SCALE EFFECT IN NUTRIENT TRANSPORT ALONG A RURAL RIVER SYSTEM - THE RIVER EDEN, CUMBRIA, UK

Fatai Oladapo Tijani

Thesis submitted for the degree of Doctor of Philosophy

Newcastle University

School of Civil Engineering and Geosciences

February 2016

Abstract

Many research studies on nutrient transfer are conducted at small scale and transferring such findings to the large scale at which planners and catchment managers work faces uncertainties because of non-linearity. There is a need therefore for multiscale studies, which define and link the transfer mechanisms across spatial scales. Such a study may also provide the answers on the processes driving it and test the answers further by using a model.

Experimental data to support the study were collected from two complementary research programmes in the Eden catchment. Spatial scale variations were investigated through seasonal and spot samples down a sequence of nested catchments, area 1 – 1400 km^2, from the NERC-funded Catchment Hydrology and Sustainable Management project (CHASM). Soil samples were also taken. These samples were analysed in the laboratories for nitrate, phosphates and suspended sediment using standard methods. The explanation of spatial variation was then supported by data from two contrasting 10 km^2 catchments of the DEFRA-funded Demonstration Test Catchments (DTC) project. A generalisation of the findings was carried out by deploying the TOPCAT-NP model.

The nitrate, phosphorus and the suspended sediment concentration, load and yield increased downstream relative to the headwaters. Nitrate sources were complex and appear dominated by groundwater source whereas phosphorus and suspended sediment were from diffuse sources. Nitrate showed the clearest increasing pattern downstream when compared with the other nutrients. A downstream increase in nutrient transfer relates to a downstream increase in flow, agricultural land use and soil type. Hydrology of Morland was adequately represented by the model but the nutrients were less accurate leading to suggestions on model improvement.

By carrying out a spatial scale related study of the Eden catchment, analysing the DTC high resolution data and modelling the data, insights into how, where and when nutrients losses occur have been gained. This encourages us, in that targeted land management and a better understanding of the hydrological processes that drive nutrient losses may be an effective way to reduce the problem.

Acknowledgements

I will like to express my heartfelt gratitude to my supervisors, Dr James Bathurst and Dr Paul Quinn for their guidance, patience and support. I am also grateful to Dr Nick Barber for showing me the way in the Eden catchment and in the laboratory. Special thanks to Mr Peter Dawber who was my kind companion throughout my field visits. I note with thanks groups of people who offered me, warm services – some academic, administrative and laboratory staff in the School of Civil Engineering and Geosciences, Newcastle University; technical advice on soil – Prof David Manning, Prof Durodoluwa Oyedele and Dr Jennine Jonczyk; publications - Prof. Phil Haygarth, and Dr Geoff Parkin; data set - the DTC team, Environment Agency, Centre for Ecology and Hydrology, Mr Gareth Owen, Dr Claire Walsh, Dr Carolyn Mills, Miss Liz Lewis; and type setting or proofread, and offer of advice on part of my thesis – Dr December Ikah, Dr Kemi Akande, Dr Ibukun Adewale, Dr Ndukwe Dickson and Captain Sola Olawuyi. I am also grateful to Mr Steve Obrike who helped me to sort out the maps of my study area on ArcMap. I wish to acknowledge Dr Russell Adams who helped me to proofread the whole thesis despite short notice.

I am indebted to the Tertiary Education Trust Fund, Nigeria and my home University, Obafemi Awolowo University (OAU), Ile-Ife, Nigeria, for providing me the fund for my doctorate studentship. I wish to also appreciate the staff of the Department of Soil and Land Resources Management, OAU, who graciously accepted to shoulder my duty in the department while I am away on study leave. I appreciate Prof Durodoluwa Oyedele and Mr Cornelius Atere who always helped me to monitor all the official paper work that made my stay here possible.

I acknowledge the kind companion of friends in the University and brethren in the Deeper Life Bible Church, Newcastle and Gospel Church of the Living God, Nigeria, who will not allow distance to separate me from their love and kind support. They all made me socially and spiritually stable to face this research.

Finally, I will like to thank my family for their supports throughout the time I have been working on this thesis and the Almighty God for inspiring me all the way and providing me the invisible loving support that rallies all human and material resources that have made this thesis a reality.

Table of Contents

Abstract iii

Acknowledgements…………………………………………………………………….....v

Table of Contents vii

List of Tables……………………………………………………………………xiv

List of Figures..xvi

List of Acronyms……………………………………………………………...xxi

Chapter 1: Introduction 1

1.1. Context…………………………………………………………………...1

1.2. Research Aims……………………………………………………….....5

1.3. Thesis Outline…………………………………………………………..6

Chapter 2: Literature Review 8

2.1. Introduction……………………………………………………………...8

2.2. Introduction to catchment nutrient dynamics……………………………..8

2.2.1. Flow-nutrient relationship 8

2.2.2. Sediment 13

2.2.3 Nutrients.. 15

2.2.4 Catchment characteristics and nutrient dynamics 22

2.3 Introduction to spatial scaling……………………………………………....25

2.4 Catchment datasets…………………………………………………….....31

2.5 Catchment hydrometry…………………………………………………….33

2.6. Studies in stream nutrient cycling using high frequency monitoring approach……………………………………………………………………...36

2.7. Hydrological modelling…………………………………………………….38

2.7.1. Deterministic models.. 39

2.7.2. Distributed physically-based models 40

2.8.Summary…………………………………………………………………………45

Chapter 3: Methodology 46

3.1. Introduction……………………………………………………………………46

3.2. Description of the Eden catchment……………………………………………....47

3.2.1. Topography 47

3.2.2. Geology 49

3.2.3. Soil 52

3.2.4. Vegetation and land use 58

3.2.5. Climate 58

3.2.6. River characteristics 58

3.3. CHASM-based field programme………………………………………………60

3.3.1. CHASM 60

3.3.2. CHASM gauge stations, experimental design and sampling 61

3.3.3. Seasonal campaign 68

3.4. Laboratory analysis and data collection…………………………………………69

3.4.1. Suspended sediment analysis 69

3.4.2. Phosphorus analysis 70

3.4.3. Nitrate analysis 71

3.4.4. Point source and septic tank in the Eden...……………………………………71

3.4.5. Soil handling and processing 72

3.4.6. Estimation of soil water extractible P, bicarbonate P and pH 72

3.4.7. Determination of soil N, total organic C and organic matter 73

3.4.8. Determination of particle size distribution of the soil 75

3.5. DTC-based programme…...……………………………………………………75

3.5.1. DTC 75

3.5.2. Eden DTC experimental design, gauging station, sampling and laboratory analyses 75

3.5.3. Data collection 77

3.5.4. Summary of spatial, hydrological and water quality data used for this study 77

3.6. Modelling 78

3.7. Summary 78

Chapter 4: A Spatial Scale Evaluation of the Nutrient and Suspended Sediment Regime of the Eden Catchment 79

4.1. Introduction 79

4.2. Hydrological Characterisation 79

4.2.1. Precipitation 79

4.2.2. Flow 81

4.3. Nutrient and sediment concentrations 86

4.3.1. The water quality variables and flow 86

4.3.2. Seasonality in the concentrations of the water contaminants 90

4.3.3. The pattern of nutrient and sediment concentrations in the nested Eden catchment and land use 94

4.3.4. Relationships between catchment characteristics and land area 95

4.3.5. Relationships between the water quality variables and some catchments characteristics 99

4.3.6. Comparison of soil data with the nutrient and sediment concentrations in the Eden 107

4.4. Evaluating sediment and nutrient loads and specific yields 110

4.4.1. Choice of method and limitations 110

4.4.2. The development of sediment and nutrient rating curve for load calculation 111

4.4.3. Calculation of specific yield 113

4.4.4. The pattern of loads and specific yields of nutrients and sediments in the nested Eden catchment 113

4.5. Summary………………………………………………………………………..118

Chapter 5: Evaluating the Nutrient and Suspended Sediment Regime of the Demonstration Test Subcatchment 120

5.1. Introduction……………………………………………………………………..120

5.2. Hydrological Characterisation…………………………………………………...120

5.2.1. Precipitation and flow 120

5.3. Nutrient and sediment concentrations, and turbidity…………………………122

5.3.1. Comparison of concentration data from the autosampler and the CM equipment 122

5.3.2. The water quality variables and flow 123

5.3.3. Seasonality in the concentrations of the water quality variables 133

5.3.4. The pattern of nutrients and sediment concentrations in response to different land use and elevation 137

5.3.5 Storm events data and period of dry spell 139

5.4. Evaluating sediment and nutrient exports and specific yields………………147

5.4.1. Calculation of the annual load and yields 147

5.4.2. The comparison of loads and specific yields of nutrients and sediment in response to some DTC catchments characteristics 147

5.4.3. Load exceedance and comparison of nutrient and sediment transfer ... 149

5.5. Summary………………………………………………………………………..151

Chapter 6: Discussion of Findings from the CHASM and DTC Studies 154

6.1. Introduction……………………………………………………………………..154

6.2. Hydrology and water contaminants transport using the spatial scale CHASM study……………………………………………………………………………………154

6.2.1. Rainfall and flow pattern in 2012 154

6.2.2. Nutrient and sediment rating curves 155

6.2.3.Point sources in the Eden catchment……………………………………159

6.2.4. Influence of the synergy between hydrology and land use on the spatio-temporal variations in the strength of rating curves………………………………160

6.3. Spatial pattern, elevation and land use effects in nutrient and sediment concentrations and yields, using a spatial-scale CHASM programme…………..163

6.3.1. Comparison between nutrient and sediment concentrations and yields in the Eden, and other catchments 163

6.3.2. Sediment and nutrient exceedance and water quality limits................. 166

6.3.3. Influence of land use distribution on the contaminant content of the River Eden: Gais Gill vs Blind Beck... 168

6.3.4. The spatial variability of nutrient and sediment concentrations in the nested Eden catchment 169

6.3.5 Spatial distribution of sediment and nutrient load and specific yields..... 171

6.4. Hydrology and contaminant transfer using the high resolution DTC study platform…………………………………………………………………………173

6.4.1. Rating curve 173

6.4.2. Point sources in Dacre and Morland………………………………………174

6.4.3. Event storms 174

6.4.4. Sediment and nutrient source 175

6.4.5. Relationship with turbidity.. 176

6.5. Elevation and land use effect using the high resolution data from the DTC study……………………………………………………………………………177

6.5.1. Dacre vs Morland 177

6.6. Linking the DTC study to the CHASM study…………………………………..177

6.7. Seasonality in the concentrations of the water quality parameter…………..178

6.7.1. Headwater system and seasonal variability……………………………179

6.8. Relationships between the concentrations of the water quality contaminants and the riparian soils in selected catchments……………………………………181

6.9. Implications for water quality management……………………………………181

6.10. Summary………………………………………………………………………182

Chapter 7: Modelling Nutrient Concentrations in a River Eden Subcatchment 184

7.1. Introduction……………………………………………………………………..184

7.2. Nutrient concentrations simulation using a minimum information requirement model…………………………………………………………………………………184

7.2.1. The hydrological model - TOPCAT…………………………………………..187

7.2.2. The N-MIR…………………………………………………………………188

7.2.3. The P-MIR…………………………………………………………………190

7.3. Sensitivity test…………………………………………………………………..193

7.4. TOPCAT-NP set-up and calibration……………………………………………197

7.4.1. Model setup.. 198

7.4.2. Calibration of TOPCAT-NP Model.. 198

7.4.3. Re-calibration of the TOPCAT-NP model.. 205

7.5. Discussion………………………………………………………………………207

7.5.1. Calibration 207

7.5.2. Sensitivity test……………………………………………………………..208

7.6. Comments on process representation and recommendations for improvement of TOPCAT-NP model…………………………………………………………………209

7.7. Summary……………………………………………………………………..213

Chapter 8: Conclusion.. 214

8.1. Introduction…………………………………………………………………..214

8.2. The CHASM study……………………………………………………………..214

8.2.1. Data sampling in a densely instrumented nested catchment 214

8.2.2. Comparison of spatial relationship of catchment characteristics, stream concentrations of N, P and SS with the catchment area and quantification of contaminant load.. 215

8.2.3. Identification of key driver of the stream contaminant content and the variability relative to catchment size 217

8.2.4. Does soil and elevation play any role? 218

8.2.5. Seasonality at the Eden headwater system at Gais Gill compared to the higher order watercourses downstream or elsewhere in the Eden.................. 219

8.3. Findings from the DTC study……………………………………………………220

8.3.1. Further investigation of catchment characteristics and processes put forward by CHASM studies by using the DTC high resolution data 220

8.3.2. Further insights gained through the DTC study 221

8.4. Modelling study……………………………………………………………………223

8.4.1. Assessing the potential of TOPCAT-NP applied to Morland in predicting impact of land use and management changes on nutrient content in rivers.... 223

8.5. Overall key findings………………………………………………………………224

8.6. Further Research…………………………………………………………………225

Appendix 227

Appendix A – Stage-discharge (or stage-flow) rating co-efficient for some CHASM catchments……………………………………………………………………………..227

Appendix B – Water quality data and rating curves………………………………..228

Water quality data at Gais Gill 228

Appendix C – Demonstration Test Catchment……………………………………..276

Appendix D – One year Flow Duration Curves (FDC) from 01/10/11 – 31/01/2012……………………………………………………………………………...282

Appendix E – Load and Yield………………………………………………………285

Appendix F - Bank-side continuous monitoring analyser…………………………..291

References……………………………………………………………………………..292

List of Tables

Table 2.1 Catchment models capable of simulating nutrient and sediment transport…………………………………………………………………………………42
Table 3.1The soil cover of the subcatchments selected for CHASM project (Thomson *et al.*, 1983). 53
Table 3.2 Summary of monitoring locations. Sites in italic are part of the nested basin system 64
Table 3.3 Summary of the spatial datasets……………………………………………..77

Table 3.4 Summary of the flow and water quality datasets…………………………...78

Table 4.1 Stage and flow monitoring equipment in the River Eden and tributaries .. 82
Table 4.2 Flow statistics for the River Eden at Kirkby Stephen (based on mean daily flow).. 83
Table 4.3 Annual and seasonal R-square values of the relationship between flow and the Water quality variables 89
Table 4.4 Variations in nitrate concentration in cold and warm weather at Gais Gill 93
Table 4.5 A Pearson correlation among soil properties at GG and BB 110
Table 4.6 Annual load for Great Musgrave using flow duration-rating curves method 112
Table 4.7 Calculated annual load and yields for Great Musgrave 114
Table 4.8 Comparison between the FDC-rating and approximate methods for estimating nitrate and SS loads in the River Eden 117
Table 5.1 Hydrological summary and elevation of Dacre, Morland and Pow 122
Table 5.2 Comparison between mean and median concentration of the contaminants generated by the autosampler and the CM equipment at Morland......................... 123
Table 5.3 R^2 values for rating relationship between the environmental parameters and turbidity and flow using data obtained from the autosampler and CM equipment respectively. 130
Table 5.4 Pearson correlation between the WQPs in Morland.............................. 131
Table 5.5 a – c Comparison of concentrations of WQPs using data obtained from both the autosamplers and the CM devices 138
Table 5.6 Comparison of the catchment characteristics in Morland and Dacre…...139

Table 5.7 Comparison of annual loads of WQPs from Dacre and Morland using the approximate method (Autosampler data) and integration of hourly estimate of the CM data 148
Table 5.8 Nutrient yields from the DTC catchments calculated using the Autosampler and CM data 148
Table 5.9 Comparison of rainfall, flow and nutrient and sediment export in Morland using Autosampler data and CM data for the period covering October 2011 – September 2012 151
Table 5.10 Comparison of rainfall, flow and nutrient and sediment export in Dacre using Autosampler data for the period covering October 2011 – September 2012 151
Table 6.1 Nitrate concentration and corresponding flow from autumn 2011 to summer 2012 at Temple Sowerby 158
Table 6.2 Estimate of point source in the Eden……160

Table 6.3 Mean of flow data for the periods spot samples were collected in CHASM and when the autosampler was in operation in the DTC (Morland) subcatchment 162
Table 6.4 Mean of near-continuous flow data for selected sub catchments covering September 2011 – August 2012 162
Table 6.5 Range of nutrient export into the UK rivers 165
Table 6.6 Maximum concentration of sediment and nutrients in selected subcatchments under both the CHASM and also the DTC Schemes 165
Table 6.7 Percent exceedance of selected Eden sub catchments 167
Table 6.8 Comparisons between contaminant yields at Gais Gill and Blind Beck .. 169
Table 7.1 Parameters for Morland (12.5 km^2) 199
Table 7.2 Nash-Sutcliffe efficiency E and Pearson correlation showing the fit of the model across seasons 202
Table 7.3 Comparison between the nitrate leaching parameters before and after recalibration 207

List of Figures

Figure 1.1 Scale and processes (A) A nested catchments from upland area (1 km^2) to lowland area (100 km2) (B) Change in land use intensity 3

Figure 2.1 Generalised hydrograph showing sampling position (Pionke *et al.*, 1996) 9

Figure 2.2 Nitrogen cycle: adapted from DEFRA (Defra, 2012) 16

Figure 2.3 Phosphorus cycle (adapted from www.defra.gov.uk) (Defra, 2012)........ 19

Figure 2.4 A conceptual framework of the P cycle in aquatic systems (Barber, 2008) 20

Figure 2.5 Conceptual framework showing process relationships between different scales for the Campos de Panes area (A) and the Schrondweilerbaach area (B) (Cammeraat, 2002) 30

Figure 2.6 Classification of hydrological models according to process descriptions (Refsgaard and Knudsen, 1996) 39

Figure 2.7 Schematic diagram of a catchment and the MIKE SHE quasi three-dimensional distributed physically-based model (DHI, 1993). 41

Figure 3.1 The River Eden Catchment (adapted from the Eden River Trust, 2014). 48

Figure 3.2 Digital Elevation Model (DEM) of the study sites in the Eden Catchment .... .49

Figure 3.3 Catchment Geology map.. 50

Figure 3.4 Eden Catchment drift geology map 52

Figure 3.5 Eden Catchment HOST soil types... 54

Figure 3.6 Dacre soil map (from Eden DTC Project:www.edendtc.org.uk)............... 55

Figure 3.7 Morland soil map (from Eden DTC Project: www.edendtc.org.uk) 56

Figure 3.8 Pow soil map(from Eden DTC Project: www.edendtc.org.uk) 57

Figure 3.9 Catchment land use map. 59

Figure 3.10 Flow, suspended sediment and nutrient monitoring locations in the Eden Catchment to Eden at Sheepmount gauge 62

Figure 3.11 Eden gauge stations at Temple Sowerby, CHASM (Mayes *et al.*, 2006)…………………………………………………………………………………...63

Figure 3.12 Dacre, Morland and Pow maps (EdenDTC, 2011) 76

Figure 4.1Subhourly rainfall pattern at Great Musgrave for period covering (a) April 2011-April 2013 and (b) October 2011- September 2012 80

Figure 4.2 Sub-hourly rainfall and flow pattern; Morland subcatchment from October 2011- September 2012 80
Figure 4.3 River Eden at Kirkby Stephen flow duration curve (based on mean daily flow) comparing the 2011 and 2012 data with data from 1972 – 2011 83
Figure 4.4 (a-b) Regression analyses used to generate flow data for Gais Gill station after the first device was lost in November 2011 84
Figure 4.5 Regression analysis used to generate flow data for Smardale station 84
Figure 4.6 Relationship between the observed flow and downscaled flow at Kirkby Stephen from the period when the two data sets overlapped 85
Figure 4.7 Regression analysis between the CHASM flow data and the EA stage data 86
Figure 4.8 Relationships of TP, RP, SS and N with flow in autumn 2011 (one of the SS data point in autumn returns zero value and was therefore excluded so as to permit the graphing of the log-transformed data) 87
Figure 4.9 The dual relationship of nitrate with flow at Temple Sowerby for the 2011 – 2012 water year (i.e. the period of the seasonal campaign) 89
Figure 4.10 Seasonal f nutrient concentrations in the Eden catchment during the seasonal campaign as a function of catchment area 91
Figure 4.11 Variation in algal growth at Gais Gill in (a) cold (27/02/2013) and (b) warm weather (31/05/2012) 94
Figure 4.12a Spatial pattern of P, SS, RP and N along the Eden nested system 96
Figure 4.12b Relationships between some Eden catchment characteristics and area……………………………………………………………………………….....97

Figure 4.13a Relationships between nutrients, suspended sediment and elevation……………………………………………………………………………...100

Figure 4.13b Relationships between nutrients, suspended sediment and some HOST classes……………………………………………………………………………..102

Figure 4.13c Relationships between nutrients, suspended sediment and grassland……………………………………………………………………………..104

Figure 4.13d Relationships between nutrients, suspended sediment and tilled land………………………………………………………………………………105

Figure 4.13e Relationships between nutrients , suspended sediment and urban land use……………………………………………………………………………………106

Figure 4.14a-d (1) A comparison of some soil properties between GG and BB and (2) Spatial distribution of HOST soil types in the Eden catchment 108
Figure 4.15 Spatial pattern in nitrate and SS, loads and yields in the River Eden using the FDC-rating technique.. 115
Figure 4.16 Loads and specific yields of TP, RP, SS and nitrate in the River Eden using the Approximate method.. 116
Figure 5.1 Sub-hourly rainfall and flow for (a) Dacre and (b) Morland (c) Pow from September 2011 – September 2012 121
Figure 5.2 Box plot comparing the contaminant concentrations from the two measuring equipment at Morland... 124
Figure 5.3 Scatter plots of hourly flow against P, TRP (Ortho-P), SS and N at Morland from samples collected using the autosampler.. 126
Figure 5.4 Scatter plots of hourly flow against P, TRP (Ortho-P), turbidity and N at Morland using the CM equipment 127
Figure 5.5 Scatter plots of hourly turbidity against P, TRP (Ortho-P), SS and N at Morland based on the autosampler sampling date.. 128
Figure 5.6 Scatter plots of hourly turbidity against P, TRP (Ortho-P), and N at Morland using the CM equipment 129
Figure 5.7 Comparison of the outliers of hourly TP, TRP and N data from the CM data (Hourly) with those from an autosampler... 132
Figure 5.8 Seasonal comparison of TP, TRP, SS and NO_3-N hourly concentrations in Dacre (subcatchment 1) and Morland (subcatchment 2) for the period covering a water year (2011 – 2012) 134
Figure 5.9a Hourly flow, TP and TRP time series recorded at Morland within the Eden catchment, northeast England in 2011 - 2012 water year…………………….135

Figure 5.9b Hourly flow, turbidity and $N0_3$ time series recorded in Morland within the Eden catchment, northeast England in 2011 - 2012 water year…………………….136

Figure 5.10 Hourly precipitation, flow, nutrients and turbidity contents of Morland in the wet period following an event on 29/11/2011. 140

Figure 5.11 Hourly precipitation, flow, nutrients and turbidity contents of Morland in the wet period following an event on 28/06/2012 141
Figure 5.12 Hourly multi-peak precipitation, flow, nutrients and turbidity contents of Morland in the wet period following an event on 25/09/2012................................. 142
Figure 5.13 Hourly precipitation, flow, nutrients and turbidity contents of Morland in the dry period following an event on 27/01/2012... 143
Figure 5.14 Hourly precipitation, flow, nutrients and turbidity contents of Morland during a dry period, March 2012. 144
Figure 5.15 Morland flow duration curve and corresponding responses of TP & TRP, N and turbidity from 01/10/2011-30/09/2012... 146
Figure 5.16 Seasonal comparison of rainfall, flow and water quality parameter transferred in Morland Beck outlet- using (a) Autosampler data and (b) CM data and –(c) the Dacre Beck outlet from October 2011 – September 2012......................... 150
Figure 6.1 Algal growth at Great Musgrave (source: Mannix, 2005)………………..168
Figure 7.1 Schematic diagrams showing the flow and nutrient components and parameters used in the TOPCAT-NP model (Quinn unpub. Lecture notes)........... 185
Figure 7.2 Screenshot of the user-friendly MS Excel interface of the TOPCAT-NP model 186
Figure 7.3 EPIC simulations showing (a) a relationship between annual nitrate loss and annual HER (b) the relationship between surface runoff and sediment losses from (Quinn et al., 2007) 189
Figure 7.4a-k Sensitivity test for the moorland catchment for parameters (a) BackN, (b) Ninitial, (c) ϕ, (d) BackP, (e) Pinitial, (f) PDC, (g) Qback, (h) Quick, (i) QuickCSA, (j) split and (k) SRMAX respectively.. 197
Figure 7.5 observed and simulated flow, N, TP and soluble P simulations for the Morland catchment in the River Eden, UK 201
Figure 7.6 observed and simulated flow (Q), nitrate, TP and Sol P for the Morland catchment during winter)... 203
Figure 7.7 observed and simulated flow (Q), nitrate, TP and Sol P for the Morland catchment during summer.. 204
Figure 7.8 (a) Observed and simulated nitrate concentration for Morland after re-calibration (note the June period) (b) simulated nitrate during the wet period following recalibration.. 206

Figure 7.9 Observed and simulated nitrate concentration in the summer period in 2012 (a) before recalibration (i.e. after first calibration) and (b) after recalibration . 207

List of Acronyms

AP	Appleby
BB	Blind Beck
BFI	Base Flow Index
BGS	British Geological Survey
CEH	Centre for Ecology and Hydrology
CHASM	Catchment Hydrology and Sustainable Management
DEM	Digital Elevation Model
DTC	Demonstration Test Catchment
FAO	Food and Agriculture Organisation
FDC	Flow Duration Curve
FSR	Flood Studies Report
GC	Great Corby
GG	Gais Gill
GM	Great Musgrave
HOST	Hydrology of Soil Type
KS	Kirkby Stephen
MLURI	Macaulay Land Use Research Institute
NERC	Natural Environment Research Council
ORSTROM	Office de la recherché scientifique et technique d'outre-mer
RD	Ravenstonedale

RP/DRP	Reactive Phosphorus (Soluble Phosphorus)
SAAR	Standard Period Annual Average Rainfall (mm)
SD	Smardale
SS	Suspended Sediment
TRP	Total Reactive Phosphorus
TP	Total Phosphorus
TS	Temple Sowerby
UNESCO	United Nations Educational, Scientific and Cultural Organisation
USDA	United State Department of Agriculture
WRAP	Winter Rainfall Acceptance Potential
WQP	Water Quality Parameter
WQV	Water Quality Variables

Chapter 1: Introduction

1.1. Context

Fresh water is very important to our everyday life. It is one of the habitats for fisheries and provides water for domestic, agricultural and industrial purposes amongst other uses. Less than 3% of the global water is fresh; a larger percentage is frozen and unavailable for consumption. Fresh water consists of rainfall, natural lakes, reservoirs and rivers (UNESCO, 2003). The world population, projected to increase to 9 billion by 2050, will require water services to meet the expanding needs in terms of drinking water, any expansion in business activity and urbanisation amongst other factors. Thus the contamination and pollution of surface water such as streams and rivers by nutrients and sediment is increasingly recognised as a serious concern that impacts water quality worldwide. The major pollutants are nitrogen (N) and phosphorus (P), and they are known to impair river ecology by causing eutrophication (Jarvie *et al.*, 1998).

