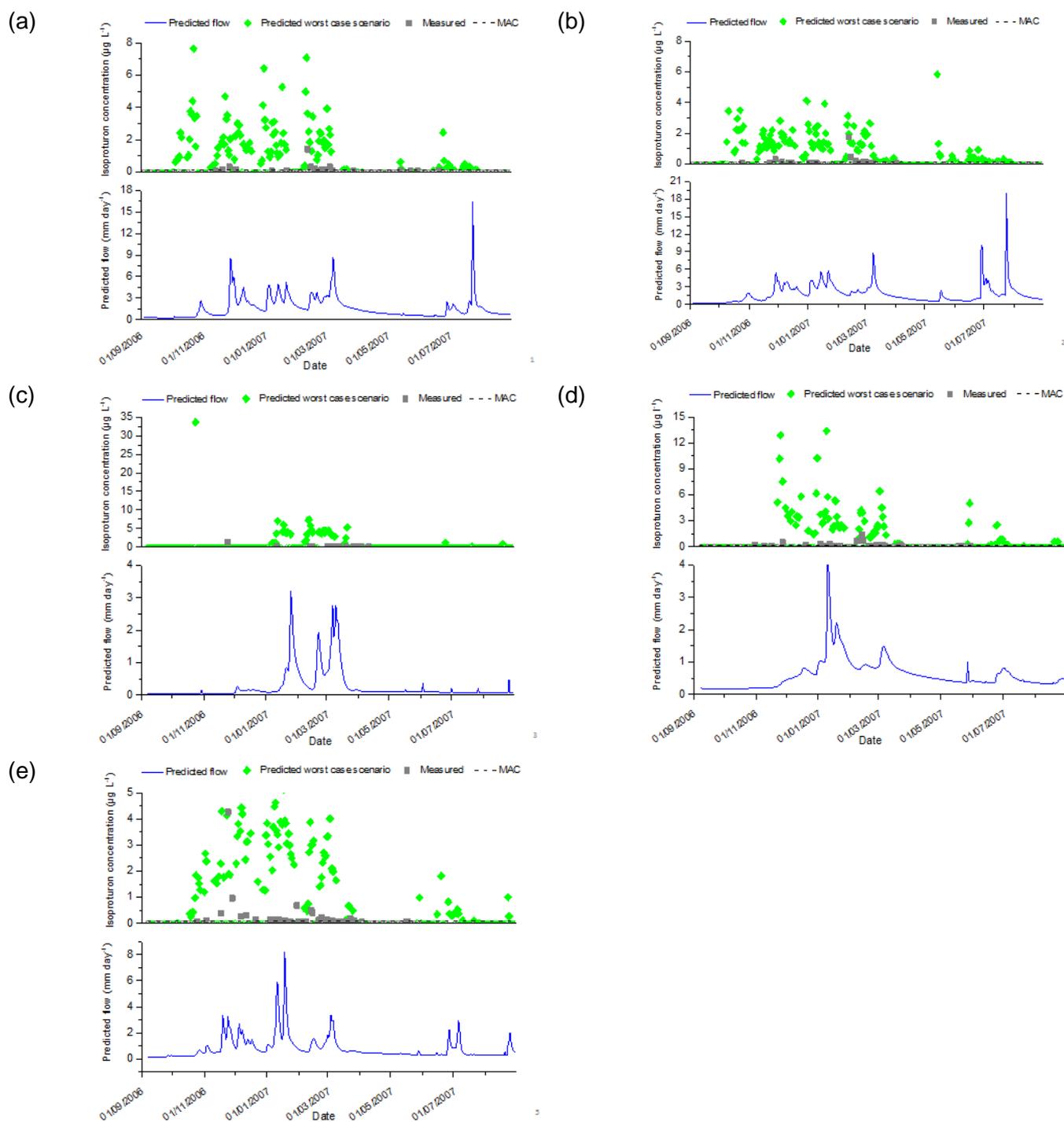


Figure H.5. Comparison of predicted and measured isoproturon concentrations and predicted flow between September 2006 and September 2007 in the (a) Lugg (b) Teme (c) Waveney (d) Wensum and (e) Yare catchments. Note the difference in scale between the catchments.

Predicted concentrations of isoproturon in all catchments occur before the measured concentrations (Figure H5), this is seen in the propyzamide results presented in Section 4.6. As in the propyzamide results, there are isoproturon concentrations predicted to occur in May and June 2007.