Eutrophication depletes the oxygen status of rivers and poses a threat to fisheries. Many UK waters are already impacted with eutrophication and P pollution arising from human activities (Jarvie *et al.*, 1998; EA, 2000). Nitrate (NO_3) is of particular concern to drinking water supplies and there are guideline targets and permissible limits set at 25 mg NO_3 l^{-1} and 50 mg NO_3 l^{-1} respectively. Reducing the level of P in sewage and cleaning up polluted waters comes at a cost. To address the problem of pollution in European rivers the European Commission produced the Water Framework Directive (WFD), whereby year 2015 was fixed as the deadline for the achievement of water having “good” ecological status for all member countries. The United Kingdom is addressing this through agencies such as the Department of Environment, Food and Rural Affairs (DEFRA) and the Environment Agency (EA), and projects such as the Catchment Hydrology and Sustainable Management (CHASM) (O'Connell *et al.*, 2002), and the Demonstration Test Catchments (DTC) (EdenDTC, 2011) amongst others.

Therefore, investigating water quality is a continuing concern and has drawn the attention of researchers from various disciplines. Quinn (2004) identifies key factors that influence nitrate losses and these occur at a range of scales (1 m^2 to 10,000 km^2). At a plot or point scale (1 m^2), agronomic, leaching and soil hydrological processes dictate pollutant transport. At the hillslope scale (1-5 ha), the role of topography, soil and human influences dominates and the dominant process evolves into a range of typical hillslope units combined at the catchment scale (1-10 km^2). As the single catchment increases to a basin scale (1000 – 10000 km^2), he proposes a large scale variability in land use, rainfall and topography. It is evident from the forgoing that there is a confluence of disciplines or professions involve in seeking understanding of the problems of water pollution and proffering solutions to this issue. Haygarth *et al.* (2005a) in their paper on the 'Phosphorus Transfer Continuum' were more specific on the discipline by matching the scale of study with the associated disciplines. They put forward a simple four-tiered model to describe the research approaches and needs for the continuum: source, mobilisation, delivery and impact. Associated disciplines identified from different scales (e.g. sub-plot to catchment-scale containing rivers or lakes) are, biochemistry, agronomy, soil science, hydrology and limnology.

Thus solving water quality problems involves deploying many research tools and scientific methods into the laboratory, field and catchment studies. However, measurements at the hillslope and catchment scales are limited in time and space and measuring techniques are still limited despite advancement in research techniques. There is therefore the need for a means of extrapolating the data obtained from those measurements, through simulations to gain broader understanding, for applications to ungauged or poorly gauged catchments, and for an assessment of the impact of future hydrological changes (Beven, 2011), land use changes and management. Modelling therefore helps to both extrapolate and make predictions and can be useful as a decision making tool. The reliability of the simulations depends on the modeller making the correct choice of model, the accuracy and validity of the input data, and concept(s) on which the model is built and trained.

Quinn (2004) argued that complex physically-based models for nitrate and soil hydrological processes are best suited for the point or plot scale because the bulk of the concepts guiding the physically-based models relate to one dimension fluxes, and can only reasonably test basic agronomic ideas and physical relationships. At the hillslope scale he suggests using quasi-physical models that can describe the

Critical Source Areas (CSAs) and Variable Source Areas (VSAs). CSAs refer to surface or near surface areas for nitrate and phosphate loss while VSA describes areas generating runoff by saturation excess. This occurs when the soil becomes saturated and any additional rainfall or precipitation triggers runoff. He proposed a Minimum Information Requirement (MIR) model that couples the physical-based and quasi-physical models, and could be used to represent large catchments. Even when the appropriate model is chosen, the scale of the measuring techniques (generating the conceptual model and the input data) still remains an issue because most field equipment measures a variable at the point scale.

One major issue in the management of water resources is the transfer of findings from the small to large scale, yet most research experiments are conducted at the small scale. Schumm (1977) theorises that sediment yield decreases with time and distance but Mills (2009) failed to find a relationship between suspended sediment yield and catchment area. Although Bloschl (2001) noted that there is spatial arrangement of flow paths and that mechanisms change with scale he still put forward the scale invariant/similarity concept where it was stated that catchment processes at both the small and large scales do not change. Blöschl then proposed upscaling as a way of transferring information from the small to large scale while conversely downscaling was suggested for transferring information from the large to small scale. Catchment processes and the factors influencing them are spatially heterogeneous and complex, and the previous discourse has shown that processes are modified as scale increases. Figure 1.1 is a simple illustration of how land use

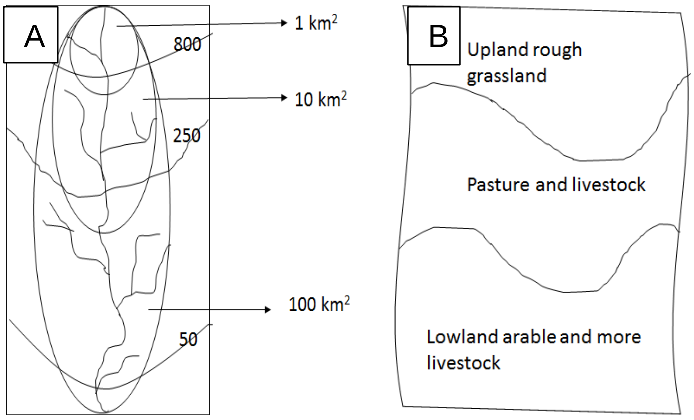


Figure 1.1 Scale and processes (A) A nested catchments from upland area (1 km^2) to lowland area (100 km^2) (B) Change in land use intensity

evolves in a catchment as the catchment size increases. With nested catchments it is then possible to relate processes and understand how catchment characteristics such as nutrient dynamics change at a range of scales.

Studies conducted at the large scale take into consideration these heterogeneities and complexities. Stakeholders in catchment management and modelling therefore, prefer using findings from research conducted at the large scale (~100 km^2 or greater). Such studies require investment in field instrumentation and data gathering. The CHASM project has a dense network of gauging stations up to a mesoscale (~100 km^2) in the Eden catchment and these stations are set up using a nested basin approach. The Environment Agency (EA) gauging stations, in the Eden catchment made it possible to extend the study area up to the basin scale. Thus, sub-catchments at a series of spatial scale can be studied along with an investigation of scaling relationships within the system. This represents a means of obtaining spatial-scale data upon which better predictions and decisions can be made.

The River Eden and its catchment is designated as a Site of Specific Scientific Interest (SSSI) and Special Area of Conservation, and is also a host to another national catchment-scale project, the Demonstration Test Catchments (DTC) that is set up to evolve cost effective ways of mitigating diffuse pollution without adversely affecting farmers' profit. Spatial scale investigations that have used the Eden catchment as the study area include a study of the spatial dependency of the flood response to high rainfall and spatial scale patterns in sediment transport (Wilkinson, 2008; Mills, 2009). The current research complements these by adding a study of the spatial dependency in nutrient yield. In doing so it advances our understanding by quantifying the variation in nutrient yields over a four orders-of-magnitude range in spatial scale by seeking process-based explanations for the variation and by examining a modelling approach for extrapolating from the case study to a more general UK application. In other words, it intends to gain an understanding on how, where and when nutrient losses occur in the Eden catchment by carrying out a spatial scale related study of the Eden catchment (CHASM study), perform an analysis of the DTC high resolution data and perform a modelling analysis in order to find an effective way to tackle the problem of nutrient losses in a more general sense.

1.2. Research Aims

To evaluate the spatial scale patterns in nitrate and phosphorus transport at a range of scales in the Eden catchment and also to identify the processes driving them. This aim is to be achieved by: (a) quantifying the spatial scale dependency through the Eden catchment using nested catchment data from the CHASM project; (b) explaining the dependencies and the controlling processes using the DTC data for catchments with different land uses; and (c) extending the findings through to a wider use by catchment modelling.

Research questions

1. Where are the SS, TP, TRP and $N0_3$ coming from and the possible transport pathway(s) in the Eden?
2. Does TP, TRP and NO_3 concentrations and yields increase with increase in catchment size?
3. Is there any role play by the weather pattern, soil-related- and in-stream-processes in the export of the SS and nutrients?
4. How is the stream concentration of the SS and nutrients related to elevation/topography, geology, soil type etc. in the Eden catchment?
5. What role does the intensity of land use and land management practise play in the pattern of the water quality determinands in the River Eden?
6. Can the key driver(s) be represented by the TOPCAT-NP and which environmentally-safe management strategy can be proposed from the result of the modelling?

Objectives

1. Conduct discrete field sampling and laboratory analyses so as to assess suspended sediment (SS), P and NO_3 concentration, load and yield using a dense network of gauge stations at a range of scales (1.1 – 1373 km^2) in the Eden catchment.
2. Compare the spatial relationship of stream concentrations of NO_3, P and SS with catchment area and quantify loads and yield (load per unit area).
3. Identify the key driver(s) of stream contaminant (SS, P and NO_3) concentrations and their variability relative to catchment size.

4. Assess any other factors directly or indirectly influencing contaminant transfer
5. Investigate seasonal effect across the Eden sub-catchments.
6. Use near-continuous data from the DTC to validate the processes driving nutrient and SS emission from the Eden catchment.
7. Assess the potential of TOPCAT-NP to represent the processes driving the nutrient transfer and therefore extend the findings beyond the Eden catchment.

1.3. Thesis Outline

Chapter 2 – focus on a literature review that provides an information base for this research. The chapter considers nutrients in a fluvial system, catchments characteristics and processes that are related to nutrient transfer, and tools that are relevant to data acquisition and modelling.

Chapter 3 - describes the deductive methodological approach leading to three studies conducted in this research: the CHASM study; the DTC study and the modelling. The CHASM study contains information on the study site, the field monitoring routines and laboratory analyses. The other two studies are desktop-based and the rest of the chapter summarises the DTC projects and the model employed.

Chapter 4 – discusses the quantification of the discharge data from stage data, calculation of load and specific yield using the concentration data obtained from the field campaigns (CHASM study). The chapter also reports the relationship of concentration and discharge linking this relationship to possible sources of the SS and nutrients, and highlights other roles play by hydrology in the catchment. Impact of the weather pattern, elevation, land use and management, and the role of in-stream processes were also considered. The chapter also demonstrates spatial pattern of concentration, load and specific yield down the Eden subcatchments under the CHASM project.

Chapter 5 – presents and quantifies the use of the data obtained from high frequency monitoring stations obtained from the DTC team. This is used to validate and expand the scope of the hydrochemical signals obtained from the CHASM study, confirm the processes and catchment characteristics responsible, and linked the results to the spatial pattern described in chapter 4.

Chapter 6 – using literatures, this chapter primarily focuses on providing details explanations on the results and quantification of hydrochemical functioning of the river Eden presented in chapters 4 and 5 with the aim of conceptualising nutrient transport in the Eden within spatial context. Here, key drivers of the nutrient that underpins modelling scenarios that is to be explored in the modelling chapter were emphasized.

Chapter 7 – explores the TOPCAT-NP model as a tool used to project the key drivers of the nutrient exports into the future management options, also beyond the spatial range obtained in the Eden catchments in a bid to generalise the findings to other catchments.

Chapter 8 – the conclusive chapter indicates to what extent the questions and objectives of this study have been achieved. Key findings are mentioned and possible future research directions are stated.

Chapter 2: Literature Review

2.1. Introduction

This chapter addresses the issue of nutrient transfer in a spatial scale context and seeks to gain insights into the processes driving it. It brings together the current state of research into nutrient loss in catchments. The challenges in measurements and scale theory will be considered, and various opportunities available for research within spatial contexts will be examined. There will also be a consideration of the modelling tools that are available for the representation of the catchment nutrient dynamics and the prediction of these.

2.2. Introduction to Catchment Nutrient Dynamics

2.2.1. Flow-nutrient relationship

Stream flow is influenced by various flow patterns: storm flow, base flow and elevated base flow. Storm flow represents the rise, peak, or early recession of a storm hydrograph. This is in itself controlled by overland flow, and near stream underground and other inflows of subsurface water. Any flows represented on the hydrograph by the stable non-storm flow or extended storm flow recession periods (usually at least two days after the hydrograph peak) are classified as base flow. In some rivers it is a typical high flow rate during late winter. Flows are classified as an elevated base flow if they coincide with the post-storm recession period usually less than two days following the hydrograph peak and characterized as atypical relative to the extended baseflow recession. Any flows that do not fall into these three categories are described as unclassified (Pionke *et al.*, 1996). This is illustrated in figure 2.1 below. Baseflow and elevated baseflow are sustained by inflows of subsurface water that are in turn characterised by varying residence times. In catchment hydrology these flows are related to the nutrient dynamics (e.g. ground water is important for nitrogen (N) but overland flow is important for phosphorus (P), and the relationship is described by various terms and expressions: nutrient concentration, nutrient flux and nutrient load or export. These terms and expressions are explained below,

i. *nutrient concentration* is the mass of nutrient per unit volume of solution at a specific time which is usually expressed in milligrams per litre

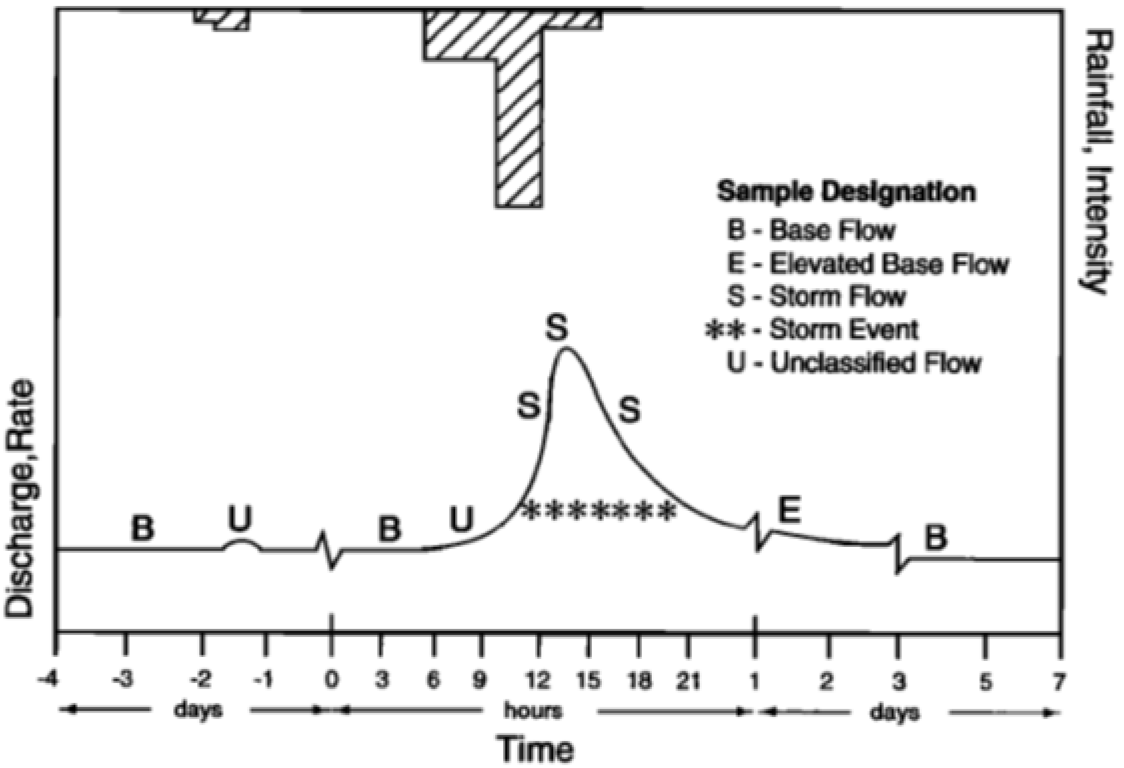


Figure 2.1 Generalised hydrograph showing sampling position (Pionke *et al.*, 1996)

ii. *nutrient load* within a river at a specific time, is the product of the river discharge (e.g. litres per second) and concentration of the nutrient (e.g. milligrams per litre) at a specific time. There is also an instantaneous load of N or P calculated by multiplying their respective concentrations and the river flow at the time of sampling. This can be expressed in milligrams per seconds (Pionke *et al.*, 1996) used the term chemical export, the percentage of which is given by

$$Chemical\,\mathrm{exp}ort\% = \left[\frac{\left(DQX\overline{Q}X\overline{C}\right)}{\sum\left(DQ_i X\overline{Q}_i X\overline{C}_i\right)}\right]X100 \qquad (2.1)$$

where DQ is the component of the flow distribution of interest (the percentage of flow e.g. base flow), mean Q is the corresponding mean flow and mean C is the corresponding mean concentration. The summation term includes the base flow, elevated base flow, storm flow and the unclassified flow components mentioned above. The export percentage fraction makes it possible to characterise the export pattern of the nutrient of interest.

iii. The *nutrient yield* from a river (e.g. grams per year per area) is the mass of nutrient transported into the river in a specific time per unit catchment area. It can also be expressed as a kilo-equivalent of nutrient per unit land area (e.g. Keq nutrient/hectare, Correll *et al.* (1992)). Therefore there are different ways by which the nutrient yield can be expressed in catchment studies.

Many studies (Pionke *et al.*, 1996; Haygarth *et al.*, 2005b; Howden *et al.*, 2010) have provided some insights into the relationships between discharge and the different fractions of nutrient yield. Such studies often considered the various species of these nutrients especially nitrogen (N) and phosphorus (P). To enhance the understanding of these fractions and how they relate to flow there is need to summarise their definitions which are in turn linked to their methods of determination. In the case of N, although the yields of the reduced forms of N (organic and ammonium nitrogen) are also reported in the literature, nitrate is mostly considered. Total N is obtained using the persulphate procedure (to be discussed under methodology). The organic nitrogen fraction is obtained by subtracting the inorganic fraction from total nitrogen. There are also soluble (Nsol) and particulate forms of nitrogen (usually in the reduced form). The soluble form is measured from the filtrate obtained by passing the sample through a membrane-filter (0.45 µm pore size).

Similarly, several P fractions exist which are: total P (TP), organic phosphorus (OP), soluble P (Psol) and particulate P (PP), and are measured by laboratory approaches similar to that of N. TP is obtained by the persulphate digestion procedure, OP by the difference between TP and the inorganic fraction. Unlike N, P fractions were given a lot of attention in many studies. Total dissolved P (TDP) is measured from the filtrate which is then subjected to a persulphate digestion procedure the same as for TP (for TP, the digestion is carried out before filtration). TDP is the sum of the poly-phosphorus, organic phosphorus and orthophosphate P or dissolved P (DP). After persulphate digestion the TP and TDP are also analysed using these colorimetric procedures. The use of a filter (0.45 µm) followed by the molybdate procedure (Murphy and Riley, 1962) is the technique employed to measure Psol (dissolved P, DP) while the PP is the difference between the TP and DP.

Apart from the P in the water phase (TDP and DP), there are P fractions in the sediment phase: labile PP, algal-available PP (AAP) and total PP. Labile PP describes Cl – resin extractible PP (while Labile P is the sum of labile PP and TDP). Labile PP is a measure of the P fraction that could be desorbed from sediment into the water phase, such as by dilution during transport (Pionke and Kunishi, 1992). AAP represents NaOH extractible PP. To measure total PP the sediment sample is digested in 70% perchloric acid using the method of Olsen and Sommers (1982) without any HNO_3 pre-treatment. This is then filtered so as to obtain the filtrate in readiness for analysis using the molybdenum blue procedure. The three sediment fractions are analysed using the molybdenum blue procedure following the initial treatments. Most studies on nutrient dynamics (including the relationship with flow components) at a catchment scale have focussed on these nutrient fractions.

The increases in nutrient concentration and flux have been linked to various factors which include flow regimes or river discharges, themselves a function of different stream flow drivers: storm flow, base flow etc. Howden *et al.* (2010) mentioned three ways to increase nitrate fluxes: by increasing either the river discharge or nitrate concentration or a combination of both. In the study of a long term nitrate data record obtained from the Thames basin (Howden *et al.*, 2010) the trends observed were explained based on the contribution of different flow components. The immediate increase in nitrate concentration was explained to be accounted for by the near-stream and shallow subsurface runoff sources in parts of the catchment, but long-residence time groundwater pathways governed a sustained shift in mean concentration that was observed in the basin (Jackson *et al.*, 2006; Howden and Burt, 2008; Jackson *et al.*, 2008). Groundwater, hillslope flow, confined and unconfined aquifers have also been found to contribute to the nitrate dynamics of the shallow sub-surface flow regime (Komor and Magner, 1996; Pinay *et al.*, 1998; Clement *et al.*, 2003). Many authors have indicated that substantial NO_3 concentrations and export result from baseflow especially when elevated. (Gburek and Heald, 1970; Pionke *et al.*, 1988; Schnabel *et al.*, 1993; Pionke *et al.*, 1996). The concentration and export of P on the other hand is driven by storm flow particularly where sediment export predominates (Gburek and Heald, 1974; Johnson *et al.*, 1976; Pionke *et al.*, 1988). High flow conditions can stimulate soil erosion, re-suspension of non-consolidated stream-bed sediments and stream-bed erosion (Jordan-Meille *et al.*, 1998). Some studies have also showed that substantial exports of TP (Johnson *et al.*, 1976) and water phase P (TDP and DP) (Pionke *et al.*, 1996) are driven by storm flow and occurred during the upper 10% of flow duration. Application of this knowledge together with the delineation of critical source areas (CSAs) is vital to the management both of P losses from the catchment and the subsequent river pollution. CSAs are areas with high soil P levels combined with a high potential for surface runoff and erosion (Gburek and Sharpley, 1998). The DTC project is also investigating various mitigation measures that will provide explanations on both how nutrient enters the river and how this can be controlled. This research stems partly from an involvement in the DTC investigations, while the Catchment Hydrology and Sustainable Management (CHASM) project provides the spatial scale context for the research. Although high flows can increase the nutrient concentrations in rivers, cases of dilution have also been reported. This is especially the case under high flow conditions (e.g. a flood).

There have been contrasting findings on the issue of dilution observed during high flows. Ballantine *et al.* (2008) compared concentrations from manual samplers used during high flows, with an in-stream time-integrated suspended sediment sampler and attributed the difference between concentrations from these samplers to a dilution effect. There is a contrast in the concentrations of PP when fractionated during high flows. The sediment-associated inorganic phosphorus (IP) has been observed to be higher compared with the sediment-associated organic fraction (Bai *et al.*, 2009). Ballantine *et al.* (2008) observed variations in the yield of these P species in relation to time and among the investigated (UK) catchments. Their observations for the River Hooke at Frome showed higher IP fractions. However, a higher OP contribution was earlier observed in the Devil's Brook in the Piddle catchment before the IP content increased later: a trend representing the initial transport of remobilised material stored within the channel bed and enriched by plant material which, after exhaustion, was later controlled by the IP component arising from recently introduced PP from the catchment surface. Pionke *et al.* (1996) reported a distinctive pattern in the responses of the concentrations of water phase P (TDP and DP) and NO_3 to water flow rate in their Mahantango Creek (USA) research watershed study. As the flow rate increased the water phase P initially decreased when the flow was still within the base flow range (probably because the channel source was diluted before the sediment source area are engaged) but the concentration increased once the storm flow dominated (probably after the sediment source area has been engaged). The reverse was the case for nitrate which exhibited a rise in concentration as the flow rate initially increased at a period coinciding with the base flow period (and even at storm flow rates) but later decreased once the storm events dominated runoff generation.

These researchers also reported seasonal nutrient concentrations in the river. They observed the highest water phase P and lowest NO_3 concentrations in the stream flow processes during summer, whereas the reverse was true during winter and spring. Both the water phase P components (TDP and DP) were similar for storm flows but significantly different for non-storm flows across all seasons. The seasonal effect was explained to be due to a change in flow rates rather than the concentrations. The bioavailable component, represented as algal available P (AAP), also fluctuated in rivers during high flow events (Pacini and Gachter, 1999; Bai *et al.*, 2009). With the contrasting land use intensity in the DTC catchments, and the large scale research platforms under the CHASM and Environment Agency (EA) projects in the Eden catchment a research question pertains to whether the observations are going to be similar or different in terms of the relationship between the stream flow processes, variable land use intensity, seasons etc., and the yield of nutrient fractions into the River Eden, including the sediment associated P.

2.2.2. Sediment

The process of erosion generates sediment. Erosion consists of different types: splash, sheet, rill and gully erosion. Splash erosion occurs as a result of the striking energy of rainfall which detaches soil particles. Sheet erosion describes a uniform movement of the detached particles over the surface of the ground as a result of the overland flow resulting from excess of rainfall over water infiltration into the soil. Overland flow tends to concentrate and scours areas where there is a weak bond holding the soil structure together resulting in channels that are termed rills. If unchecked it widens and deepens into channels that cannot be closed by agricultural activities and machinery: at this stage it is no longer regarded as rill but rather gully erosion. There is also stream channel erosion that occurs in the natural channels. These various types of erosion differ in erosive power but all have the capability to detach and transport soil particles which are later deposited as sediment either within the catchment or into the river draining the catchment, depending on the size of the materials and the hydrological connectivity of the catchment. Sediment engaged from land can be natural (resulting in e.g. denudation over geologic time scales) or from anthropogenic sources. Anthropogenic sources can occur from construction, mining, agricultural activities etc. but agricultural activity poses the biggest problem.

Apart from the sediment entrained from land surfaces an appreciable quantity can also be generated from the bank and in-stream i.e. what are termed in-channel and in-stream sediment sources. Walling *et al.* (1999) came up with the following order of sediment contribution to suspended solid yield in the River Ouse catchment in Yorkshire: Woodland area (0%) < uncultivated topsoil (25%) < channel bank (37%) < cultivated land (38%). Though most of the land use contributed an appreciable amount of sediment into the river, agricultural activity dominated despite having the least areal extent in this catchment. Sediment is transported in solution (< 0.45 µm) and as solid materials in rivers, with each having both organic and inorganic nutrient components associated with them. The solid sediment materials are subdivided into bedload and suspended load. The suspended load is less dense and finer having size < 2 mm (sand-sized and other finer particles) with size < 63 µm (silt- and clay-sized particles) predominating (Baldwin *et al.*, 2002; Barber, 2008). The < 63 µm-sized particles are the chemically reactive component of the solid load and are carriers of contaminants and nutrients (Owens *et al.*, 2005). This is because the particles in this size range possess a large surface area for reactions and are negatively charged. Thus they are characterised by the adsorption and desorption of organic and inorganic chemical substances (nutrients and contaminants) and cation exchange reactions. These nutrients through various stream flow components (discussed in the previous section) will find their way into the river.

The association between sediments and some forms of nutrient pollutant is vital to an understanding of the mechanism of nutrient fluxes at different spatial scales. PP (a sediment associated fraction of P) is known to be entrained into the runoff and find its way into stream channels and this has been found to account for a larger proportion of TP in some rivers. For instance, it has been reported that PP accounted for a larger percentage of TP load with a proportion up to 75% recorded in Great Britain and Ireland (Walling *et al.*, 1997) while Bowes *et al.* (2003) suggested a higher proportion of 76% transported in rural catchments. These authors also explained that increased TP concentrations observed in the lower reaches of a river system were due to P adsorption by fluvial sediment. PP, together with DP has been linked to the bioavailable fraction (AAP). Sharpley and Smith (1992) reported that the bioavailability of PP often exceeds that of soluble P. Corroborating this, Ballantine *et al.* (2008) reported an algal available P (AAP), that was unusually high (77%) at the Bovington sampling site in the Frome catchment which corroborated this.

2.2.3 Nutrients

Nitrate and ammonium nitrogen - sources and sinks in a catchment

Nitrogen (N) exists in the atmosphere as nitrogen gas (N_2). Its cycle begins (figure 2.2) when it is connected to the soil phase (and the biosphere at large) through a number of processes: symbiotic nitrogen fixation, non-symbiotic nitrogen fixation, and nitrogen deposition (e.g. N in rain and snow precipitation). Nitrogen gas is not useful to most plants with the exception of the leguminous species that are capable of tapping it in association with nitrogen-fixing bacteria (typically members of the genus *Rhizobium*) in a process termed symbiotic nitrogen fixation. These plants requires the nutrient for protection from oxygen that would otherwise poison the enzyme (nitrogenase) required for nitrogen fixation, while the bacteria fix nitrogen from the atmosphere in a form that is eventually nutritionally beneficial to the host plant. There are also free-living (non-symbiotic) nitrogen fixers, chiefly *Azotobacter* and a few other species of bacteria such as *Klebsiella pneumoniae*. They are free-living in soil and water, and utilize atmospheric N_2 for synthesising cellular proteins. Cell proteins are mineralised in soil after the death of the Azotobacter cells into a form of N that crops can utilize. Nitrogen deposition occurs in the presence of both nitrogen oxides (NO_x) and NH_3 gases which are emitted into the atmosphere. NO_x in the atmosphere is also formed by the action of lightning on atmospheric N_2 molecules (atmospheric nitrogen fixation) which contributes about 5 – 8% of the fixed nitrogen. These nitrogen gases are deposited into the terrestrial or aquatic environment in what are described as either wet- (scavenging of gases and aerosol by rainfall) and dry- (direct deposition of gases and aerosol) deposition (Fowler *et al.*, 1989; Hornung and Sutton, 1995). Although an aerosol of the reduced form of N (NH_x) could be dispersed in fact NO_x is more widely dispersed. NH_x tends to concentrate around agricultural areas (generally within 1 – 500 m of the point source) and along the roadside (as it is emitted by vehicles fitted with catalytic

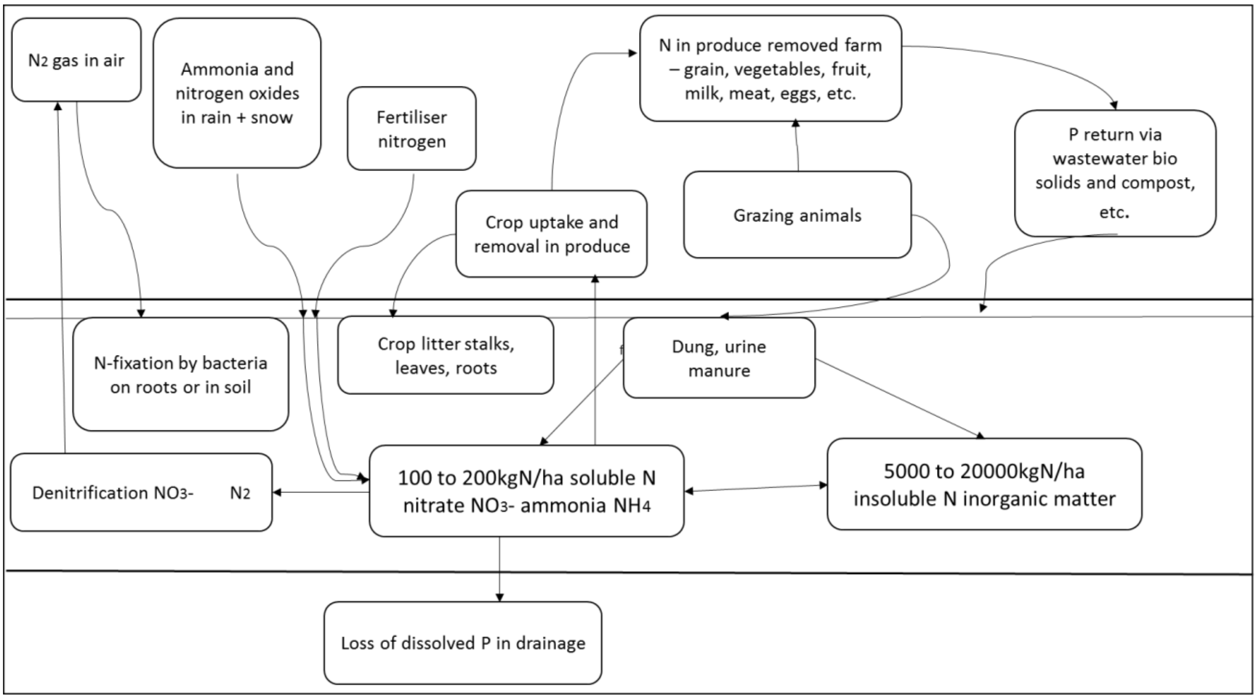


Figure 2.2 Nitrogen cycle: adapted from DEFRA (Defra, 2012)

converters), and it is often deposited in high quantities detrimental to semi-natural vegetation in intensive agricultural areas (Shepherd *et al.*, 2008).

With the concern for food security for an ever-increasing world population efforts have been directed at improving soil productivity which include manuring and fertilisation. One of the limiting major elements needed by plants and produced as fertiliser is N. The processes leading to the production of some of the nitrogen fertiliser (urea and ammonium nitrate) involve the combination of atmospheric N and H (usually derived from natural gas and petroleum respectively). Other sources of nitrogen are driven by land use that encourage N mineralisation or ammonification and discharges from sewage effluent (Howden *et al.*, 2009), microbial decomposition and bedrock weathering (Holloway *et al.*, 1998). Once N from these sources finds its way into the soil and is taken up by plants animals and humans can feed on the plants and their products. The excreta and remains of animals together with plant debris (and litter) and dead microbes are mineralised and returned as nutrients to the soil. Thus the sources of nitrogen are both natural and anthropogenic. An excess of these nutrients in the soil and those that are added directly to the water bodies (e.g.

nitrogen deposition and free-living bacteria fixation) may constitute potential pollutants in these media.

There are different ways in which nitrogen (particularly the highly soluble nitrate) in the soil is linked to a water body. These includes: surface runoff, sub-surface runoff and leaching. Surface runoff is very important in the transport of particulate nitrogen in the form of organic N and ammonium which can be adsorbed to suspended particles in heavily-grazed grassland. However, most N from grassland and cropped fields is transferred through subsurface pathways (Heathwaite *et al.*, 1993; Anderson *et al.*, 2001). N is transferred to the subsurface pathway through a process termed leaching. Leaching is the downward movement of nutrients (nitrate) through the soil body. It is termed percolation if it advances beyond the root zone into the groundwater. Leaching is the pathway of N transfer from hillslope to streams and groundwater via either the soil matrix or a preferential flow pathway (e.g. biopores, cracks in the expanding clay soils). Studies have shown that the nitrate - flow relationship varies with seasons. The nitrate concentration is greatest in the early winter when the unused nutrients from the autumn are flushed away. This declines later because of a limited time for interaction of the flowing water with the soil matrix. It is also high in the spring reflecting the application of manure and fertilizer (Armstrong and Burt, 1993). High nitrate concentration is indirectly toxic to humans, livestock, and damaging to industrial processes (Hayes and Greene, 1984; Canter, 1997; Scandor *et al.*, 2001) and constitutes a threat to both river and marine ecology (Burt *et al.*, 1993).

Nitrogen is lost from “pools” through: plant uptake, leaching, erosion, microbial immobilisation, bush burning, volatilisation and denitrification. Clemente *et al.* (2003) observed nitrate reduction during transport along a riparian transect, a finding that supported previous research (Peterjohn and Correll, 1986; Daniels and Gilliam, 1996; Hodge *et al.*, 2000; Lyons *et al.*, 2000; Asadi *et al.*, 2002) This reduction occurred due to mixing of water from hillslope flow and groundwater (confined and unconfined aquifers), nitrate-nitrogen uptake by vegetation and microorganisms, and microbial denitrification. Microbial denitrification describes the conversion of nitrogen in an oxidised form (e.g. nitrate) into a gaseous form (N_2O) through the action of denitrifying bacteria in an anaerobic environment. Thus nitrogen is returned into the atmosphere (figure 2.2).

Phosphorus – forms, sources and sinks in catchment system

Sources of phosphorus can be broadly classified as inorganic and organic as shown in its cycle (figure 2.3). Rock phosphate and fertilizers constitute the inorganic sources. The weathering of rock phosphate, an important natural inorganic source could not meet the global demand for P, that is required to support the vigorous crop production that matches the food and raw materials. Also, rock phosphate is not ubiquitous and therefore there is a need for other sources. The discovery of inorganic fertilizer and its adoption has been one of the major approaches directed at meeting this need, leading to the accumulation of P in the soil due to the adsorption properties of the soil matrix when it comes to the reactive forms of P. Thus P can be found in soil as occluded P in the mineral lattice and can also be held by calcium (Ca-P), aluminium (Al-P) and iron (Fe-P) at soil exchange sites. Plants can take up nutrients from the soil and their products are in turn used by animals and humans alike. The wastes and remains of these animals, together with crops, stalks and wastes from plants constitute the organic P in the soil P “pool” when decomposed by microorganisms. In a broader sense this comprises manure, dung and urine from grazing animals, crop litter and debris, wastewater bio solids and the microbial mineralisation of organic matter and microbial biomass (figure 2.3). Phosphorus is also linked to point sources such as sewage effluent, farmyard manure disposal and other landfill sites. The relative contribution of point or diffuse sources of P has been found to be important in the understanding of the differences among TP fluxes into individual rivers (Walling *et al.*, 2001b; Ballantine *et al.*, 2008). Point sources affect the TP loadings in catchments that have a significant urban, sewage and industrial inputs compared with rural settlements downstream of the river reaches (Owens *et al.*, 2001; Owens and Walling, 2002; Demars and Harper, 2005). PP is partitioned into inorganic and organic fractions; the increased inorganic fraction has been linked to intensive agricultural activities while the increased organic fraction is related to the presence of organically rich plant materials (McComb *et al.*, 1998). The latter was also associated with catchments having a higher percentage of moorland or unimproved upland pasture (Russell *et al.*, 1998b).

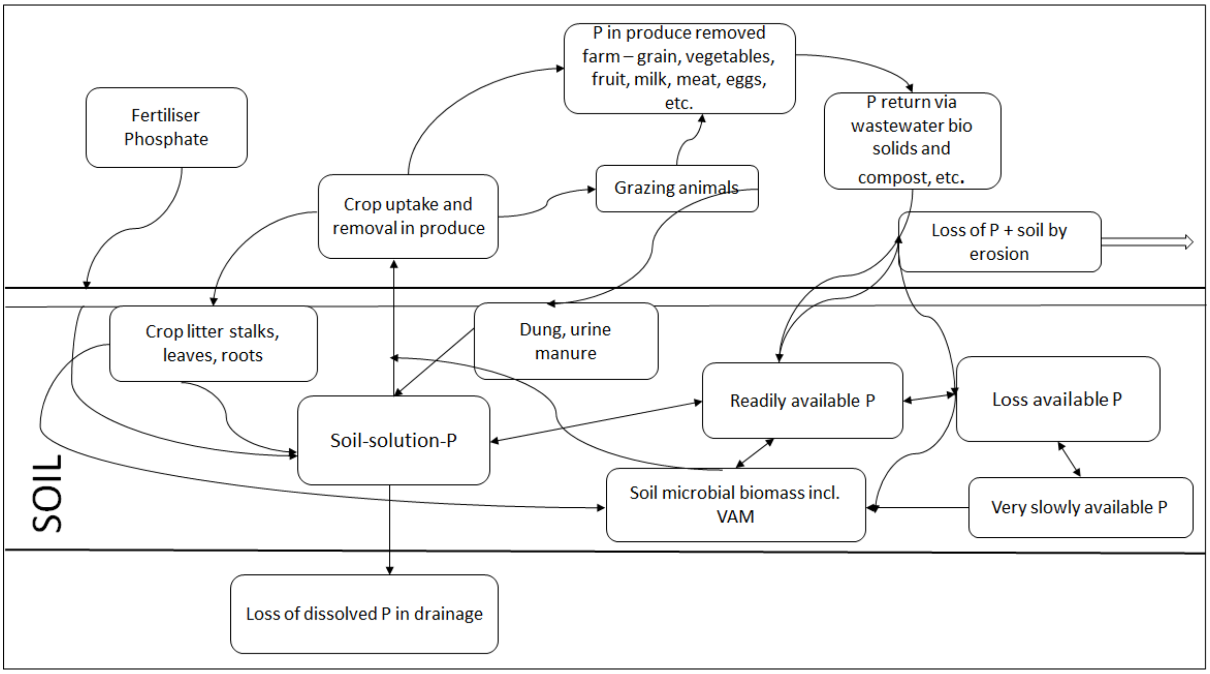


Figure 2.3 Phosphorus cycle (adapted from www.defra.gov.uk) (Defra, 2012)

In-stream water processes also act as sinks and sources of P (figure 2.4). Discharges from upstream represent an external source of P (A) into this aquatic system (DP and/or PP). River flows in the early stages of storm events result in an increase in the amount of P due to the dissolution- (DP) and suspension- (PP) of pre-existing P stored in the bed sediments. Other sources of in-stream P are mineralised dead aquatic plants and microbial biomass (B - G). Conversely, bed sediment (B, D), living aquatic plants and microbes (E) are also potential sinks reflecting a complex system of in-stream P dynamics (Baldwin *et al.*, 2002).

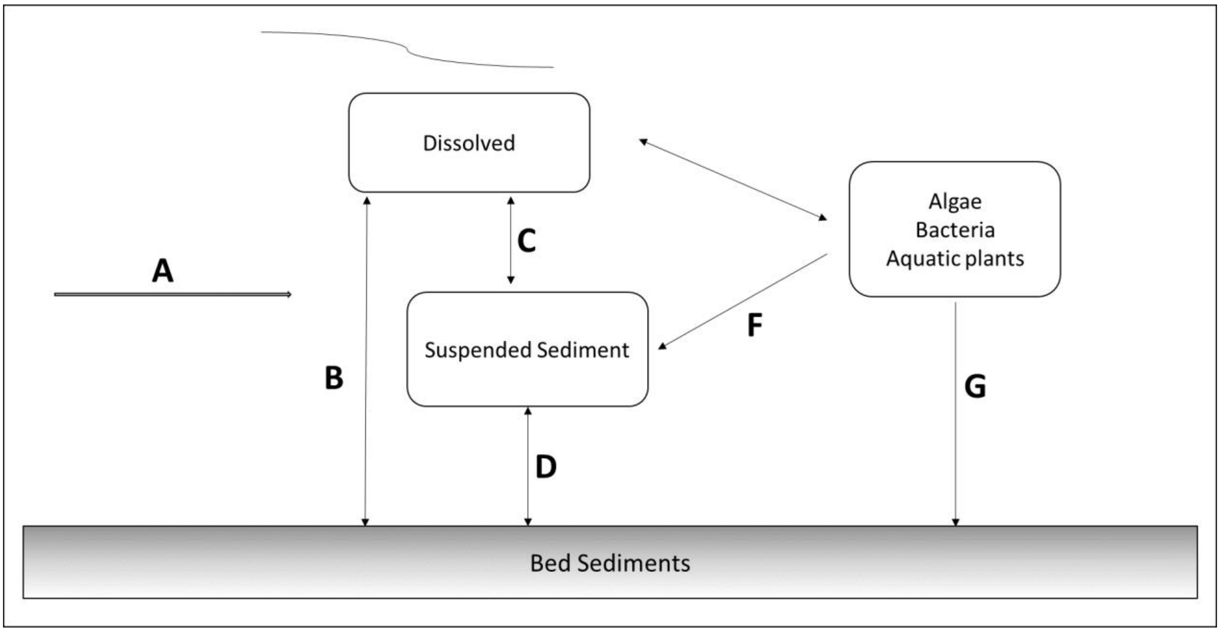


Figure 2.4 A conceptual framework of the P cycle in aquatic systems (Barber, 2008)

The available P is found in the soil solution and is either taken up by plants or eroded away as reactive P, a component of the total P (TP) in the fluvial system. A fraction of the P held at the soil exchange sites is also lost from the soil mass as colloids and/or sediment-associated P, or particulate P (PP) due to erosive forces. Unlike nitrate, soil erosion is a major pathway of P loss in aquatic systems (40 – 88%) whilst there are comparatively minor losses through sub-surface runoff (12 – 60%) (Ulén *et al.*, 2007). The P lost through erosion is highest where there are areas of high P concentration in the catchment coinciding with areas of highest runoff generation, and these are delineated as critical source areas (CSA). This situation is capable of leading to high P concentrations in the river resulting in a process termed eutrophication that compromises the good ecological status of the aquatic and marine environments. This underscores the need to identify these CSAs for PP in addition to all the other forms of P. Having adequate data about these sources combined with their interactions with soil and sediment, and their transport at different catchment scales should provide the baseline information for the necessary mitigation measures, including erosion and runoff management. The output of such studies should also provide adequate technical information for policy makers who are concerned with the management of river basins at large. The UK Demonstration

Test Catchments project is currently working with the UK Government's Department for Environment, Food and Rural Affairs (DEFRA) in this regard.

Nutrients and the catchment ecosystem – European and UK policy implication

Excess nitrogen can be toxic to an ecosystem. Nitrate ingestion has been linked to gastric cancer (Scandor *et al.*, 2001) and nitrite is indirectly toxic to humans causing a form of oxygen starvation that in extreme cases leads to death. Excessive levels of nitrate in groundwater also pose problems for livestock, crops, industrial processes and river ecology (Hayes and Greene, 1984; Canter, 1997). A case of nitrogen pollution occurred when ammonium sulphate was permitted to discharge into a ditch which led to a small tributary of the River Eden, Ploughlands Beck. This incident caused the largest recorded fish kill in one of the most pristine rivers in England (Shaw *et al.*, 2011). There are a number of major directives put in place by the UK to control nitrogen levels in water bodies and drinking water supplies. These include the Drinking Water Directive (98/83/EFC), Groundwater Directive (80/68/EFC), and the Nitrates Directive. The Drinking Water Directive sets a permissible range of nitrate concentrations from 25 to 50 mg NO_3 l^{-1} with the latter as the maximum admissible concentration. It is in agreement with the 1993 WHO guidelines (Defra, 2012). The Groundwater Directive deals with point sources while the Nitrate Directive (91/676/EC) focuses on pollution from agricultural activities. The Nitrate Directive applies only to designated Nitrate Vulnerable Zones (NVZs). NVZs are identified as all known areas of land draining into nitrate polluted waters, which are identified through monitoring data (Osborne and Cook, 1997; Jackson *et al.*, 2008). These three Directives operate in harmony with the European Commission Water Framework Directive (WFD, 2000/60/EC).

The threats to aquatic systems from P constitute the encouragement of algal blooms, loss of aesthetic value(s), and eutrophication amongst others. To address these threats, the UK, as a signatory to the WFD, came up with some initiatives. One is the setting of a drinking water standard for phosphorus which must not exceed 2200 µg P l^{-1} (UK Water Supply [Water Quality] Regulations 1989, Shaw *et al.* (2011)). DEFRA has been in the vanguard of sponsoring projects (e.g. DTC, Beven *et al.* (2005)) to understand the mechanisms governing P pollution in an attempt to tackle the problem. In Beven *et al.* (2005) the issue of P solubilisation as it relates to its delivery is described as being plagued with uncertainty, yet it is very vital in policy making and also informed the development and operation of mitigation measures. This uncertainty has been linked to a difficulty in arriving at generally acceptable routine measurements of the relevant fraction(s) of P and the challenge of only having insufficient dissolved P and PP data to allow for a probabilistic estimate of the uncertainty. The prospect of using the previously acquired experience to represent the P delivery ratio in another catchment, or even the same catchment under different circumstances may still not remove the uncertainty because of limited information availability. Furthermore the potential number of coefficients that will be required to represent certain catchment attributes such as different management practices, flow pathways and landscape variables, is very large. The challenges to the latter option are that the source term and the assignments to different flow pathways will be left out. These challenges lead these authors (Beven *et al.*, 2005) to suggest site-specific measurements to estimate P loads under different management strategies whenever the need arises. These findings call for more studies to provide more data to aid the understanding of mechanisms of nitrogen losses, P solubilisation, sediment detachment and delivery to the river, in order to adequately inform the policy makers in their drive to have rivers of good quality and ecological status as stated in the WFD.