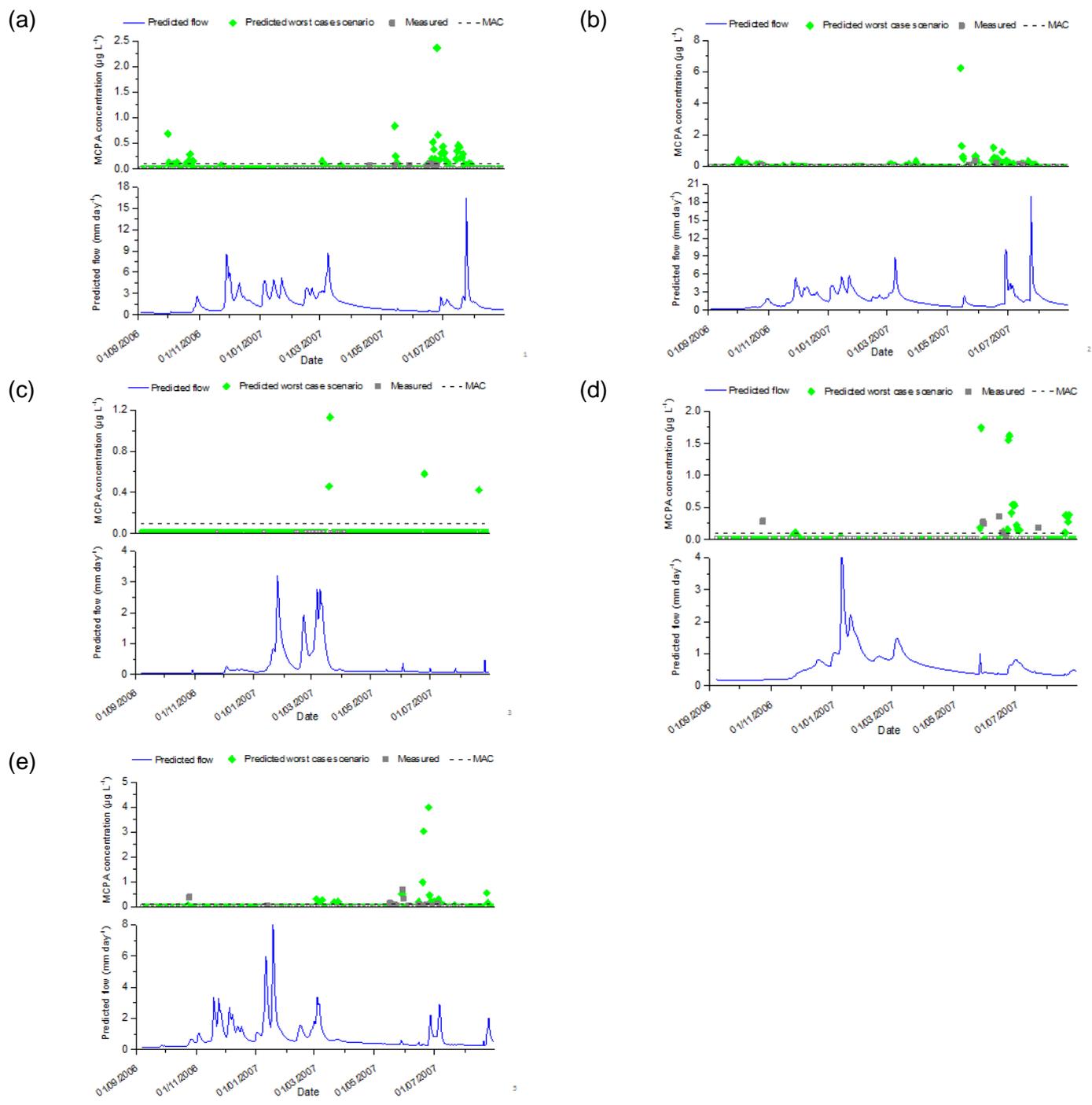


Figure H.6. Comparison of predicted and measured MCPA concentrations and predicted flow between September 2006 and September 2007 in the (a) Lugg (b) Teme (c) Waveney (d) Wensum and (e) Yare catchments. Note the difference in scale between the catchments.

The timing of the predicted MCPA concentrations corresponds well with the measured data.