2.2.4 Catchment characteristics and nutrient dynamics

Land use and management

Mills *et al.* (2008) investigated the spatial variability in catchment characteristics relating to suspended sediment yield (SSY) in the Upper Eden catchment, and reported a weak positive relationship ($R^2 = 0.2$) between the SSY and the percentage of managed grassland in the catchment which. They observed a higher stock density pattern in the pasture of this catchment and in a field survey they also discovered significantly higher densities of channel bank poaching, a sediment source in the grazed area. This and larger proportions of bare soil near the channel due to livestock trampling led them to conclude that land use practices might affect sediment supply and transport rates in this catchment. Ammonium-nitrogen transport and PP that are likely to be adsorbed to this sediment are expected to share the same fate in this catchment. Ballantine *et al.* (2008) attributed significant increases in TP content in the lower reaches of the Frome and Piddle catchments to intensive agricultural activities which tend to increase in the downstream direction. There were low TP concentrations in the Bovington stream, in the Frome catchment, where the heathlands are used for military training and agricultural activity was primarily absent. Therefore it is not enough to consider the land use alone as guide to locating sampling sites for a study, but the influence of topography on the spatial pattern of agricultural intensity within and between catchments should also be considered. Many studies have implicated land use as the determinant of nitrate pollution. In their historical study covering 1868 – 2008 Howden *et al.* (2010) indicated persistently high nitrate concentrations since World War II that have defied all interventions including those based on the EU Nitrate Directive (91/676). They attributed the stepped increase not just to an increase in fertilizer input but rather long-term processes following the changes in land use, because both the release of soil nitrogen and groundwater transport operate at decadal timescales. Activities such as the conversion of grassland or forest to arable land, drainage (which prevents denitrification) etc., enhance microbial mineralisation making nitrogen potentially available for movement into the water bodies. Land use plays a significant role in soil properties, another important catchment characteristic that influences nutrient loading rates.

Soil and its properties

Soil mineral matter, organic matter, and its biological, physical and chemical properties (e.g. soil solution) all represent a major control of nutrient and sediment (together with its sorbed nutrients) production, transport and delivery. For instance soil organic matter, soil structure and texture, govern soil solution chemistry/solubilisation (which depend on soil cation exchange capacity, CEC, or nutrient retention capacity), sediment detachment and its transportability across the catchment. Jackson *et al.* (2008) identified the need to monitor data on topsoil nitrogen speciation and leaching for further data for the INCA-Chalk model, used in a nitrate study of a chalk catchment.

Mills *et al.* (2008) identified the presence of a large proportion of fine materials in the flood plain as a potential source of SSY. Ballantine *et al.* (2008) observed a positive correlation between the specific surface area (SSA) and TP of suspended sediment samples in the Frome catchment. Beven *et al.* (2005) reasoned that P delivery depends on a good estimation of its mobilisation which in turn depends on soil properties, soil moisture condition, vegetation cover, rainfall intensity, surface and sub-surface flow rates. Soil types are known to have their unique properties which play a significant role in their behaviour in relation to the natural environment. Ballantine *et al.* (2008) in their work at the Upper Tern catchment, that is underlain by sandstones covered by sandy soil and subjected to intensive agriculture, observed an elevated level of P. They explained that sandy soils while easily worked and free draining are known to have little structure making them easily mobilised and transported to the river channel. However, there was high TP concentration in the Frome and Piddle catchments that are mostly underlain by chalk which tends to cause high binding capacities on the soil above it. Soil and its related properties are often closely related to the underlying geology. It is well known that the parent material formed in-situ is one of the factors behind soil formation.

Geology

Some authors have established the influence of geology on the nutrient content and sediment-associated P (e.g. Dillon and Kirchner (1975)). Walling *et al.* (2001) reported the influence of geology on the TP and AAP attached to fluvial, suspended sediments in UK rivers. TP levels were reported to be significantly different between catchments of varying geology (Ankers *et al.*, 2003) in south west England while (Ballantine *et al.*, 2008) observed similar variations between the Upper Tern catchment underlain with sandstone and the Frome/ and Piddle catchments that are underlain with chalk. The underlying geology can also play a significant role in nitrate behaviour in a catchment. Many researchers agreed that chalk, a common aquifer and landscape type over England and indeed northwest Europe, can retard decades of prior nitrate loading within its deep unsaturated zones. This has been viewed to render WFD timeline unrealistic for areas underlain by chalk (Foster, 1993; Mathias *et al.*, 2006; Jackson *et al.*, 2007; Jackson *et al.*, 2007, 2008). Other studies have reported a layered bedrock control on groundwater discharge which divided the subsurface discharge into shallow and deep components. The shallow, NO_3 contaminated (i.e. rich) groundwater layer contributed more until the NO_3 contaminated (i.e. less rich) deeper layer dominated at the higher non-storm flows and even at storm flows (Pionke *et al.*, 1988; Gburek and Urban, 1990; Schnabel *et al.*, 1993; Pionke *et al.*, 1996). Other structural influences on NO_3 concentration were observed in its decrease with depth from soil water at the top of the profile into the deep aquifer underlying it (Schnabel *et al.* (1993)). The geology of a catchment indirectly controls its hillslope routing through its influence on its topography (e.g. Beven (1986)).

Topography

The role played in sediment and nutrient transport coupling by a hillslope varies with catchments. “Hillslope coupling” describes the combined effect of overland flow, vertical flow, sub-surface runoff and groundwater flow in a direction controlled by the slope that produces a net discharge to the streams or river draining the catchment. Although Soulsby *et al.* (2006) reported that the soil hydrological processes control the hydrologic responses of the Scottish Feshie catchment they mentioned the possibility of larger scale hillslope flow routing driving the hydrological functioning of other catchments having different soil units and climatic conditions. Mills *et al.* (2008) observed a weak negative relationship ($R^2 = 0.3$) between the SSY and the percentage of hillslope-to-channel coupling in the Eden catchment. This will affect nutrient fluxes as discharge and sediment are directly involved in nutrient export to rivers. The hillslope flow is enhanced by the frequency and magnitude of hydrological events.

Hydrological events

An analysis of both event and seasonal precipitation totals and the attendant flows into the river are crucial for evaluating nutrient loadings into stream channels. (Beven *et al.*, 2005) stressed the role of event frequency and magnitude in the delivery of nutrients to stream channels. They reasoned that this might be an important controlling factor for the delivery of both the dissolved and particulate P. The hydrological event controls both flows and the river regime (see Section 2.1.1. above).

2.3 Introduction to Spatial Scaling

A theory that allows the information from a point scale to be applied at a larger scale remains an unresolved issue in hydrology. A temporary solution is often to linearly interpolate and approximate the findings of models that assume that the small scale theory can be used at a large scale (Shaw *et al.*, 2011). Yet it is well known that spatial and temporal heterogeneities are the case as the catchment scale increases. The varying behaviour of the catchment processes with scale is thus non-linear, and it is still a subject of scientific debate, a situation Blöschl back in 2001 rightly stated will be with us for another few years. Nonlinearity describes the dynamics or a rate and direction of the system response that is neither additive nor proportional in magnitude to the agent causing it. A non-linearity as it relates to some catchment processes has been reported.

Burkett *et al.* (2005) linked nonlinear behaviour in ecological phenomena (biological, geological and hydrological processes) to some threshold values. These values if exceeded by even small differences are capable of triggering rapid disproportionate changes. For instance, the nonlinear stream flow was described as a long term implication of permafrost melting when snowmelt occurring earlier (a reduction in snow pack by 50% resulting from a 4^0C rise in temperature) was modelled in the Loch Vale watershed (Baron *et al.*, 2000a). Although Baron *et al.* (2000b) explained that climate change is capable of ameliorating both eutrophication and the onset of acidification in aquatic systems, by switching the effect to terrestrial systems through the increase in biotic uptake as a result of an earlier spring there was a contrasting report of a nonlinear increase in nitrogen in an aquatic environment, when climate change may cause the snowpack to warm earlier.

An increase in emission of reactive nitrogen to the atmosphere, specifically ammonia and nitrogen oxides as was the case post – 1950 caused a major disruption of the global nitrogen cycle (Galloway *et al.*, 1995; Vitousek *et al.*, 1997). This could have far reaching effects on vulnerable environments such as rocky, mountainous basins. Though such an environment is generally considered as oligotrophic (an environment deprived of nutrients), a slight introduction of limited nutrients such as from atmospheric nitrogen deposition, can lead to a marked change (Baron *et al.*, 2000b). Elevated N deposition in forest areas can also display high foliar N, a low C:N ratio, a low lignin:N ratio, and the high potential for net (positive) mineralisation rates (Rueth and Baron, 2002).

The application of fertilizer to soil is another contributor to inorganic nitrogen availability that can be lost to streams or lakes (Rueth *et al.*, 2003). These processes may result in eutrophication of the water body draining their basin and in many lakes could eventually lead to acidification (Baron *et al.*, 2000b; Fenn *et al.*, 2003). The crossover between eutrophication and acidification has been described as another good example of nonlinear dynamics brought about by human-initiated N deposition

(Stoddard, 1994). The acidification of a medium (e.g. catchment and its river) could be capable of altering its nutrient dynamics, an issue to consider when making inferences on the nutrient behaviour of such a medium.

Phosphorus is another nutrient causing eutrophication whereby if the concept of nonlinearity is not considered in its modelling, erroneous conclusions may be drawn which may misinform decision makers. Carpenter *et al.* (1999) in their analyses of management policies for lacustrine ecosystems subject to alternate states, thresholds and irreversible changes, focused on the problem of lake eutrophication due to excessive P inputs and discovered that analyses based on deterministic lake dynamics usually led to higher allowable P input rates compared with analyses that allowed for various nonlinear relationships, uncertainties and interactions. Consequently, these authors suggested that P input rates should be reduced below the levels derived from traditional deterministic models. Burkett *et al.* (2005) argued that a better understanding of linear and nonlinear ecosystem processes and patterns will improve science-based management of natural resources. They therefore sought advancements in the ability to simulate nonlinear ecosystem dynamics in order to adequately support adaptive management, and to provide strategies for mitigation of- and adaption to- the interactive effects of climate change or human activities on biological systems. Thus adequate research information that provides an understanding of the nonlinear behaviour of stream flow processes and river discharges, nutrient and sediment yields as scale increases, are *sine qua non* to an effective river basin management strategy that targets achieving a “good ecological status” of water.

Bloschl and Sivapalan (1995) described scaling as related to a characteristic area or a length of time, that defines a system or observation or a model. Scaling thus refers to a rough indication of an order of magnitude rather than an accurate figure. There are several terms linked to this subject: scale invariance, upscaling/data aggregation, downscaling/data disaggregation and regionalisation. According to Bloschl (2001), scale invariance occurs when processes behave similarly at small and large scales. Upscaling refers to transferring information from a given scale to a larger scale, whereas downscaling refers to transferring information from larger to a smaller scale. Regionalization involves the transfer of information from one catchment (location) to another (Gupta *et al.*, 1986; Bloschl and Sivapalan, 1995; Kleeberg, 1992).

The concept of scale has been further subdivided into process, observation and modelling scales. Process scale is defined as the scale that natural phenomena exhibits and is beyond our control (e.g. a cycle for snowmelt, a return period for flooding). An observation scale is described as a scale relating to the necessity of a finite number of samples and this dictates the type of instrumentation to be employed (e.g. spatio-temporal extent of a dataset; spacing between samples; resolution of a dataset). Model scale mainly refers to hydrological modelling and this scale is parametised in the model.

The common spatial model scales are: the local scale (1 m^2); the hillslope scale/reach (100 m^2); the catchment scale (10 km^2) and the regional scale (1000 km^2). In terms of time, typical model scales are: A short rainstorm event (1 hour), the event scale (1 day); the seasonal scale (1 year) and the long-term scale (100 year), (Dooge, 1982; Dooge, 1986; Bloschl and Sivapalan, 1995). The CHASM project (its instrumentation in the Eden catchment was used for this research) uses a modelling scale designated thus: the patch (~50 m^2); the microscale (~1 Km^2); the miniscale (~10 Km^2) and the mesoscale (~ 100 Km^2) (O'Connell *et al.*, 2002; Wilkinson, 2008). Efforts are also being made to draw inferences at global scale using remote sensing technology. Therefore, scaling in hydrology involves observations at point or local scale to large catchment scale which forms the practical basis for most hydrological applications.

Point scale concepts characterise many measurement techniques and parameter estimation techniques in hydrology and hydrological modelling respectively. For example, rainfall and soil moisture are measured at a point scale while hydraulic conductivities and cross-section measurements of the roughness coefficient in rivers represent some hydrological model parameters measured at a point or local scale (Shaw *et al.*, 2011).

As previously mentioned, it is the information obtained at the catchment scale that is preferred for practical purposes. This is because the larger scale catchment captures all the variability, heterogeneity and complexity of the points within (Cammeraat, 2002). However, processes and properties at point scale (and small scales) are not only non-linear but merge into each other as scale increases (Cammeraat, 2002; Clark *et al.*, 2009). For instance macroporosity resulting from fauna activities would likely evolve into improved drainage and subsurface erosion which can in turn give rise to sediment flux and channel processes that dictate catchment development (figure 2.5).

It was explained further that biological processes dominated at the lower levels but graduated into abiotic processes at large scales. Building on this concept and in attempt to address the debate surrounding scale issues, Cammeraat (2002) applied hierarchy theory and response units as an approach towards scale-transcending environmental studies on degradation and geomorphological development. Using hierarchy theory, a specific scale of study was selected and finer-scale processes are incorporated at this central level of scale enabling the emergence of patterns derived from the finer-scale processes. The broader scale, which he later used as a response unit, constrained the development of patterns at the smaller scale by prescribing the boundary conditions. The author described the response units as several land units that have a characteristic response with respect to hydrological and geomorphological processes. It is upon these response units that the watershed was built. In identifying such units key indicators that reflect dominant processes within a response unit should be selected.

These could be vegetation structure or spatial patterns in biological activity, differences in soil characteristics, or others, depending on the geo-ecosystem (Imeson and Cammeraat, 1999) or depending on the landscape processes to be analysed. In a hydrological sense, the dominant processes concept (DCP) mentioned here is what Bloschl (2001) described as the process that controls hydrological response in an environment, and he linked it to a similarity approach (scale invariance) defined earlier.

Lazarotto *et al.* (2006) used this hydrological response unit (HRU) concept in a study carried out in the humid region of Switzerland and noted that discharge data from seven small agricultural catchments was strongly influenced by the areal fractions of well and poorly drained soils. The Hydrology of Soil Type (HOST), a soil classification system specifically developed for hydrological studies in which soils are grouped into classes based on the soil physical properties and underlying geology, linked to some hydrological variables (e.g. base flow index), that are comparatively easy to apply at catchment scale, has been used in a similar context.

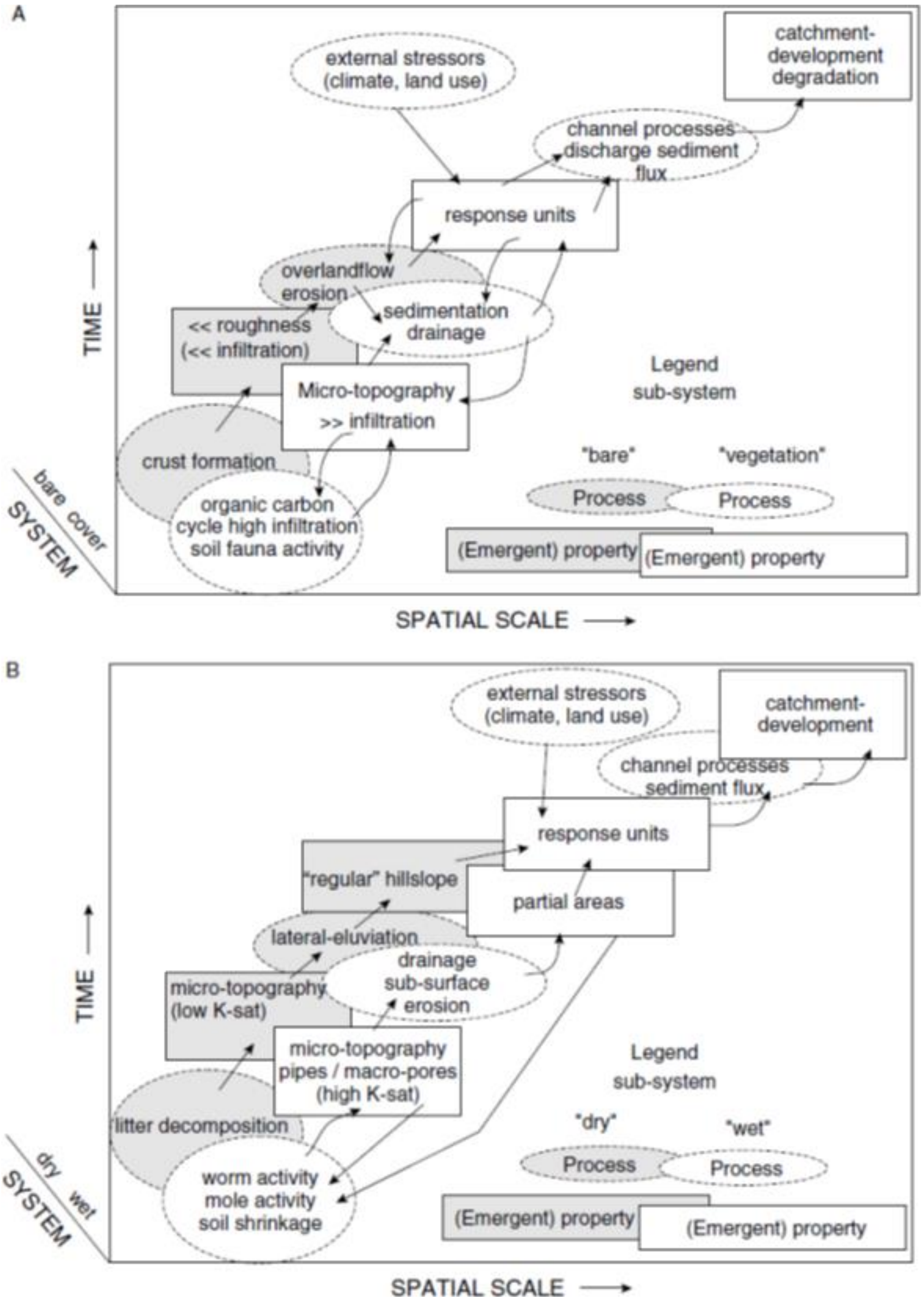


Figure 2.5 Conceptual framework showing process relationships between different scales for the Campos de Panes area (A) and the Schrondweilerbaach area (B) (Cammeraat, 2002)

This has been used in some studies in a manner similar to the DCP and HRU to explain the hydrological functioning of a nested catchment (Soulsby *et al.*, 2006).

2.4 Catchment Datasets

Catchment data sets refer to databases/sources and other data acquisitions/holdings that represent the catchment characteristics, and are capable of providing an explanation for the observed patterns in the properties or processes being investigated in the catchment. These datasets can be broadly categorised into hydrometeorological and landscape classification data. Basically the former pertain to precipitation and evaporation and discharge data and are acquired through hydrometeorological networks in the study area. Such data can also be obtained through the appropriate regional and central agencies or institutions having responsibility over the measurement stations (e.g. EA, Meteorological (Met.) Office etc.). There are two UK national programmes that have the infrastructure that also provide data within their domains that are relevant to the current research. These are CHASM and DTC (defined above) which both have an Eden catchment-based component among other locations. CHASM used a multi-scale nested catchment approach, providing a context for studying spatial scales, while the DTC project operates at a smaller scale (2 – 10 km^2) and is investigating cost effective measures to curtail pollution from diffuse sources to ensure good water quality, whilst food security from the agricultural production activities is not compromised. DTC thus provides a platform for the understanding of the processes of nutrient transfer into the rivers. Combining the spatial scale studies using CHASM initiatives and DTC offers holistic and unusual opportunities for performing (i) a detailed and spatial scale study; understanding of (ii) the mechanism(s) governing nutrient transfer within a catchment and; (iii) the associated processes at a larger spatial scale. For landscape classification, data are required on the topography, land use, geology and soil. Topographical data are supplied in the form of a digital elevation model (DEM) and the DEM data are a raster grid of elevation values. Elevation data can be sourced from EDINA, land use from the Centre for Ecology and Hydrology (CEH), geology from the British Geological Survey (BGS) and soil from the Macaulay Land Use Research Institute (MLURI). These sources have been used in the characterisation of the Upper Eden catchment by a Doctoral study that used a processed based approach to investigate spatial variability and scale dependency of sediment yield in this catchment (Mills, 2009), and there have been a number of Doctoral and other studies that described the Eden landscape (Younger and Milne, 1997; Walsh, 2004; Wilkinson, 2008; Mills, 2009; Barber, 2013). Other important Eden catchment characteristics described include its climate (Office, 2009) and the river characteristics (Mills, 2009b; CEH, 2014). These characteristics are vital to the understanding of catchment behaviour. For instance, experience elsewhere has revealed that topography can drive stream flow processes (e.g. overland flow), land use can influence nitrate concentration in rivers (Howden *et al.*, 2010), geology is capable of moderating groundwater flow (Pionke *et al.*, 1996) and chalk aquifers can store and influence nitrate concentrations in groundwater (Ballantine *et al.*, 2008). Soil can also influence hydrological functioning of the catchment. For instance, landscape controls particularly catchment soil cover influenced the catchment hydrological functioning in the Feshie catchment, Scotland. The soil cover was mapped using the Hydrology of Soil Type (HOST) digital base (Soulsby *et al.*, 2006). Based on the links between discharge, sediment and nutrient transport, soil has the potential to play a significant role in nutrient transport in a catchment.

Although many soil classifications exist some are more widely used than others: USDA Soil Taxonomy, FAO/UNESCO legend, ORSTROM (commonly used in France and in Francophone Africa) among other classification systems (FAO, 1992). In the United Kingdom, there is also the soil classification system of England and Wales developed by Cranfield University, and some specific classifications for engineering and hydrological purposes. The first attempt to classify soils according to their hydrological response was the Winter Rainfall Acceptance Potential (WRAP) scheme developed for the Flood Studies Report (FSR, NERC, 1975). When the need for its second revision arose the Soil Survey of England, now the Soil Survey and Land Research Centre (SSLRC) and the Soil Survey of Scotland, based at the MLURI completed the national reconnaissance mapping of soils at 1: 250,000 and used the large hydrological databases held by the Institute of Hydrology (IH) for the definition of the classes that constitute the HOST.

According to these authors the HOST classification was developed, at the soil mapping resolution mentioned above, by primarily using soil physical databases related to- and expressed as- catchment scale hydrological variables particularly the base flow index (BFI) and standard percentage runoff (SPR). HOST has 29 classes in all and its computer-based data set (on a 1 km grid that covers the whole of UK and available for lease) is capable of greatly speeding up the process of abstracting these classes for catchments or sites of interests (Boorman *et al.*, 1995). Also a map of BFI can be sourced from EDINA. As briefly mentioned earlier this has been used for some hydrological studies in the Feshie (Soulsby *et al.*, 2006) and Dee catchments (Tetzlaff and Soulsby, 2008) in Scotland and it should be a useful tool in relating nutrient yield to soil properties in this current research in the Eden catchment.

2.5 Catchment Hydrometry

This section describes the measurement of the hydrological variables, a number of which have been mentioned above. Although the details of the hydrometric network specific to this research will be discussed under the methodology, an overview and a brief mention of the general considerations in hydrometric network design as they relate to this research is presented below. The measurements are broadly divided into those that measure water quantity and quality. The variables most considered in water quantity measurements are precipitation, evaporation, overland flow, subsurface flow, river flow and groundwater. Variables often considered in water quality measurement include nutrients, sediment, contaminants from farming, mine sites and other industrial activities, etc. This discussion focuses on nutrient and sediment measurements at the catchment scale.

A network approach has long been adopted in hydrometric designs for effective measurement and it takes some issues into consideration. For instance, there is the need to consider the physical features (land characteristics including the climate) of the area where the hydrometric network is to be installed. Information about the existing stations and data is equally vital, and this brings in the use of the topographical map which serves another purpose in being used for the plotting of the locations of the new stations. Another is the need for a budgeting and cost-benefit evaluation of the project while the purpose of the research infrastructure is kept in perspective (Shaw *et al.*, 2011). This purpose could be a need for studies or information on heterogeneity/variability of catchment physical characteristics and response, that are relevant to sustainable water resources management, scale issues etc.

A key issue in hydrology which currently influences hydrometric network design is the scale concept. There are various scales in hydrology (see section 2.2) but most catchment experimentation has been largely confined to a scale less than 10 km^2. The application of the findings derived from such experiments and subsequent models developed from such hydrological understanding are limited, as only some of their aspects can be transferred to larger scales and are difficult to extrapolate. A large scale research provides a framework that incorporates anthropogenic influences (e.g. abstractions, socioeconomic activities), the fate of pollutants, overall water cycle functioning and the improvement of the predictive capacity of models by reducing their uncertainties (O'Connell *et al.*, 2002). In the UK, the CHASM programme instrumented four multi-scaled catchment hydrological experiments (with a nested structure up to a mesoscale, ~100 km^2) at different locations with varying physical characteristics. Mesoscale catchments represent a range of climatic conditions, physical characteristics and anthropogenic impacts. They play a key role in the functioning of larger basins, and are frequently the major sources of runoff for water supply. This initiative adopted a methodological framework that permits a coherent research that can infill the gaps associated with research at small scale (earlier itemised) including the reduction of uncertainties in modelling, extrapolation to other basins and the understanding of catchment behaviour under future climate conditions (O'Connell *et al.*, 2002).

The CHASM instrumentation, for instance, employed a Generic Experimental Design (GED) which at a range of scales involved an adaptive, staged approach to enhance the understanding and resolution of the significant spatial variations in catchment response (e.g. hydrological response). The approach to instrumentation entailed deploying mobile, permanent and staged instrumentation. The understanding of the hydrological response(s) arising from data obtained- and models developed- from this instrumentation led to the reclassification and redeployment of instruments to sample the unresolved variability. Along with the digital maps (of topography, soils, vegetation and geology), mobile instrumentation (an all-terrain vehicle for rapid field surveys) was used for land classification. The land units defined from this land classification aided the instrumentation in the microscale catchments (1 km^2) where the spatial variability in responses could be resolved. The instrumentation at this stage could be permanent (as it is the case with miniscale [10 km^2] and staged. The miniscale catchments were pooled together to form the mesoscale (100 km^2) in a nested structure. The permanent instrumentation includes river gauging stations with nested structure, observation boreholes and stream-aquifer interaction experiments, hydrometeorological stations and raingauges, hillslope instrumentation (soil moisture probes), suspended sediment and water quality monitoring equipment. Staged instrumentation comprises raingauges, multilevel piezometers, gypsum blocks and suction lysimeters. “Staged instrumentation”, in this sense, refers to a scheme in which after the variability in responses is resolved some instruments are retained while others are moved to another location, where the procedure is repeated again.

The DTC is another UK project that focuses on the reduction of diffuse agricultural pollution, the improvement of ecological status of freshwaters and the development of models based on this local understanding. DTC projects are at micro- (2 km^2) and mini- (10 km^2) scales. There are DTC projects within the UK including the Eden catchment component and there is emphasis on collaboration with many stakeholders. The Eden catchment component concentrates on the effects of livestock and mixed farming on diffuse pollution while the other two (in different locations) are concentrating on lowland mixed farming and arable farming respectively. Although located in the Eden catchment with links to both the EA and CHASM, the Eden DTC has its own unique instrumentation. There are high and low specification monitoring stations with telemetry that are capable of measuring and transmitting real time data (i.e. hydrological and water quality data) at a high resolution to an internal database located on a server at Newcastle University. There are also mobile water quality instruments that are also used to measure flow along with turbidity, and there are ISCO autosamplers. With this intensive instrumentation, it has been possible to obtain information that provides explanations for the mechanism of how nutrients enter the river. The combination of the DTC study with EA and CHASM projects (with large scale coverage, ~1000 km^2) provides an unusual study platform and is expected to result in an appreciable detailed understanding of the mechanisms controlling nutrients (with associated sediment) concentrations and yields in the Eden catchment.

2.6. Studies in Stream Nutrient Cycling using High Frequency Monitoring Approach

The occurrence of rapid changes in hydrochemical and ecological dynamics, and processes (e.g. in-stream biological processes) in water bodies necessitate the deployment of high frequency (HF) or continuous or *in-situ* monitoring equipment that can measure these processes at sub-daily timescales. Historically, high frequency or bank side monitoring include both manual and automated measurements. Although impractical in term of human and financial resources required, it is interesting that Schloefield *et al*., (2005) in Devon, southwest England and Neal *et al*., (2012b) in Plynlimon, mid-Wales conducted a sub-hourly discrete sampling campaign manually. Their research demonstrated complex diurnal patterns and contributed new ideas on temporal dynamics in nutrient content of these rivers. However, manual sample is plagued with an additional problem of sample instability apart from human and financial resources required. Therefore, the emergence of technology that can measure river hydrochemical and ecological properties appears promising.

Stream nutrient and water quality property are measured using a range of bank side or *in-situ* equipment. There are multi-parameter sondes (e.g. YSI 6600) and high-frequency nutrient monitors. Different types of *in-situ* nutrient monitor are available. Common ones are Systea Micromac C, the Hach Lange Phosphax Sigma, the Hach Lange Nitrax etc. It is possible to programme them on-site manually or remotely using a Meteor Burst system (Meteor Communications, 2011) and transmit measurements by the telemetry system which are accessed in real time through the web host. The YSI 6600, for instance, draws water sample from a flow cell that is in turn continuously fed using a peristaltic pump and measures *in situ* dissolved oxygen, pH, water temperature, conductivity, turbidity and chlorophyll concentration (YSI, 2007). The Micromac got its water through a black tubing (to exclude light and prevent algal growth) that pump the water from a flow cell. The equipment uses colourimetric technique to determine unfiltered total reactive phorphorus (TRP), by developing phospho-molybdate blue colour (Murphy and Riley, 1962), and also measures nitrite (NO_2) and NH_4 (Krom, 1980). The Hach Lange phosphax Sigma uses its sampling unit, the Sigmatax module, to draw sample from the flow cell and is determined colourimetricaly as TRP after persulphate digestion within the system

(Hach-Lange, 2002, 2003). An *in situ* filtration system, Hach Lange Filtrax, using 0.15 µm that enable the determination of the soluble P fractions (the soluble reactive phosphorus, SRP, and the total dissolved phosphorus, TDP) has also been reported (Wade *et al.*, 2012). Unlike others, the Hach Lange Nitratax probe is designed to be placed directly into a river and uses an ultra-violet (UV) absorption technique without any need for reagent (Hach Lange, 2007). Details of the setup of the instrumentation can be found in Wade *et al*. (2012). The ongoing Demonstration Test Catchment (DTC) uses these instruments and there are some research that has been carried out using these equipment.

Wade *et al.* (2012) deployed these research tools in lowland rivers below two contrasting catchments in the River Thames, southeast England: The rural Enborne catchment and an Urbanised catchment, The Cut. The equipment tested both the hydrochemical and ecological dynamics of the river. A good relationship between the data from the grab sample and the high frequency data were observed. The diurnal nutrient dynamics and biological processes, made possible by the HF data particularly during the low flow period, showed complex diurnal dynamics with two nutrient peaks coinciding with the peak period of domestic consumption. This is a pointer to Sewage Treatment Works (STWs) as a significant nutrient source in The Cut. Further work carried out in the Enborne catchment, a rural system, indicated diffuse source (agricultural fertilizers) as the predominance source of phosphorus and nitrogen while some degree of contribution was recorded from the STWs and septic tanks (Halliday *et al*., 2014). During period of low flow in River Enborne, TRP was STWs-driven while nitrate was controlled by groundwater and to a lesser extent STWs (Bowes *et al.*, 2015). Bowes *et al.*, (2015) observed a clockwise hysteresis for P following dry period and attributed this to a near channel source which involve contribution from the re-suspension of nutrients from bed sediment, field drains, septic tanks, animal faeces, soil/bank erosion and dead organic matter. Nitrate response was complex. Elsewhere in the River Hafren, Plynlimon, Wales, Halliday *et al.*, (2013) also observed prevalence of different processes controlling the complex diurnal nitrate dynamics in the upper and lower reaches/subcatchments of the river. The diurnal dynamics in the Upper Hafren, a moorland, indicated the importance of instream biological processes that correspond with peak air temperatures. However, the diurnal signals at the downstream site were a composite type depicting the influence of advection, dispersion and soils nitrate processing under forest.

2.7. Hydrological Modelling

The inclusion of modelling in these projects is to broaden both the practical uses of the findings from this study and to further test the predictive capacity of the TOPCAT-NP model. A model is useful in simulating and predicting hydrological events and their consequences. It is an important tool that enables the transfer of findings among catchments. Modelling provides a simplified way of representing a natural system such as catchment hydrology and aids robust decision making. If supplied with the correct dataset, modelling is a quick and cost effective result-generating tool to guide end users on what to expect when various natural or management options are combined. In a similar manner, a good model supports the generalisation of findings obtained from experimentation. Unlike empirical models that are not built on process-based equations and lumped conceptual models having less spatial detail, physically based models incorporate detailed catchment hydrological process which can be critical to erosion and water quality evaluations.

Refsgaard and Knudsen (1996) identified two classical types of model: stochastic and deterministic (figure 2.6). There is also the joint stochastic – deterministic model type (figure 2.6). A stochastic model includes a minimum of one component of random character that is not explicit in the model input but only hidden or implicit. A typical stochastic model is generated from a time series analysis of a historical record and it is able to produce long hypothetical sequences of events having the same statistical properties as the historical record - a technique that is described as the Monte Carlo technique. Because of the absence of process descriptions (unlike the physically-based models) and its dependence primarily on data, classical stochastic simulation models are comparable to the empirical or “black box” models. For the deterministic model, two equal sets of input if run through the model under identical conditions will generate the same output. This category is subdivided into empirical, lumped conceptual and distributed physically-based models (figure 2.6), and these are described below. Basically, the joint stochastic – deterministic model combines a deterministic core (the lumped conceptual or the distributed physically-based type) within a stochastic framework. An example of this model type are state

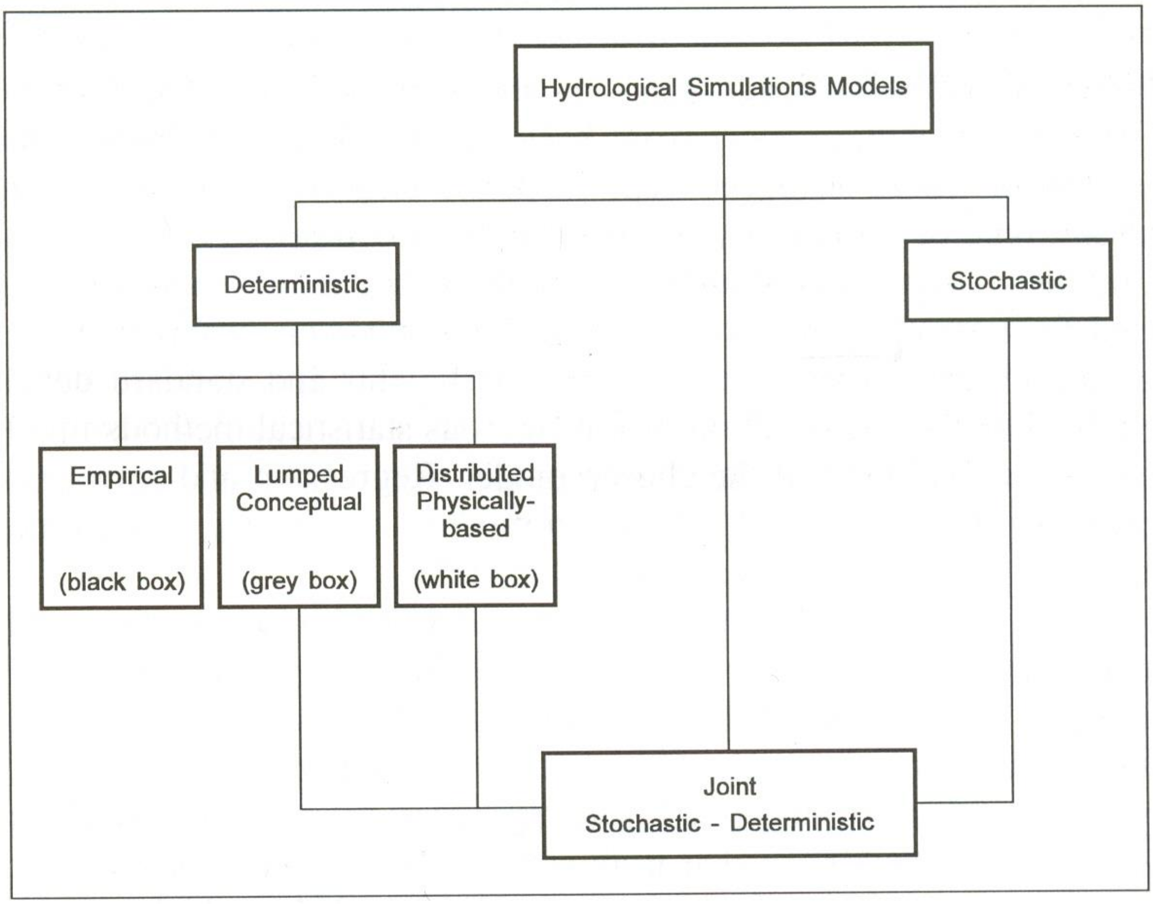


Figure 2.6 Classification of hydrological models according to process descriptions (Refsgaard and Knudsen, 1996)

space formulations and Kalman filtering techniques (Gelb, 1974). A modelling system based on this is the Sacramento modelling system (Georgakakos *et al.*, 1988) which combined Kalman filtering with a lumped, conceptual rainfall-runoff model. Another example is the SPDE-type model; spatial variability of parameter values and stochastic partial differential equations. This theory was incorporated into MIKE SHE, a distributed physically-based model, and applied to catchment scale problems (Sonnenborg *et al.*, 1994).

2.7.1. Deterministic models

In terms of areal description, deterministic models can be categorised into lumped and distributed models, and then they are subdivided into empirical, conceptual and physically-based models if described in terms of hydrological processes. Because conceptual and physically-based models are often associated with lumped and distributed models respectively, three divisions of deterministic models eventually emerged as shown in figure 2.6: empirical (“black box” or transfer function models), lumped conceptual (“grey box”) and distributed physically-based (“white box”) models. Brief descriptions of the first two divisions are below.

Empirical models employ mathematical equations developed from the analyses of concurrent input and output time series rather than process-based equations. There are three major divisions of the empirical methods used in these models namely:

(i) empirical hydrological methods (e.g. the unit hydrograph and Nash cascade model (Nash and Sutcliffe, 1970)),

(ii) statistically based methods including the regression and correlation models (e.g. Antecedent Precipitation Index, API, model, WMO, 1994) and,

(iii) the hydroinformatics based methods – e.g. artificial neural networks .

Lumped conceptual models are constructed based on the modeller’s understanding of the physical processes in their catchment but using averaged parameters and variables over the entire catchment, where the averaging takes place over larger units of space than the individual soil column. Thus it incorporates both a physical structure and equations with a semi-empirical approach. Examples are the Stanford Watershed modelling system, and TOPCAT model. Although lumped conceptual models represent an advance over empirical models in terms of sophistication and incorporation of physical processes in their construction (at the catchment scale) they include less detailed and precise descriptions of the hydrological processes in the catchment compared with physically-based distributed models. Physically-based models have been advocated to be more important for soil erosion and water quality modelling which requires a more detailed and physically correct simulation of water flows (Wicks and Bathurst, 1996; Birkinshaw and Ewen, 2000; Ewen *et al.*, 2000)

2.7.2. Distributed physically-based models

The description of this group of models entails two things: one is the subdivision of the computational domain into smaller parts (figure 2.7) both at the domain boundaries and also at internal points (e.g. a grid or discretisation point). The other part is the description of the flow response in the catchment using sets of equations representing flow of mass, momentum and energy. For instance, the flows of water

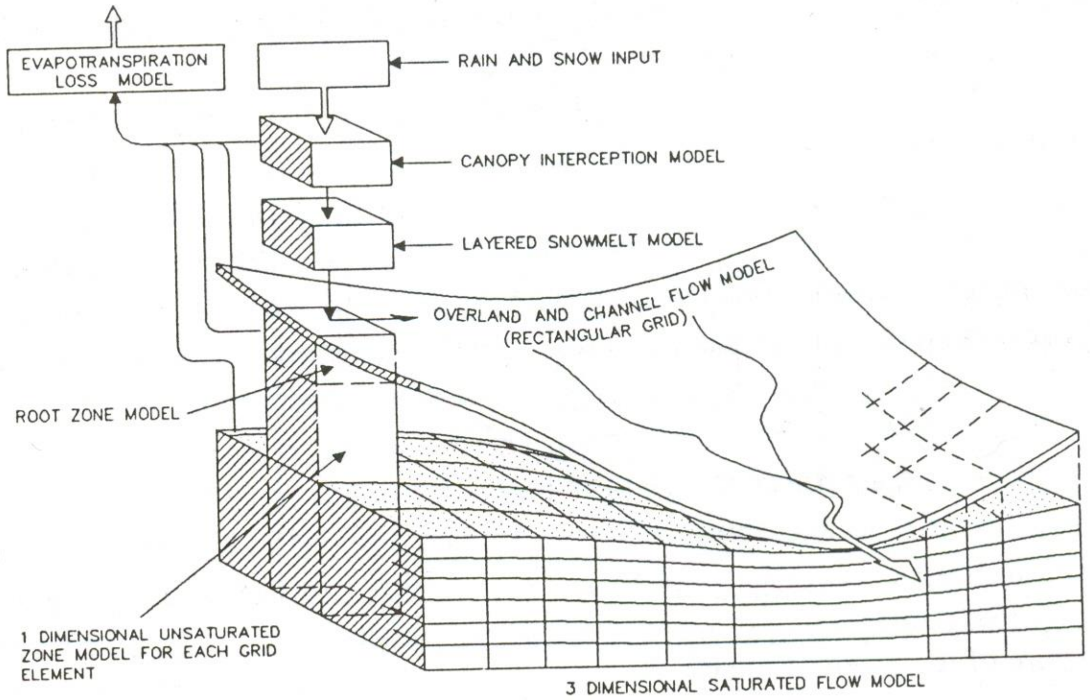


Figure 2.7 Schematic diagram of a catchment and the MIKE SHE quasi three-dimensional distributed physically-based model (DHI, 1993).

and energy are calculated from the continuum or partial differential equations: Saint Venant’s equations for overland and channel flows, Richard’s equation for unsaturated zone flow and Boussinesq’s equation for groundwater flow. Some of these models have also incorporated equations that allow the simulation and prediction of sediment and nutrient yields e.g. SHETRAN (Wicks and Bathurst, 1996; Birkinshaw and Ewen, 2000; Ewen *et al.*, 2000) and SWAT (Neitsch *et al.*, 2005; Gassman *et al.*, 2007; Pohlert *et al.*, 2007). SHETRAN has been extensively used in the UK, NZ and Chile, and SWAT is credited globally as an effective tool for assessing water resource and nonpoint-source pollution problems for a wide range of scales and environmental conditions.

Apart from SHETRAN and SWAT that are catchment models, there are other physically-based models such as ANSWERS (Beasley *et al.*, 1980), WEPP (Laflen *et al.*, 1991), LISEM (De Roo and Jetten, 1999) etc., all of which differ from one another in model features (e.g. simulation type, capability in terms of representation of erosion process, land use, output etc.). Physically-based models also interface with GIS packages, databases etc. (Lane *et al.*, 2006; Gassman *et al.*, 2007).

Despite the huge advantages that physically-based models possess, they are plagued with the problem of over parameterisation which may lead to equifinality. Equifinality results when the model structure is such that many representations of a catchment may be equally valid in terms of their ability to produce acceptable simulations of the available data (Beven, 2000).

Another group termed metamodels, based on physically-based models, which involves the reduction in the amount of parameters compared to the full models. Some of these are carved out of the 'bigger' physically-based model (e.g. TOPCAT - NP model from EPIC, MIRSED from WEPP) (Brazier *et al.*, 2001; Quinn *et al.*, 2007). They are also termed minimum information requirement (MIR) models. A MIR model is defined as the simplest model structure that address the need of policy maker while still ensuring that its parameter maintain physical significance (Quinn, 2004). They have less problem of over-parameterisation and equifinality. They are user friendly, time and cost effective. Table 2.1 gives a summary of some catchment nutrient models indicating the model type, the nutrient or water quality parameters they are capable of simulating, issues about their parameterisation and a general comment on their weakness and/or strength.

Apart from combining simple parameterisation using soil moisture stores to represent various hydrological pathways and mimicking process-based EPIC model to represent catchment nutrient loss processes, using TOPCAT-NP for this study also have the additional advantage of modeller co-operation. One of the modeller is in the Newcastle University and one of the lead researchers in the River Eden version of the DTC project. This agrees with the suggestions of Hesse *et al*. (2013) who stated that a closer co-operation between model user and modeller is one of the solutions to the problem of model failure. Therefore, this research will explore the use of TOPCAT-NP a MIR model, to transfer the insights gained from the current research to other catchments.

S/N	Model options	Type	Author(s)	Determinand simulated	Parameters	Remark
1.	SHETRAN, NITS,	PBSD	Birkinshaw & Ewen (2000)	NO_3, suspended sediment (SS)	Complex	Calibration is time Consuming
2.	Daisy/MIKE-SHE	PBSD	Styczen & Storm (1993,	NO_3	Complex	Detail parameterisation

S/N	Model options	Type	Author(s)	Determinand simulated	Parameters	Remark
			Refsgaard, 1999)			extensive calibration
3.	NMS	PBSD	Lunn *et al.*, (1996)	NO_3	Complex	Include SHETRAN etc.
4.	INCA	PB	Whitehead *et al.*, (1998, 2011), Wade *et al.* (2002, 2007b), Lazar *et al.*, (2010), Jackson-Blake *et al.*, 2015	NO_3, phosphorus, SS	Complex (>100)	Wide application but calibration is time Consuming
5.	PSYCHIC	PB	Davison *et al.*, (2008), Stromqvist *et al.*, (2008)	Phosphorus	Complex	Detail parameterisation extensive calibration
6.	SWAT	PBSD	Arnold *et al.*, (1998)	NO_3, phosphorus	Complex	Detail parameterisation extensive calibration
7.	Nutrient export coefficient	Black box	Johnes (1996), Jordan and Smith (2005)	NO_3, phosphorus	Less complex or simple	No physical sense i.e. empirical
8.	Load apportionment Model	Black box	Bowes *et al.* (2008)	NO_3, phosphorus	Less complex	Unike export coefficient, simple not needing GIS application. However, assumption of continuous point source and conservative P may not always hold, and masks diffuse source in point source-dominated catchment
9.	PIT	Black box	Heathwaite *et al.* (2003)	Phosphorus	Less complex or simple	No physical sense i.e. empirical
10.	SWIM	PB	Krysanova *et al.*, (1998), Hesse *et al.*, (2008, 2013)	NO_3, NH_4 and phosphorus	Intermediate to complex	Need more information on management etc. for improvement and wider applicability. Addition of nutrient retention translates to more complexity.

S/N	Model options	Type	Author(s)	Determinand simulated	Parameters	Remark
11.	EveNflow & PSYCHIC	CM/PB	Anthony *et al.* (2008) Davison *et al.* 2008, Silgram *et al.* (2008)	NO_3, phosphorus	Complex	Detail parameterisation extensive calibration
12.	Fuzzy National P Export model	Black Box	Jang (1993), Nasr and Bruen (2013)	Phosphorus	Less complex, parsimony	Better than ordinary empirical model but less physical sense
13.	Geospatial regression-kriging model	Black Box	Greene *et al.*, (2013)	Phosphorus with potential for water quality of river	Simple	Better than ordinary empirical model but less physical sense
14.	STONE	PB	Wolf et al., 2003	NO_3, phosphorus	Compound.	An hybrid model & unified a number of modelling efforts in the Netherland but often over-estimate N & P.
15.	MACRO	PB	Jarvis (1994), McGechan *et al.*, (2005)	Pesticides, phosphorus	Complex	Targeted livestock system & P transport through soil macropore. It is also weather driven. However, still require further testing at catchment scale
16.	SCIMAP	Black Box (risk-based)	Reaney *et al.* (2011), Milledge *et al.* (2012)	NO_3, phosphorus	Parsimonious	Less complex, improved model performance for N than P but perform less well in groundwater dominated catchment
17.	TOPCAT-NP	LCM (MIR)	Quinn *et al.* (2007)	NO_3, phosphorus	Simple	Hybrid model but simple user-friendly and time saving parametrization; with additional advantage of the co-operation of the modeller

Table 2.1 Catchment models capable of simulating nutrient and sediment transport

2.8. Summary

The literature reviewed reveals the link between nutrient delivery and hydrological processes and draws attention to other catchment characteristics and processes that control nutrient transfer in various catchments including soil, land use, atmospheric processes etc. Beven *et al.* (2005) in advancing the need for site specific measurement in addressing nutrient pollution problem, not only identified the variation in different catchment processes and responses, but also recognised the variation within the same catchment when circumstances change in such a catchment. The spatial heterogeneity in catchment characteristics adds another important dimension into the complexity and the call for site-specific measurements. Some researchers have identified downstream variations in nutrient transfer in some catchments while contrasting findings and limitations of the measurements or research to smaller catchments implies that the question of scale theory remains. The need for findings derived from studies at large scales by policy makers to address ecological challenges and key into regional policy in relation to water pollution problems have been reported. The use of existing data sets, field measurements and modelling tools as a means of extending findings and developing theories in new areas including the merit and demerit of the different model types was mentioned. National projects that are set up to address water pollution problem and scale issues including the one used in this research were highlighted.