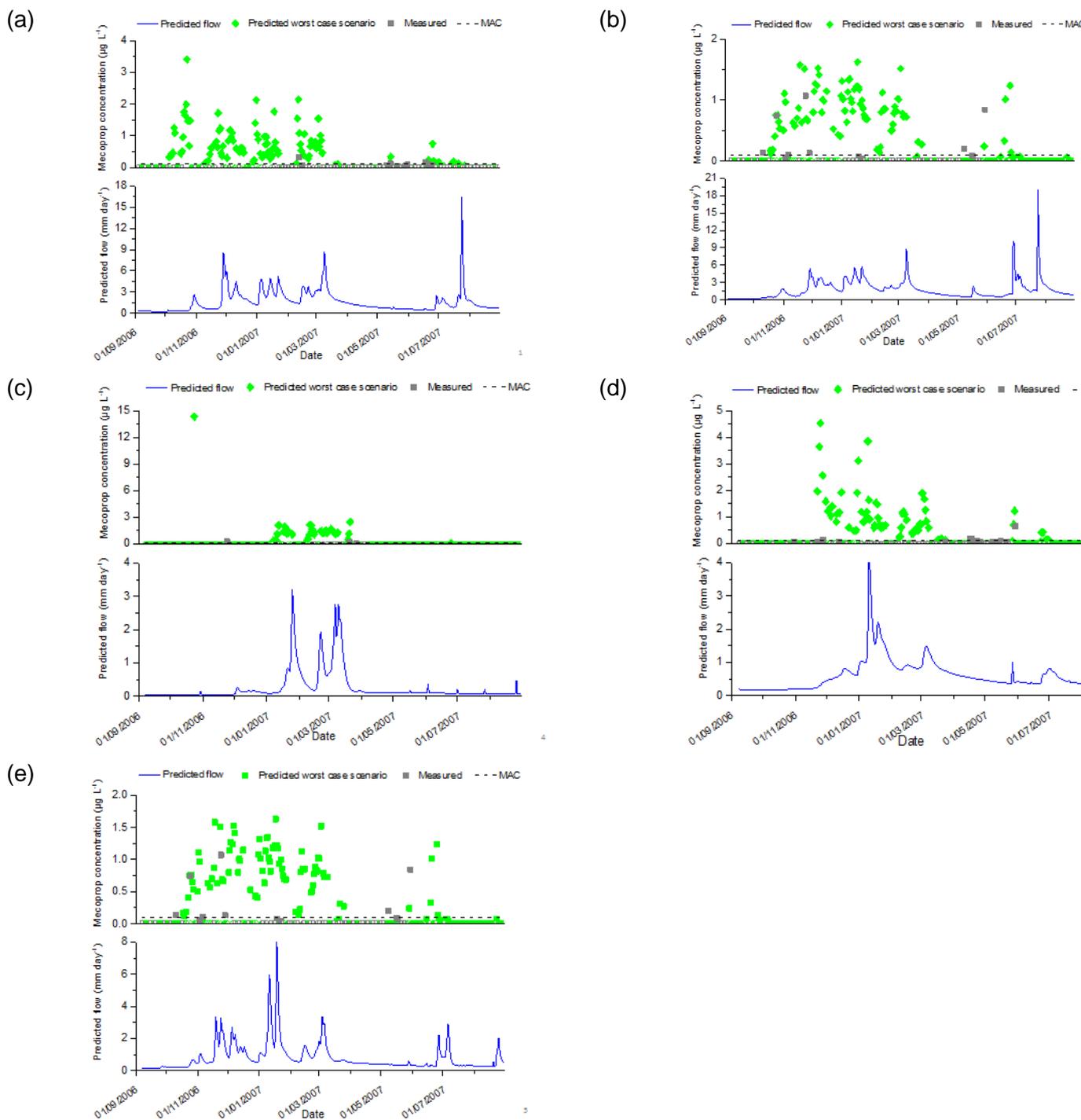


Figure H.7. Comparison of predicted and measured mecoprop concentrations and predicted flow between September 2006 and September 2007 in the (a) Lugg (b) Teme (c) Waveney (d) Wensum and (e) Yare catchments. Note the difference in scale between the catchments.

Predicted concentrations of mecoprop in the Lugg, Waveney and Wensum catchments occurs before the measured concentrations (Figure H.7), this is also seen in the propyzamide results presented in Section 4.6. In the Teme and Yare catchments the timing of the predicted concentrations compares well with the measured concentrations (Figure H.7), although predicted concentrations continue to occur after the measured concentrations have stopped being detected over the LOQ. As in the propyzamide results, there are mecoprop concentrations predicted to occur in May and June 2007, this is also reflected in the measured data in the Lugg, Teme, Wensum and Yare catchments.