Better understanding of nutrient transfer in spatial context through field measurement and modelling is critical to the understanding the mechanism of nutrient loss and proffering solutions to water pollution problems. The current research combines the unusual opportunities provided by the spatial scale study platform provided by CHASM and the high resolution nutrient data that is made possible through the DTC projects to gain an understanding of both the spatial pattern of nutrient losses in the Eden catchment, and also the processes leading to it. The advantage of the user-friendly nature of a MIR model, specifically the TOPCAT-NP, will be explored to aid the generalisation of the findings from this research

Chapter 3: Methodology

3.1. Introduction

In the sequence of studies in this nested sub-catchment, the spatial pattern in nutrient transport in the Eden catchment sub-catchment relates the spatial scale patterns to the catchment characteristics and hydrology. This chapter describes the deductive methodological approach used to achieve this. Broadly, there are two key themes explored: the field study and the application of a model to capture variations in the different sub-catchments as a basis for a more general application. The methodology for the field study is itself conducted under a combination of two national catchment management projects. These are the Catchment Hydrology and Sustainable Management (CHASM) and the Demonstration Test Catchment (DTC). Most UK field research is conducted at the small scale (<10 km^2) and transferring key findings to a larger scale, a scale at which policy makers prefer to make decisions on water resources management, is difficult because of nonlinearity. CHASM was set up to address this by providing a spatial scale dimension to this research. DTC provides water quality and quantity data at 15 minute time steps making it possible to investigate the detailed process of nutrient transfer in the catchment. The two projects share the Eden catchment as their study area and Newcastle University is one of the major stakeholders. The CHASM network allows the scale dependencies to be studied along the length of the river, from a 1.1 km^2 headwater catchment to the order of 1000 km^2. The DTC sites contrast land use and provide a basis for explaining the variations observed through the CHASM sites.

The description of the Eden catchment forms the first section of this chapter. This will be followed by the specific research approach deployed in each of the projects. For CHASM the following are considered: sampling location and associated gauging stations (i.e. the experimental design), data collection, handling and laboratory analysis. For the DTC project: gauging stations and data collection are considered; while the laboratory analyses conducted in the Environment Agency (EA) laboratories are also mentioned. The last section provides brief information on the model deployed.

3.2. Description of the Eden Catchment

The study area is the River Eden catchment located in Cumbria in northwest England (figure 3.1). The valley is 50 km in length and the catchment covers an area of around 2300 km^2. The landscape represents a northern England type having peat moorland in the Pennine headwaters progressing into pasture, woodland and arable land at lower elevations (Mills, 2009). It is home to a number of designated landscape including the Lake District and Yorkshire Dales National Parks, North Pennines the Solway Coast Areas of Outstanding Natural Beauty (AONB's), and the Hadrian's Wall World Heritage Site. In addition it also designated as a Special Area of Scientific Interest (SSSI)

The River Eden rises near the border of Cumbria and North Yorkshire at an altitude of 675 metres above sea level on Mallerstang Common. There is combination of two streams, Red Gill and Little Grain, forming Hell Gill Beck. This flows until Hell Gill Force downstream from which it forms the River Eden. The river continues its course from the south part to the north where it empties into its estuary in the Solway Firth at Carlisle. Apart from some invertebrate species that the river is known for, it also has a Special Area of Conservation status for white-clawed crayfish, Atlantic salmon etc. in addition to providing habitats for different breeding birds. The biological properties are completed with rich aquatic flora numbering 183 plant species (Eden Rivers Trust, 2014).

The basin characteristics such as topography, geology, vegetation, land use, climate and soil are described below.

3.2.1. Topography

The highest elevations of over 700 AOD are commonly found at the eastern and southern borders of the Eden catchment. Some of the sub-catchments studied such as Gais Gill, Ravenstonedale and Smardale are the closest to the southern border. The elevation drops towards the centre of the catchment where other sub-catchments are located. The lowland topography and gentler gradients extend all the way through Temple Sowerby to and Great Corby (figure 3.2).

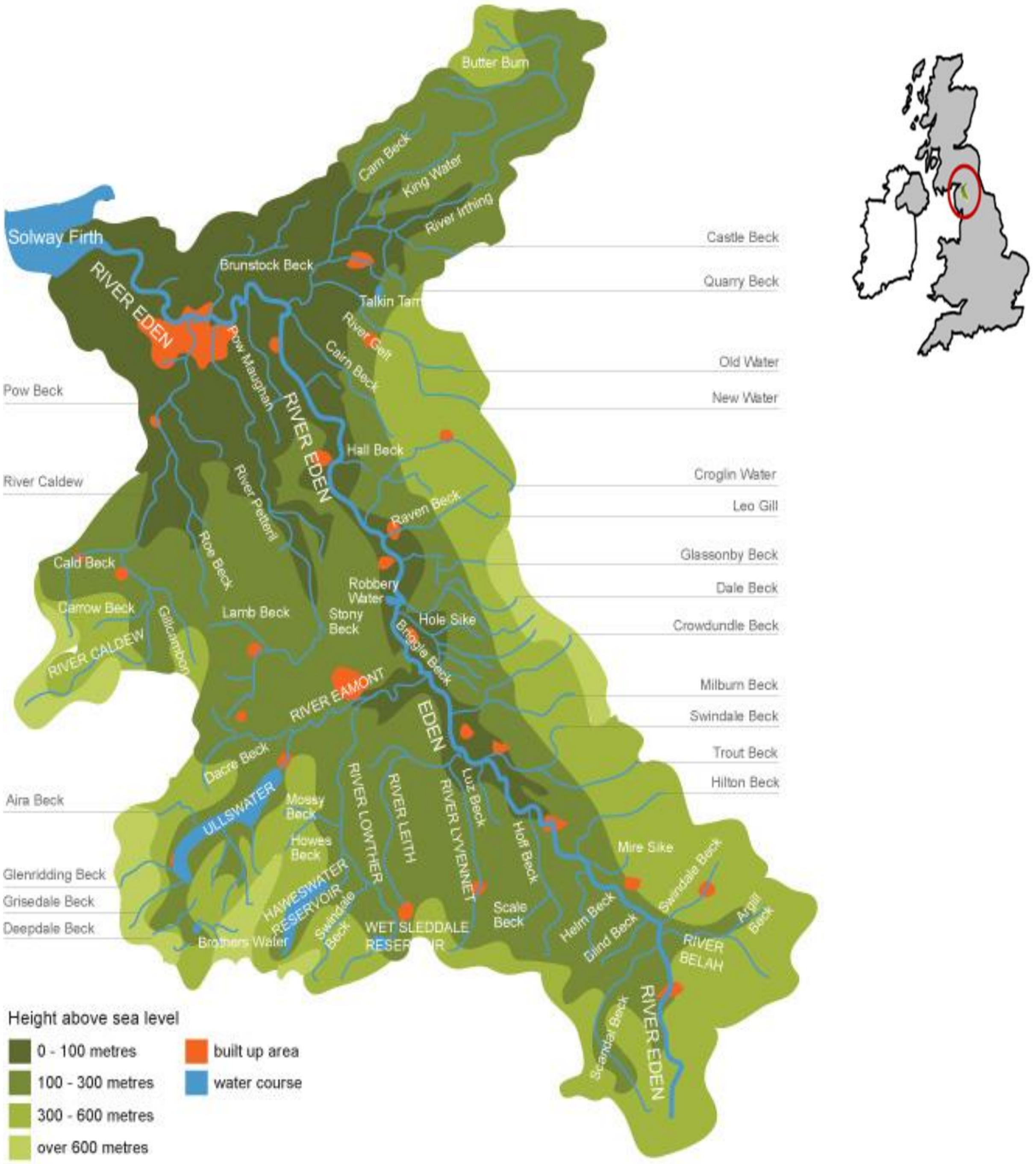


Figure 3.1 The River Eden catchment (adapted from the Eden River Trust, 2014)

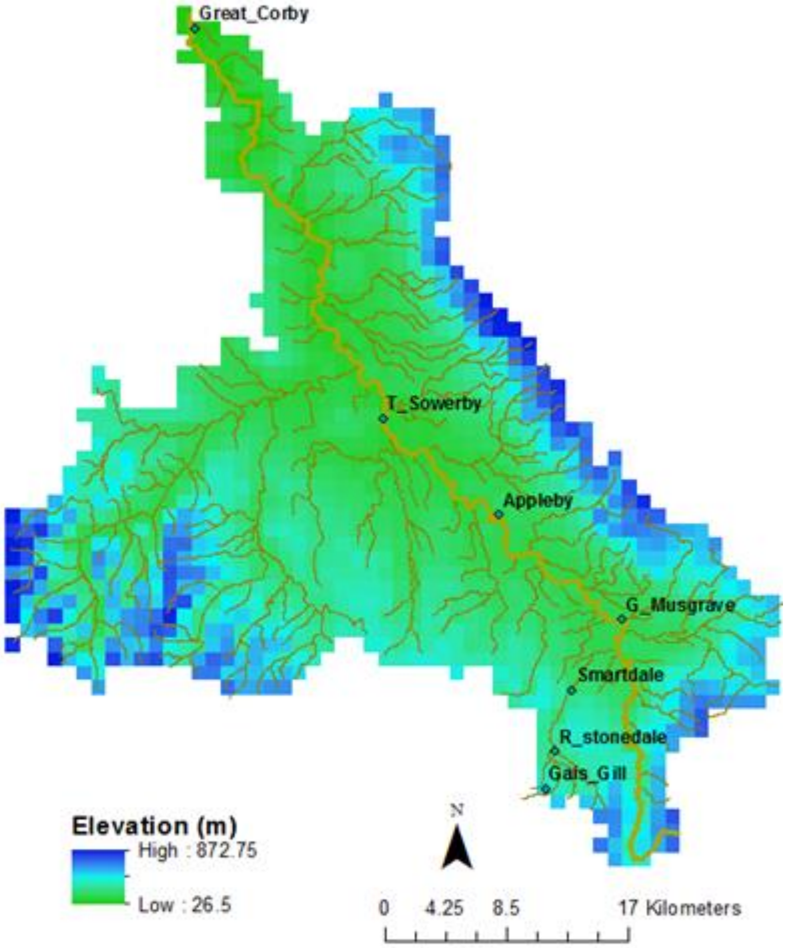


Figure 3.2 Digital Elevation Model (DEM) of the study sites in the Eden Catchment

3.2.2. Geology

The Eden valley is located between the Lake District to the west and the Pennines to the east. At the western zone, the solid geology is predominantly made up of Permian Penrith Sandstone and at the east is the Triassic St. Bees Sandstone. The two are separated by the Eden Shale. They are largely bordered by the Carboniferous limestone; this covers a larger area at the western part of the Eden. The fringe of the sub-catchment is underlain by mudstone and in some areas in the west by igneous rock and conglomerate. The 30 m wide Cleveland-Armathwaite Dyke, an igneous intrusion, crosses the valley north of Penrith, from Dalston in the SE, to NW near Carlisle towards Renwick. Apart from acting as a natural weir, it also significantly affects the topography of the catchment. The vale of Eden opens northwards into the NW-SE trending Solway Basin (Chadwick *et al.*, 1995). The geological map of the Eden Catchment up to Great Corby is shown in figure 3.3.

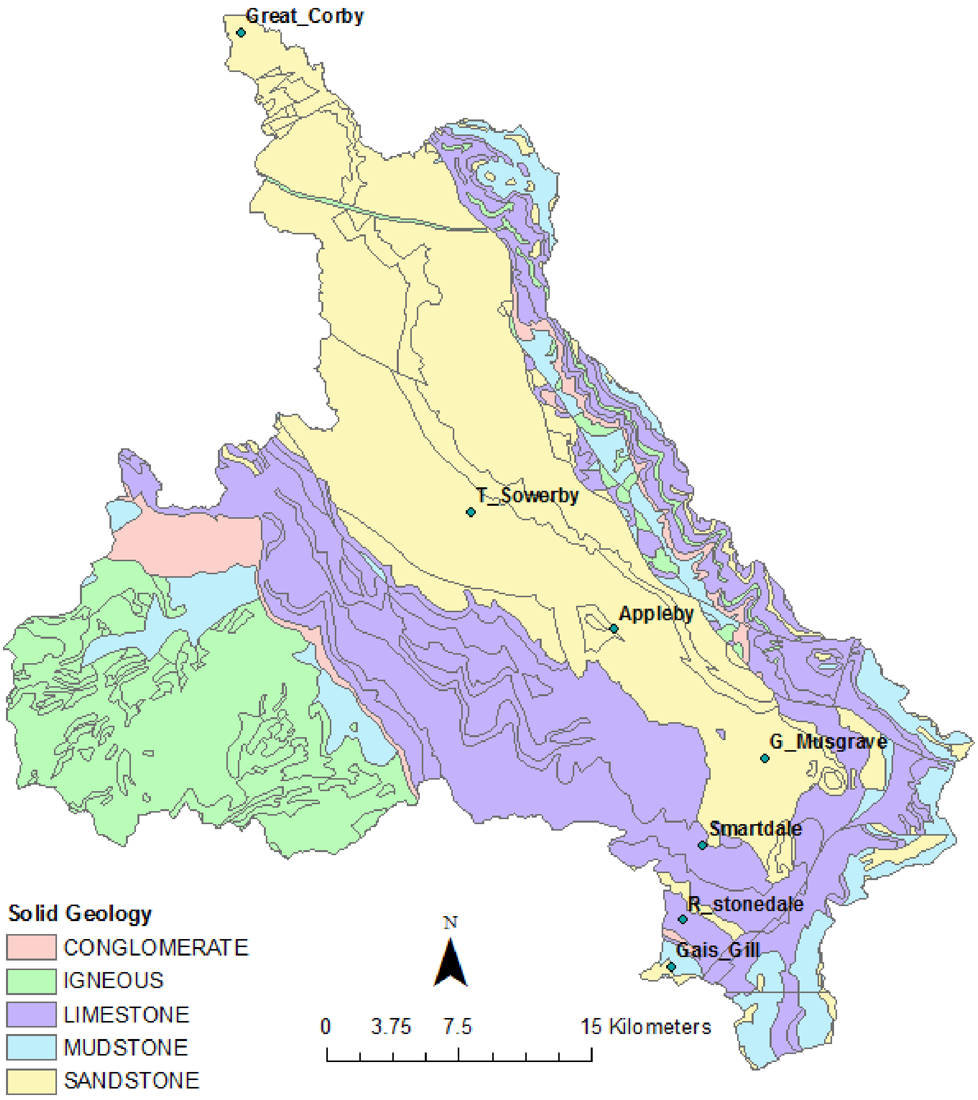


Figure 3.3 Catchment geology map

The detailed description of the DTC sub-catchment characteristics was provided by Allen *et al.* (2010). The Pow sub-catchment, for instance, is underlain by solid geology consisting of: carboniferous mudstone, Eden Shale, Penrith Sandstone, St Bees Sandstone and Carboniferous limestone. St. Bees Sandstone and Carboniferous limestone occupy the larger area. The solid geology at Morland sub-catchment is a combination of limestone, sandstone and mudstone cyclically interbedded together. Bedding dips towards the north east and is considered to influence the geomorphology of the sub-catchment. In Dacre sub-catchment, sub-catchment west of Penrith, the solid geology comprises volcanic andesite and Devonian conglomerates forming the conical hills of Great Mell Fell and Little Mell

Fell at the sub-catchment outlets and has hard, rocky outcrops. The conglomerates were developed from alluvial fans along the flank of the Lake District massif.

Overlying the major portion (over 75%) of solid geology of the Eden basin are the quaternary superficial deposits (figure 3.4). They were deposited by glacial and surface waters (streams, lakes and rivers). Based on the mode of deposition, they are classified into glacial till, glacio-fluvial outwash, river terrace deposits and alluvium. The predominant superficial deposit in the Eden basin is the glacial till and much of it forms high mounds typically described as ‘drumlinoid’. Borehole logs indicate that it comprises red-brown, stiff, silty sandy clay to friable clayey sands with pockets of lenses of different particle sizes/grades (up to cobbles) of the bedrock described earlier. This complexity creates varied piezometric levels and complex perched water tables in the catchment. Sand layers in the till, as reported for instance, may exceed 5 – 6 m in thickness. The glacio-fluvial outwash consists of stratified, well-sorted sand and gravel deposits. It occurs north of Penrith and is related to landforms such as eskers etc. Associated with the modern rivers and streams are the river terrace deposits, comprising sand and gravel. Another superficial deposit that is linked to the major streams and rivers in the Eden basin are alluvium deposits. Its composition is fine sand and gravel south of Penrith; it is a brown sandy loam north of Penrith where it is more prominent. There is a mosaic pattern of bare solid geology in this basin which it is more prominent towards the fringes particularly at the section underlain by volcanic igneous rock to the west of the basin. Peat is also found at the fringes and in some abandoned channels together with organic silts (figure 3.4).

In the DTC sub-catchments, the superficial geology in the Pow sub-catchment is glacial till primarily consisting of clay with some arenaceous materials; however, there are also some glacio-fluvial wash channels. The river channel is underlain by alluvium. In Morland sub-catchment, it is covered predominantly by glacial till that is moulded into drumlins at the north east corner with a strong south east elongation. Glacial till covers the centre of the land drained by Dacre Beck sub-catchment but the higher fells are bedrock. The valleys and hollows resulting from the dissected hummocks at the floor of the sub-catchment are filled with sands, gravels, peat and silty alluvium (Allen *et al.*, 2010).

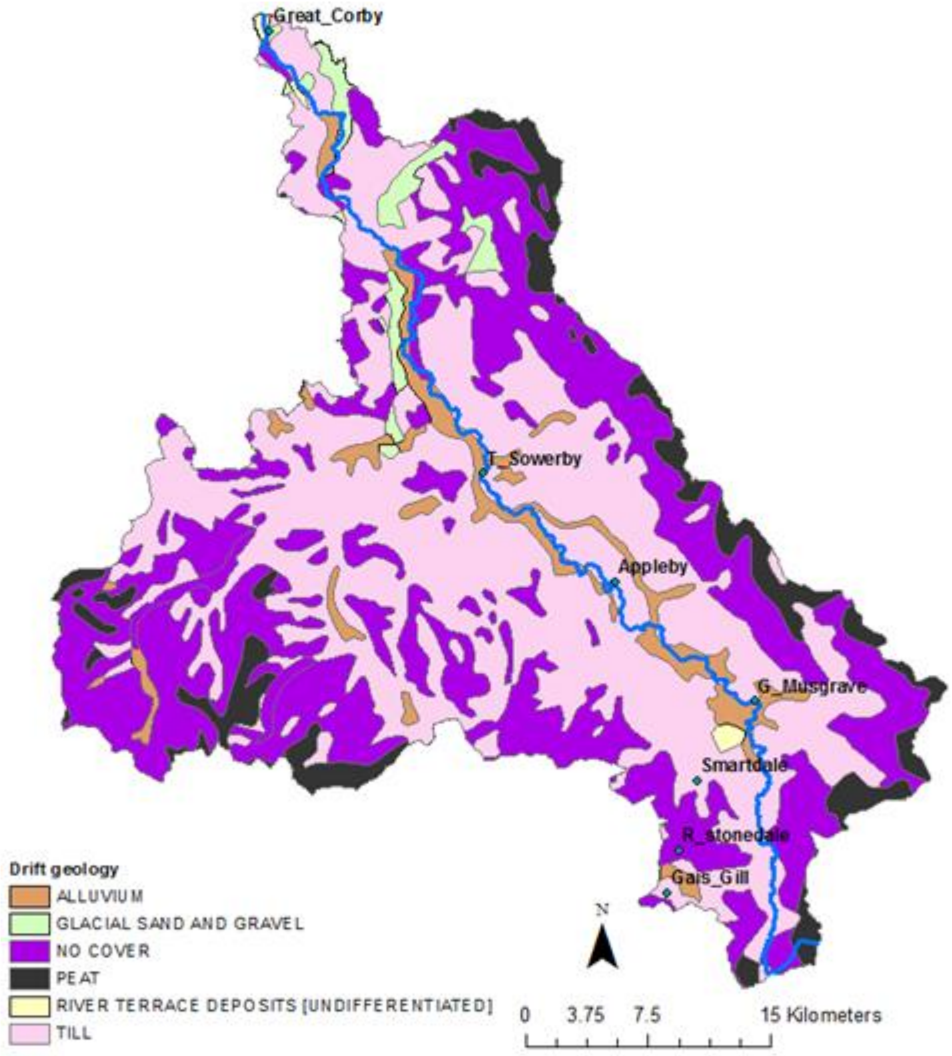


Figure 3.4 Eden Catchment drift geology map

3.2.3. Soil

There are many soil associations (a collection of "series" in UK nomenclature) in the Eden Catchment but a broad overview shows two descriptions (table 3.1). Soils described as typical brown earths dominate the south of the catchment and stretch more towards the northwest beyond Penrith. The others, "typical Stagnogley" soils, are situated between the former in the south of the catchment and extends towards the north where they are predominant (Thomson and Avis 1983, Soils of England and Wales: Sheet 1 Northern England). Another type that is prominent, "typical" brown sand, covers the immediate south of Penrith, the west of the catchment and more extensively north of Penrith in the eastern part of the catchment. Raw oligo-fibrous peat soils, "typical" brown podzolic soils and humo-ferric podzols are usually

S/N	Sub-catchment	Area (km^2)	Elevation (m)	Surrounding Soil Association (E-W of the sub-catchment)	Soil Description (E-W of the sub-catchment)
1.	Gais Gill	1.1		Briekfield, Hafren	Cambic stagnogleysols, ferric stagnopodzols
2.	Ravenstonedale	26		Eardiston1, Brickfield	Typical brown earths, cambic stagnogleysols
3.	Smardale	37		Eardiston1	Typical brown earths
4.	Great Musgrave	233		Wick1, Clifton, Enborne (river neighbourhood), Wharfe (embedded in Clifton)	Typical brown earths, typical stagnogleys soils, typical alluvial gley soils, typical brown alluvial soil
5.	Appleby	337		Wick1, Clifton, Crannymoor (embedded in Wick1)	Typical brown earths, typical stagnogleys soils, typical alluvial gley soils, humo-ferric podzols
6.	Temple Sowerby	616		Clifton, Blewbury, Enborne (river neighbourhood), Crannymoor (embedded in Blewbury)	Typical stagnogley soils, typical brown sands, typical alluvial gley soils, humo-ferric podzols
7.	Great Corby	1373		Clifton, Salwick	Typical stagnogley soils, stagnogleyic argillic brown earths
8.	Blind Beck	9.6		Clifton	Typical stagnogley soils,
9.	Kirkby Stephen	69		Wick1, Eardiston, Waltham (south)	Typical brown earth

Table 3.1 The soil cover of the sub-catchments selected for CHASM project (Thomson et al., 1983).

found at the fringes of the catchment south of Carlisle (table 3.1). Figure 3.5 shows the Hydrology of Soil Type (HOST) version of the catchment. The HOST classification is a system of soil classification in the United Kingdom that is based on soil physical properties that have hydrological significance and also incorporate catchment hydrological response (Boorman *et al.*, 1995). This together with the other soil classification can give an idea of degree of agricultural activity and nature of hydrological processes in a catchment.

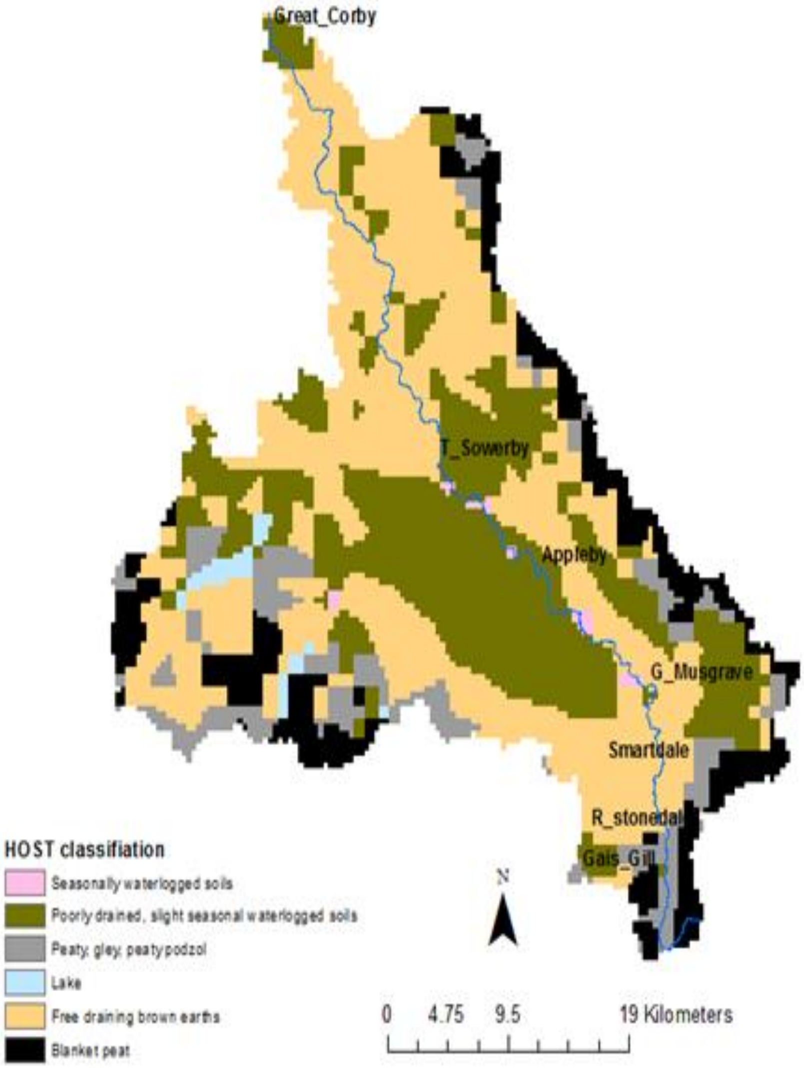


Figure 3.5 Eden Catchment HOST soil types

The soil types in the DTC sub-catchments are shown are shown in figure 3.6 to figure 3.8. The predominant soil series in Dacre and Morland is Brickfield whereas the Pow sub-catchment is predominantly covered by the Clifton series and this soil type is inherently fertile, and comparatively more intensively cultivated than the Brickfield series.

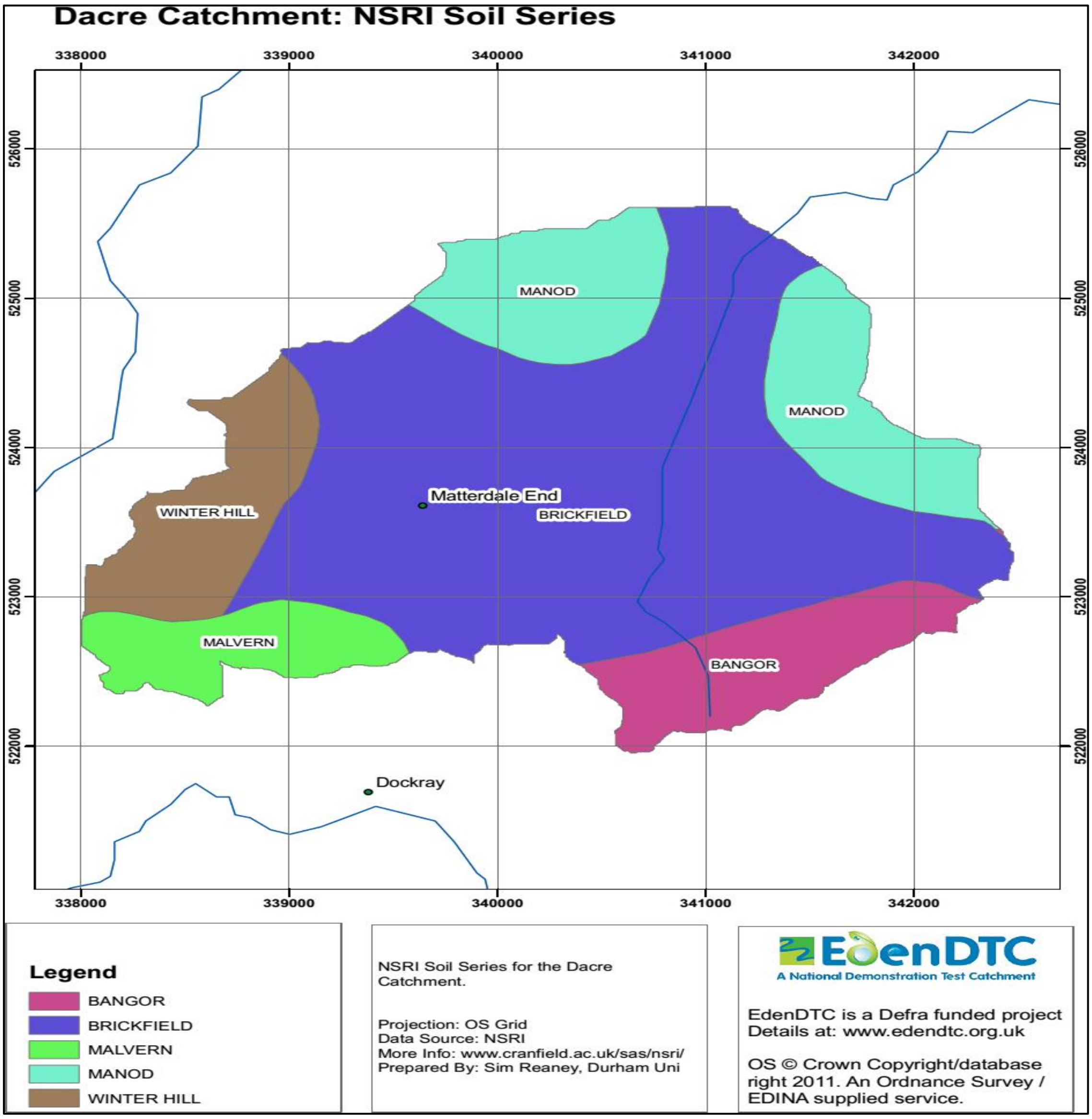


Figure 3.6 Dacre soil map (from Eden DTC Project:www.edendtc.org.uk)

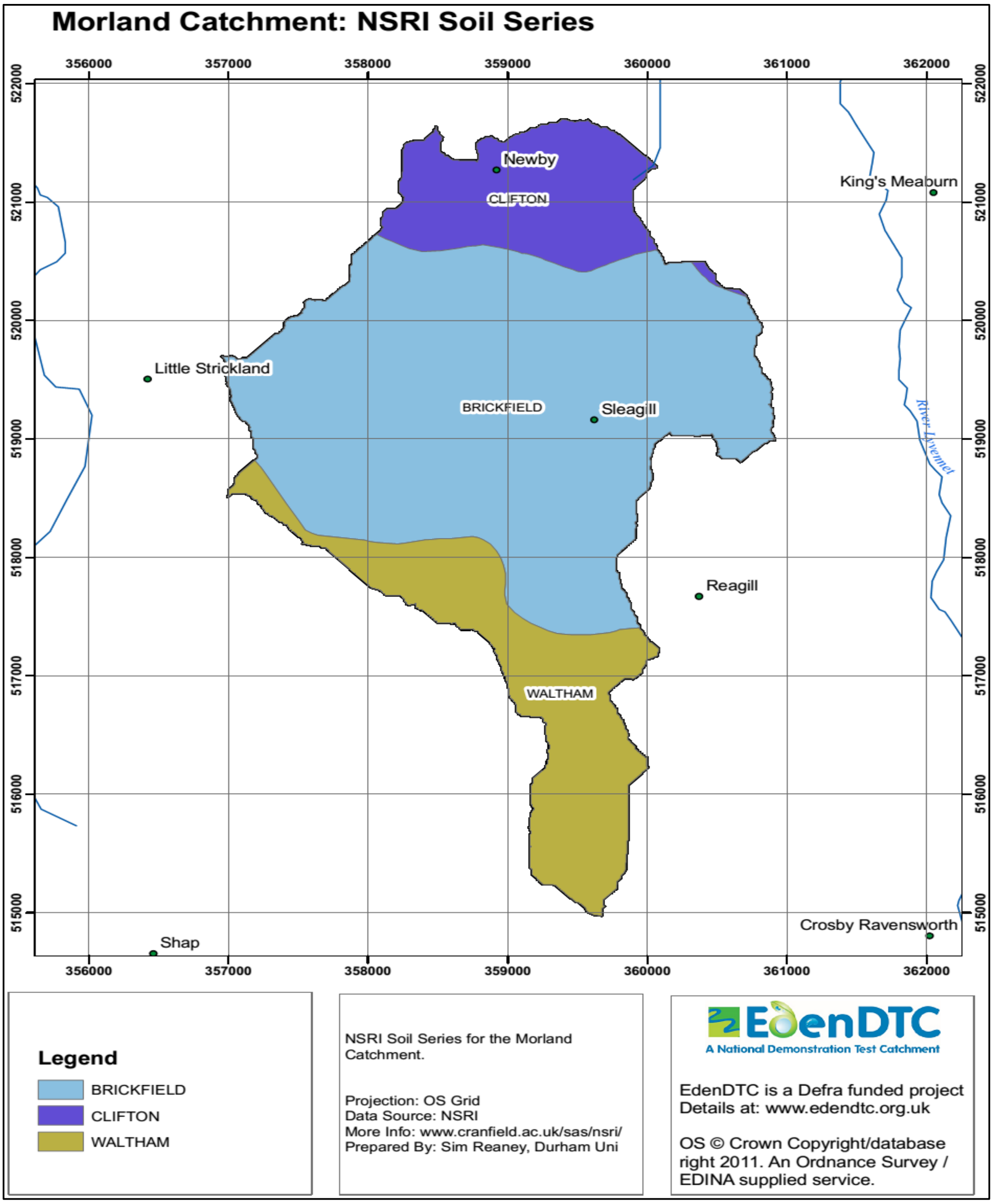


Figure 3.7 Morland soil map (from Eden DTC Project: www.edendtc.org.uk)

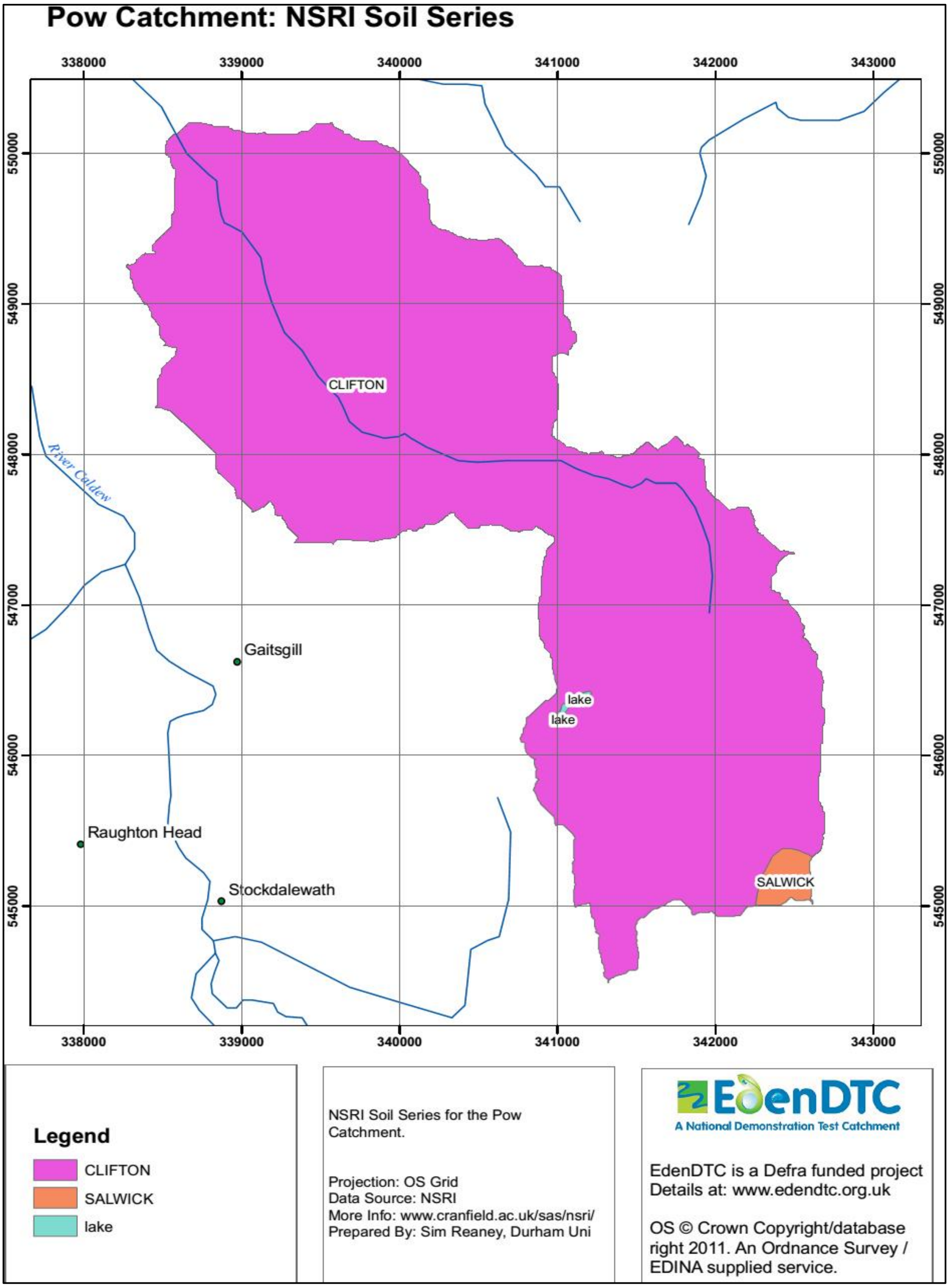


Figure 3.8 Pow soil map (from Eden DTC Project: www.edendtc.org.uk)

3.2.4. Vegetation and land use

The area of high elevation in the Eden catchment on the eastern and southern portion, is covered by unmanaged grassland (moorland) and bracken/shrub moorland. The central part of the catchment and a larger part through Temple Sowerby to the north have a higher percentage of the land covered by managed grassland along with a mosaic distribution of tilled land with higher intensities in the downstream (lowland) sub-catchments. There are pockets of woodland, bog, inland water and bare land in the catchment. Urban areas are found scattered across the catchment particularly towards the centre. Some notable settlements are found in Kirkby Stephen, Brough, Appleby, Penrith and the city of Carlisle (figure 3.9) (CEH, 2000).

3.2.5. Climate

Northwest England where the Eden catchment is located has a humid temperate climate influence by exposure to frontal systems from the Atlantic, although there is variation within the catchment due to differences in altitude. Records by the Met Office Carlisle (lowland) and Shap stations (upland) spanning 1981 – 2010 show an annual rainfall range of 872 – 1779 mm. Average monthly temperatures in July within the same period were as high as 19.6 ^{0}C (Carlisle station), 18.7 ^{0}C (Warcop station) at a relatively low site and in February as low as -2.9 ^{0}C (Loadpot Hill, Lake District area) at relatively high site (Met. Office, 2014). Snow remains in the lowlands for 0-5 days per year and longer (15-30 days per year) in areas with elevations above 300 m (Barber, 2008; Barber, 2013).

3.2.6. River characteristics

The River Eden originated from the carboniferous Limestone Fell of Mallerstang Common in the south and flows towards the Solway Firth in the north. It exhibits pool and riffle sequences. Fine sands or gravels are deposited on the river bed with gravel being predominant. Scandal Beck, where there are two of the gauging stations used in this study, is one of the tributaries that discharges into the main Eden channel before Great Musgrave. The River Eden flows into its lowland area

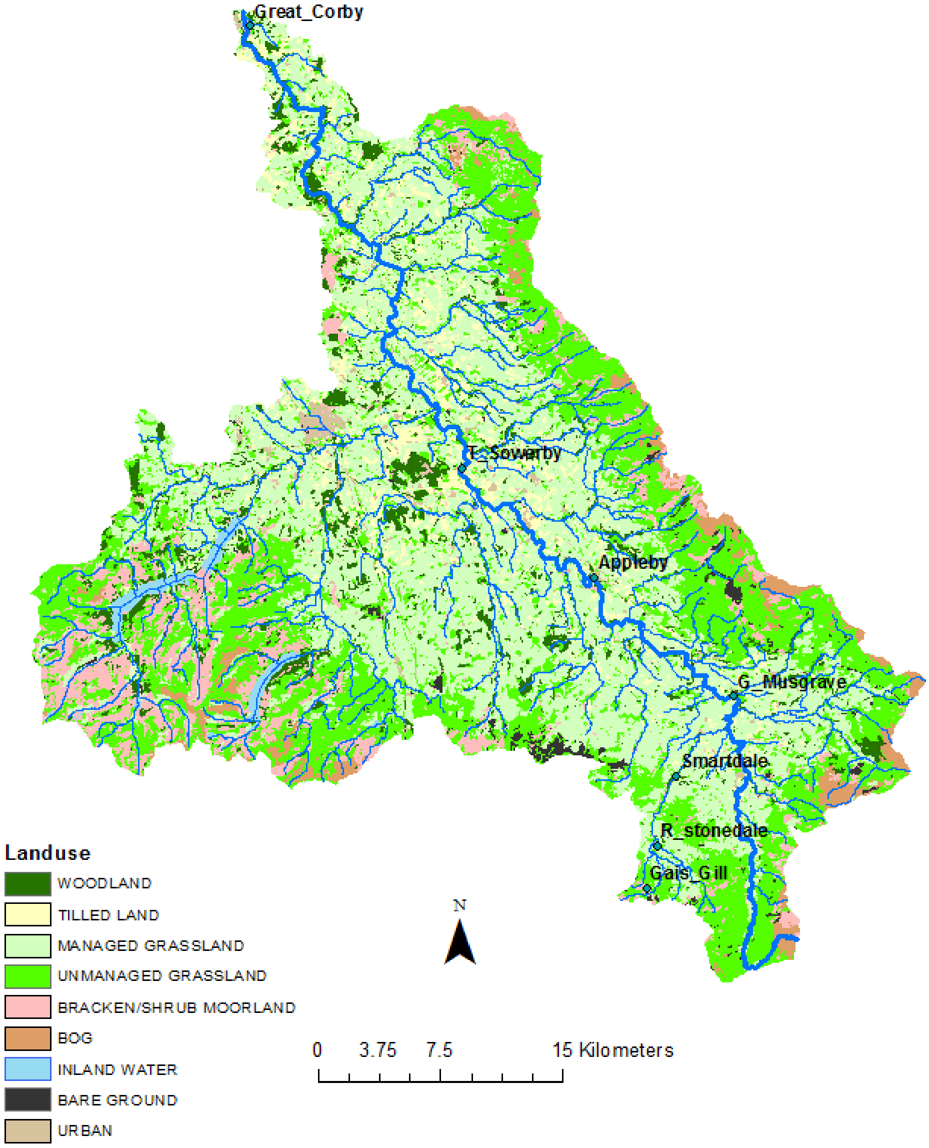


Figure 3.9 Catchment land use map

from this point, draining areas subjected to intensive farming including improved grassland, more cattle and arable production. In the upland zone, storm runoff to the river is flashy as a result of frequent intensive rainfall, steep slopes and thin soils. Aquifers in the lowlands provide base-flow that dominates the runoff pattern. The mean flow, Q10, Q95 and base flow index at Kirkby Stephen in the south for the period of record from 1971 - 2011 were 2.615 $m^3 s^{-1}$, 6.57 $m^3 s^{-1}$, 0.167 $m^3 s^{-1}$ and 0.26 respectively. At the sub-catchment outlet at Great Corby, the values were 40.556 $m^3 s^{-1}$, 88.2 $m^3 s^{-1}$, 8.08 $m^3 s^{-1}$ and 0.47 respectively (CEH, 2000; Mills, 2009b; Barber, 2013; CEH, 2014).

For the DTC sub-catchments, the source of Pow Beck is a spring near Monkcastle and it initially flows towards the north, later turning west around Foulbridge before turning north-west at Sprunston to join the Caldew near Dalston. Because a preliminary report (Allen *et al.*, 2010) showed that the rest water level in the bore holes was at a relatively low elevation relative to the nearest stream reach, it is suggested that the bedrock aquifer is not contributing to the streamflow but that the converse is occurring. The report indicated that the presence of springs suggested that groundwater discharge from the superficial deposits and surface runoff contributes to Pow Beck.

A number of small streams primarily flowing northward join to form Newby Beck which in turn forms Morland Beck which in turn eventually forms the River Lyvennet in Morland. There are some springs that supply the Morland Beck via its tributaries. Unlike the two other sub-catchments described above, Dacre contains no observation boreholes. There are a number of springs and it was reported that these are likely to feed the Dacre Beck; the bedrock itself is impervious and unlikely to yield much potential as an aquifer. The sub-catchment drains to an outlet at Nabend between Great Mell Fell (altitude 537 m) and Little Mell Fell (altitude 507 m) (Allen *et al.*, 2010).

3.3. CHASM-Based Field Programme

3.3.1. CHASM

An understanding on how nutrient concentration and export change with scale can be made possible through studying a set of connected sub-catchments. CHASM was a national programme initiated over a decade ago that instrumented four different catchments in the United Kingdom. The Eden catchment is one and Newcastle University was the lead University both for that catchment and for the CHASM programme overall. The upper part of the Eden catchment was instrumented using a nested basin ($\sim$1 km^2 through $\sim$10 km^2 to $\sim$100 km^2) approach up to 337 km^2 at Appleby. The CHASM hydrometric network was based on Generic Experimental Design (GED) and has evolved over time so as to support the understanding and resolving of significant spatial variations in hydrological/geomorphological response. The design adopted an iterative process leading to an understanding of the heterogeneity in catchment characteristics (e.g. soil, geology etc.) that eventually resulted in the classification of the landscape into hydrologically homogenous domains (O'Connell *et al.*, 2002). This is in agreement with the hydrological response units (HRUs) canvassed by some authors mentioned in the literature reviewed (Cammeraat, 2002; Lazarotto *et al.*, 2006) and the homogenous units that were identified formed the basis for the installation of the gauging stations and sampling protocols. Therefore the experimental units for this study were designed around this network of gauging stations.

The extension of this study further down to Temple Sowerby (616 km^2) and Great Corby (1373 km^2) was made possible by Environment Agency (EA) gauging stations. The nested instrumentation was established to investigate the problem associated with scientific information transfer from small sub-catchments (<10 km^2) to large ones. The design also captures the catchment characteristics (e.g. land use) as they relate to spatial dependencies observed in nutrient transport.

Past research carried out in the River Eden catchment using the CHASM programme and experimental design (GED) included the simulation and analysis of flow regimes (Walsh, 2004a), nutrient loadings at Blind Beck and the entire Upper Eden (Barber, 2008; Barber, 2013), scale dependency of rainfall on peak flood prediction (Wilkinson, 2008), groundwater and recharge processes (Fragala, 2009) and sediment transport (Mills, 2009).

3.3.2. CHASM gauge stations, experimental design and sampling

A total of nine nested monitoring sites were identified from the existing CHASM network design (GED) to provide a spatial platform for this study (figure 3.10). More detail information about the catchment and the catchment characteristics described in previous section is presented in table 3.2. The field research instruments in the Eden include river gauging stations, observation boreholes, hydrometeorological stations (Automatic Weather Stations, AWS) and rain gauges, suspended sediment and water quality monitors. Specifically, this study uses fine resolution data (at 15 minutes time step) from the flow gauging stations, AWS and raingauges (figure 3.11).

A nested system was identified for the spatial scale study, running down the Scandal Beck and then the River Eden. The relevant gauging stations are at Gais Gill

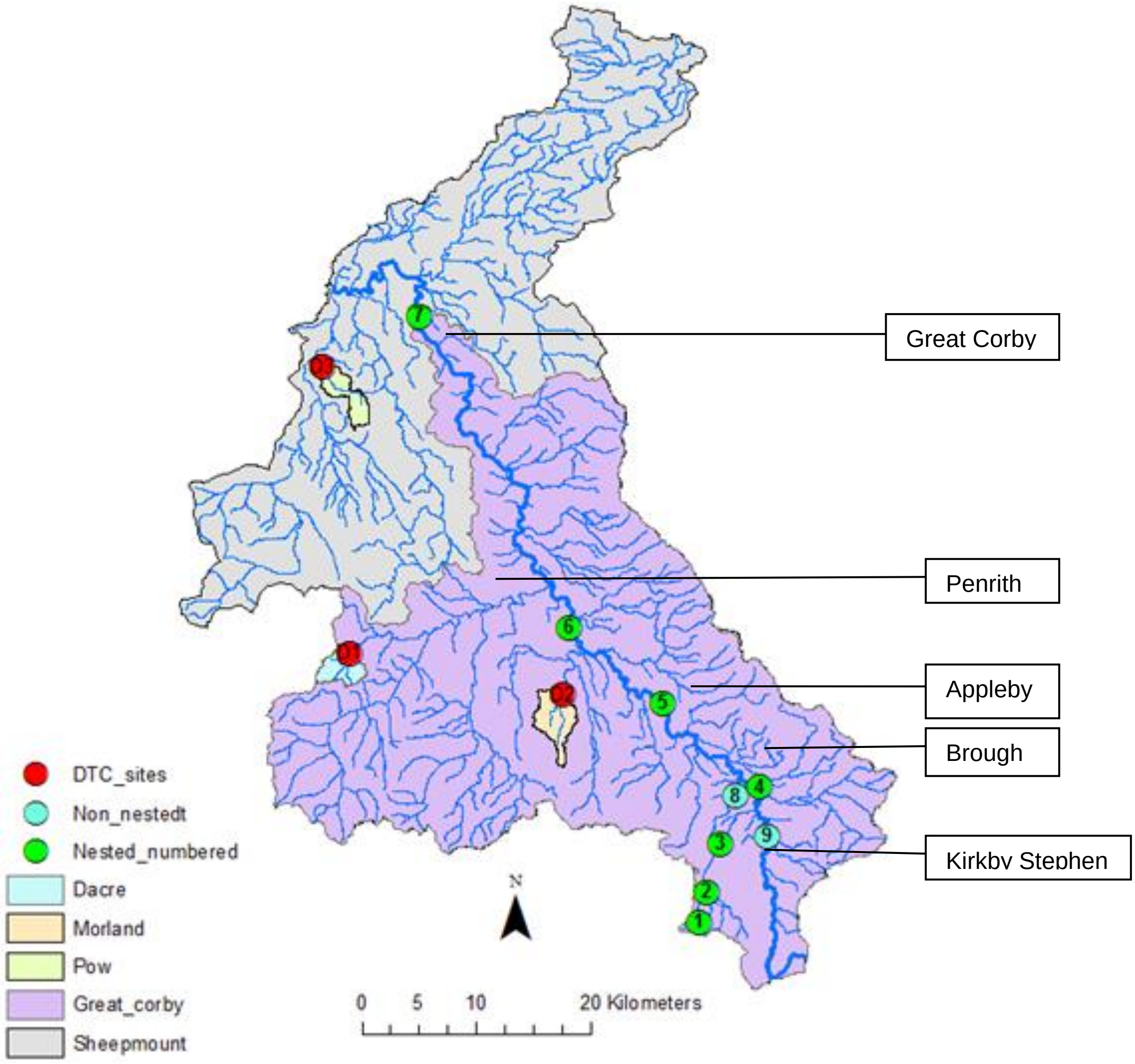


Figure 3.10 Flow, suspended sediment, nutrient monitoring locations and major settlement (in box) in the Eden Catchment to Eden at Sheepmount gauge (see Table 3-2 for the catchment names represented by numbers on the map)

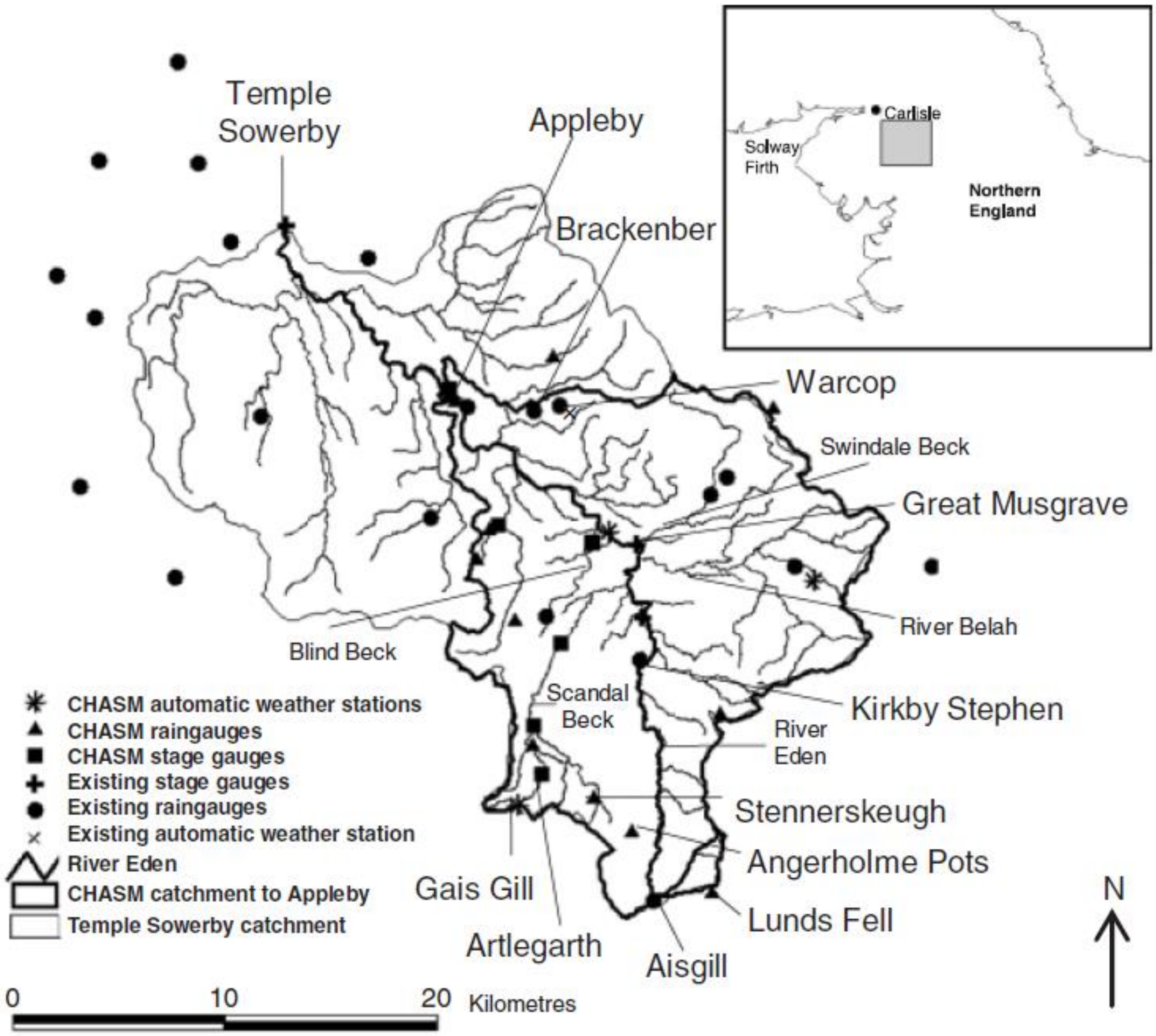


Figure 3.11 Eden gauge stations at Temple Sowerby, CHASM (Mayes *et al.,* 2006)

Name	**Area (km2)**	**Number on map**	**Dominant soil type (HOST)**	**Mean elevation (m)**	**Max. Elevation (m)**	**Dominant & Selected Land cover**	**Dominant Geology**	**SAAR (mm)**
Gais Gill	1.1	1	Blanket peat (100%)	470	602	Unmanaged grassland (70%), managed grassland (0%), urban (0%) and tilled land (0%)	Mudstone, sandstone	1882
Scandal Beck at Ravenstonedale	26	2	Free draining brown earth (35%), poorly drain slight seasonal waterlogged soil (28%)	351	707	Unmanaged grassland (55%), managed grassland (35%), urban (0.3%), tilled land (0%)	limestone	1612
Scandal Beck at Smardale	37	3	Free draining brown earth (56%), poorly drain slight seasonal waterlogged soil (19%)	331	707	Unmanaged grassland (50%), managed grassland (39%), urban (1.2%), tilled land (0.02%)	Limestone	1544

Eden at Great Musgrave	233	4	Free draining brown earth (37%), Blanket pit (25%), poorly drain slight seasonal waterlogged soil (21%)	345	707	Unmanaged grassland (44%), managed grassland (37%), tilled land (2%), urban (0.9%)	Limestone sandstone	1271
Eden at Appleby	334	5	Free draining brown earth (38%), poorly drain slight seasonal waterlogged soil (30%)	307	715	Managed grassland (42%), unmanaged grassland (40%), tilled land (3%), urban (1%)	Limestone sandstone	1189
Eden at Temple Sowerby	616	6	poorly drain slight seasonal waterlogged soil (42%), Free draining brown earth (35%)	283	796	Managed grassland (48%), unmanaged grassland (31%), tilled land (5%), urban (1%)	Limestone sandstone	1143
Eden at Great Corby	1373	7	Free draining brown earth (45%) and poorly drain slight seasonal waterlogged soil (31%)	284	945	Managed grassland (42%), unmanaged grassland (31%), tilled land (6%), urban (2%)	Sandstone limestone, igneous	1274

Blind Beck	9.2	8	Free draining brown earth (80%) and poorly drain slight seasonal waterlogged soil (20%)	220	376	Managed grassland (42%), unmanaged grassland (31%), tilled land (6%), urban (1.5%)	Sandstone Limestone	1053
Eden at Kirkby Stephen	69	9	Blanket peat (35%), Free draining brown earth (34%), peaty, Gley, peaty podzol (29%)	385	707	Unmanaged grassland (54%), managed grassland (27%), tilled land (2%), Urban (1%)	Limestone mudstone	1515
Dacre	10.2	D1	poorly drain slight seasonal waterlogged soil (53%), Free draining brown earth (18%)	505*	537	Managed grassland (42%), Unmanaged grassland (38%), Tilled land etc. (0%)	Igneous Conglom-erate	1587
Morland	12.5	D2	poorly drain slight seasonal waterlogged soil (84%), Free draining brown earth (16%)	234	392	Managed grassland (84%), Unmanaged grassland (9%), Tilled land (3%), Urban (0.6%)	Limesone sandstone	1165

Pow	10.5	D3	poorly drain slight seasonal waterlogged soil (100%)	-	155	Managed grassland (72%), Unmanaged grassland (4%), Tilled land (17%), Urban (3%)	Sandstone limestone	856

Table 3.2 Summary of monitoring locations and their characteristics. Sites in italic are part of the nested basin system

(1.1 km^2) linking up with Scandal Beck (Ravenstonedale, 26 km^2, and Smardale, 37 km^2), extending through Great Musgrave (233 km^2) on the Eden, Appleby-in-Westmorland (337 km^2) and Temple Sowerby (616 km^2) to the system outlet at Great Corby (1373 km^2). Kirkby Stephen is outside the nested system but can form another continuum of sub-catchments from Great Musgrave through to Great Corby. There is also an important tributary, Blind Beck (9.2 km^2, see location no 8 on the map), that is outside the nested system to the west. It is chosen for this study also because work has been done there that shows that it has been impacted by intensive agricultural activity (i.e. it shows the impact of agricultural land use) in the sub-catchment which it drains. The information from the research conducted in this sub-catchment is also linked to the DTC sub-catchments (Pow, Morland and Dacre) which are of a similar size.

More details about the sampling locations and gauging stations are as shown in figure 3.10, figure 3.11 and table 3.2.

3.3.3. Seasonal campaign

In the CHASM sub-catchments continuous sampling was not feasible. Therefore a set of seasonal campaigns were planned to capture the variability in conditions throughout a year. The sampling campaigns were in two forms: seasonal and monthly campaigns. There were four seasonal samplings, in November (01/11/2011 – 24/11/2011), March (06/03/2012 – 21/03/2012), May (02/05/2012 – 21/05/2012) and late July/early August (23/07/2012 – 06/08/2012). These represented autumn, winter, spring and summer respectively. These sampling periods also took into consideration farming activities including ploughing, fertilizer and manure applications, livestock movements, etc. For instance there was ploughing, fertilizer and manure application in various forms throughout the sampling periods except in spring when there was less ploughing. Some of the livestock was kept in pens over winter and returned to the fields during the summer. For each campaign, the sampling was alternated with laboratory analyses because nutrients such as dissolved reactive phosphorus (DRP) and nitrate require analysis within 24 hours. Therefore, each seasonal campaign comprised four visits in three weeks to allow for these analyses. The seasonal campaigns were ideal considering the time and money involved, and the availability of a technician anytime the need arose, when compared with the intensive characterisation all year round. The campaigns were augmented by additional data collected by monthly or spot sampling (16/11/2011 – 26/04/2013). For each visit a coherent grab sampling protocol was adopted at all the locations on the same day. The grab sampling was an instantaneous sampling whereby a plastic bottle was dipped into the river manually to collect a water sample. The water sample was preferably collected at the centre of the river where possible.

The soil sampling at Gais Gill (GG) and Blind Beck (BB) was also carried out during the seasonal campaigns. GG is a headwater sub-catchment and represents the upland Eden region with less intensive farming. BB is a tributary located further downstream and known to be in a sub-catchment subjected to intensive agricultural land use and at a low elevation, and therefore it was chosen to represent a lowland Eden sub-catchment. These soil sampling locations were chosen to capture the variations in land use as they relate to other relevant landscape characteristics that influence soil behaviour. The lower slopes comparatively receive more sediment and other materials from upslope including nutrients. The finer a soil, the larger the overall particle surface area it has for reactions to occur. Soil at the lower slope consists of finer particles and is expected to exhibit the properties of the soil of the area more readily. Considering the labour and resource constraints that detailed soil sampling entails, these locations were chosen as the Eden catchment soil sampling areas. The soil was collected from the lower slopes in the two sub-catchments during the autumn, winter, spring and summer of the water year (October 2011-September 2012). A soil auger was used and samples were collected at 0-15 cm, 15-50 cm and 50-100 cm (depending on the terrain) at those representative locations.

3.4. Laboratory Analysis and Data Collection

3.4.1. Suspended sediment analysis

A gravimetric technique was deployed in the laboratory. It involved the weighing of oven dried filter paper before and after filtration using a vacuum pump. The filter paper used was Glass microfiber paper (Whatman GF/C 70 mm) and was dried in an oven at 105^{0}C. After cooling in a desiccator, the oven-dried weight of the filter before and after the filtration process was recorded. The suspended sediment (SS) concentration was obtained using the following equation:

$$C_{ss} = \frac{(W_a - W_b)}{V_f} \qquad (3.1)$$

where: C_{ss} – suspended sediment concentration (mg/L), W_a – weight of filter paper after filtration (mg), W_b – weight of filter paper before filtration (mg), V_f – volume of sample filtered (L) (APHA, 1992)

Quality control

The suspended sediment data were compared with the data earlier obtained by Mills (2009) in the same sub-catchment. The two-sample t test conducted with Great Musgrave data at the same range of discharge indicates that they were not significantly different ($P=0.05$).

3.4.2. Phosphorus analysis

The molybdate colorimetric procedure was employed in the laboratory. The reaction of soluble phosphorus (orthophosphate) with acid molybdate and ascorbic acid produces a blue colour of molybdate complex. The intensity of the colour is proportional to the P concentration in the sample. The technique requires all P fractions to be in soluble form. The three measurable P fractions include the total P, total dissolved P and soluble, reactive P. It implies that total P must first be digested to soluble form using peroxodisulphate solution ($K_2S_80_8$).

In more details, for total P determination the unfiltered sample has to be digested and then subjected to the colorimetric procedure. For total dissolved P, the water sample has to be filtered through a 0.45 µm membrane filter, before digestion and the colorimetric procedure. Soluble reactive P does not require digestion but needs to be filtered through a 0.45 µm membrane filter before running the colorimetric procedure (APHA, 1992). Standards of known P concentration are subjected to the same colorimetric procedure. The absorbance of all the P fractions and standards are measured using an UV Spectrophotometer at a wavelength of 880 nm. The absorbance of the P standard is plotted against the known concentration. The calibration relationship between the absorbance and standard P concentration is then used to calculate the concentration of the water sample in milligrams per litre (British Standard EN 1189, 1997)

3.4.3. Nitrate analysis

A Dionex Ion Chromatography (IC) machine was deployed in the laboratory to measure nitrate concentrations. The sample was filtered using a 0.2 µm syringe filter and the filtrate was pipetted into a 5ml vial that was fed into the IC machine for the determination.

Quality control

The accuracy of the water quality analysis was checked three times using an electrical (Charge) balance (E.B.) test between 2012 and 2013. Samples of known concentrations of anions and cations were embedded among the water samples collected from the field. The charge (Electric) balance is given by:

$$E.B.(\%) = \frac{\left(\sum cations + \sum anions\right) * 100}{\sum cations - \sum anions} \qquad (3.2)$$

where cations and anions are expressed in meq/l and inserted with their charge sign. The cations are Na^+, K^+, Mg^{2+} and Ca^{2+} while the anions are Cl^-, HCO_3^-, SO_4^{2-} and $N0_3^{-1}$. For the cations, the water samples were filtered with 0.45 µm membranes then were acidified (pH<2) and then analysed using an Inductively Coupled Plasma Optical Emission Spectrometry (Varian Vista MPX axial ICP-OES). With the exception of HCO_3^-, all other anions were analysed along with nitrate as stated in the previous section. An attempt was made to analyse indirectly inorganic carbon using a Shamdzu analyser. This was converted to HCO_3^- by this equation:

$$HCO_{3^+}(mg/l) = InorganicC * \frac{61}{12} \qquad (3.3)$$

However, due to the requirement to collect the sample in an acidified bottle for this technique and the time and labour constraints this entailed, the procedure was abandoned and a water sample of known HCO_3^- value was analysed to complete the balance.

3.4.4. Point source and septic tank in the Eden

Industrial discharges and sewage treatments works (STWs) are traditionally classified as point source. Depending on the circumstance, septic tank system (STS) can be viewed as either diffuse or point source (Wither *et al.*, 2012; Bowes *et al.*, 2015). Recent studies suggest that STS contributes to point source (Palmer-Felgate *et al.*, 2010; Wither *et al.*, 2011). Jarvie *et al.* (2010) shows that STS also represents multiple point sources of nutrients in surface waters. Recent work in the Eden catchment (Barber, 2013) excluded both STW and STS in the nutrient export coefficient modelling stating that the septic tanks are notoriously difficult to estimate and that the population density is low. In this study, it was assumed that the septic tank in the Eden are multiple point sources. The Eden catchment is rural and the potential point sources of nutrients are STW and STS. A rough estimate of nutrient load from STSs and STWs was considered for the Eden using the population of the major settlements within some of the Eden sub-catchments and the values of per capita annual nutrient loads reported by Halliday *et al.* (2014). The values are 0.54 kg P person^{-1} yr^{-1} and 2.5 kg N person^{-1} yr^{-1} for P and N respectively. Factors of 95/31 and 62/14 can be used to convert these values to phosphate and nitrate respectively.

3.4.5. Soil handling and processing

The soil properties that were analysed were bicarbonate P, water soluble P, pH, N, total organic carbon (TOC), organic matter (OM) and the particle size distribution (soil class/texture).

The first process in the soil analysis after sampling was air-drying. This was followed by sieving and the mesh size used varied depending on the soil property under consideration. For bicarbonate P, water soluble P and pH the soil went through a sieve of 2 mm mesh size. Samples for N and TOC quantification (leading to the OM estimation) passed through a 0.5 mm mesh size, while soil used to determine the particle size distribution was sieved over an appropriate range of mesh sizes.

3.4.6. Estimation of soil water extractible P, bicarbonate P and pH

The water extractible P is expected to be a measure of labile P and should represent the soluble P loss during erosion. Estimation of this P fraction involves the addition of deionised (DI) water at a mass: volume ratio of 2 g soil: 10 ml water. It was shaken overnight by a mechanical shaker. After centrifuging at 12000 rpm for 15 minutes, it was filtered using “Whatman Qualitative filter paper 12.5 cm diameter”. The filtrate was further drawn through a 2 μm syringe filter before it was analysed in the IC machine. A blank sample was also run. The P concentration is expressed as:

$$P(PO_4 mg/kg) insoil = \frac{((Concentration(s) - Concentration(blank) * 10ml))}{wtofsoil(g)} \qquad (3.4)$$

where *s* represents concentration of the filtrate from the soil sample that was measured by the IC machine (British Standard 7755 Section 3.6, 1995)

Spectrometry determination of P soluble in sodium hydrogen carbonate solution ($NaHCO_3$, bicarbonate P) was achieved through the development of a phosphate-molybdate complex. Before the colour reagent was added, the soil was pre-washed in an activated charcoal and bicarbonate solution for the removal of any organic substance that may interfere with the analysis. The filtrate (filtered using Whatman paper: Qualitative circles of 150 mm diameter) and the standard are extracted with bicarbonate while a bicarbonate solution without P is used as blank. Thereafter the colour reagent is added and left for an hour before it is heated in a water bath to 90^0C for 10 minutes. The colour developed in 5 minutes and was read as reported under water analysis in a UV spectrophotometer. P is given by,

$$Pinsoil(mg/kg) = \frac{(100ml * (A_s - A_{bl}) * dilutionfactor)}{slope * wtofsample(g)} \qquad (3.5)$$

where A_s represents the absorbance of phosphate-molybdate blue complex from the sample and A_{bl} represents the complex from the blank ($NaHC0_3$). The slope is the gradient of the calibration relationship of the absorbance and concentration (mg/l) of the standard. It should be noted that the dilution factor in the equation is necessary only if the P concentration in the filtrate from the soil is high (British Standard 7755 Section 3.6, 1995).

For the pH determination in water, combined electrode was used to measure the supernatant solution of a volume: volume ratio of 5 ml soil: 25 ml water that was shaken for 15 minutes and left overnight. The quantification in calcium chloride ($CaCl_2$) followed a similar procedure except that 0.25 ml of molar $CaCl_2$ was added before shaking (British Standard 7755 Section 3.2, 1995).

3.4.7. Determination of soil N, total organic C and organic matter

For nitrogen and total carbon determination, 1 g soil samples sieved in a 0.5 mm mesh size were weighed in duplicate into 10 ml glass vials and analysed using a varioMAX CNS Macro Elemental Analyzer (British Standard section 3.8, 1995; Elementar Analysensysteme GMbH, 2005). The technique operates by the principle of catalytic tube combustion in which the presence of a metallic catalyst raises the level of oxidation of carbon by orders of magnitude. In an Elemental Analyzer, a heat-up reaction was performed in He/O_2 gases. The sample is heated at 10^0C/minute from 30 to 900^0C. Organic carbon volatilises between 200 and 600^oC and beyond this carbonate is liberated. The amount of carbon is determined via weight loss. It may also be possible to determine the proportion of organic carbon simply by heating at 550 to 600^oC overnight and re-weighing. The desired measuring components are separated from each other with the help of specific adsorption columns and determined in succession with a thermal conductivity detector (TCD). Helium (He) serves as a flushing and carrier gas. For quality control purposes, some of the samples were taken randomly and run in duplicate to check if they were repeatable. A paired T-Test showed that the duplicate samples for nitrogen and total carbon were not significantly different (p=0.05).

The soil organic matter was estimated from total organic factor using an organic carbon: organic matter conversion factor of 1.724 (Page *et al.*, 1982). The total soil organic carbon quantification was carried out in a LECO CS230 Carbon-Sulphur Analyser after the pre-treated soil was sieved through 0.5 mm mesh size. The experiment started with a CS 244 model but this was replaced (British Standard section 3.8, 1995). The principle is similar to that of the Elementar Analyzer described earlier. The metallic catalysts used are tungsten and iron chips that enable the soil to combust in a stream of oxygen. The infrared sensor detects the carbonate that is liberated. Sulphate is capable of interfering with the carbonate whereas carbonate does not. Therefore, sulphate is analysed first. The absorbents for carbonate from gas, water vapour and sulphate are incorporated external to the equipment. A (internal) compartment converts carbon monoxide (CO) liberated to CO_2 so that all the carbonate from the soil is recovered by the infrared sensor at the appropriate wavelength. As a check, some of the samples were taken randomly and ran in duplicate to check if they were repeatable. Paired T-Test for the total organic carbon shows that the duplicate samples were not significantly different (p=0.05).

3.4.8. Determination of particle size distribution of the soil

Dry sieving and sedimentation methods were used for soil particle size distribution (British Standard ISO11277, 2009). The dry sieving method covers the quantitative determination of the particle size distribution in cohesionless soil (oven-dried) down to fine-sand size using a set of test sieves placed in a mechanical shaker. The sedimentation technique covers the quantitative determination of the particle size distribution in a soil from the coarse sand size up to the clay size. This is achieved via the hydrometer method or pipette method. For this study the pipette method was used. The analysis is done such that the soil used in the sedimentation method is linked to the soil used in the dry sieving technique leading to form a continuous curve. The data obtained from the sedimentation techniques were also used to derive the soil texture using textural triangle.

3.5. DTC-Based Programme

3.5.1. DTC

The DTC project is a national project established by the Department for Environment Food and Rural Affairs (DEFRA) with the aim of evolving cost effective approaches to mitigating diffuse pollution without hampering agricultural productivity (www.edendtc.org.uk). Three locations or catchments are involved: the Hampshire Avon, River Wensum and River Eden (Eden DTC). The Eden DTC consists of three sub-catchments each covering approximately 10 km^2 and they are the Pow, Morland and Dacre sub-catchments. The Pow is located south of Carisle, Morland is at west of Appleby while Dacre is west of Penrith (EdenDTC, 2011) (figure 3.12).

3.5.2. Eden DTC experimental design, gauging station, sampling and laboratory analyses

The three Eden DTC sub-catchments apart from being hydrologically homogenous, have variations in elevation relating to the upland and lowland feature of the CHASM sub-catchments in this order Dacre>Morland>Pow. Another key sub-catchment characteristic in the experimental design that is also related to CHASM sub-catchments is the variability in agricultural intensity which is in the reverse order to elevation: Dacre<Morland<Pow. This inverse association between elevation and agricultural intensity was similar to the pattern observed in the CHASM sub-catchments. Although there are smaller sub-catchments within each of the Eden DTC sub-catchments, this study focussed on the gauging stations at the outlets. The

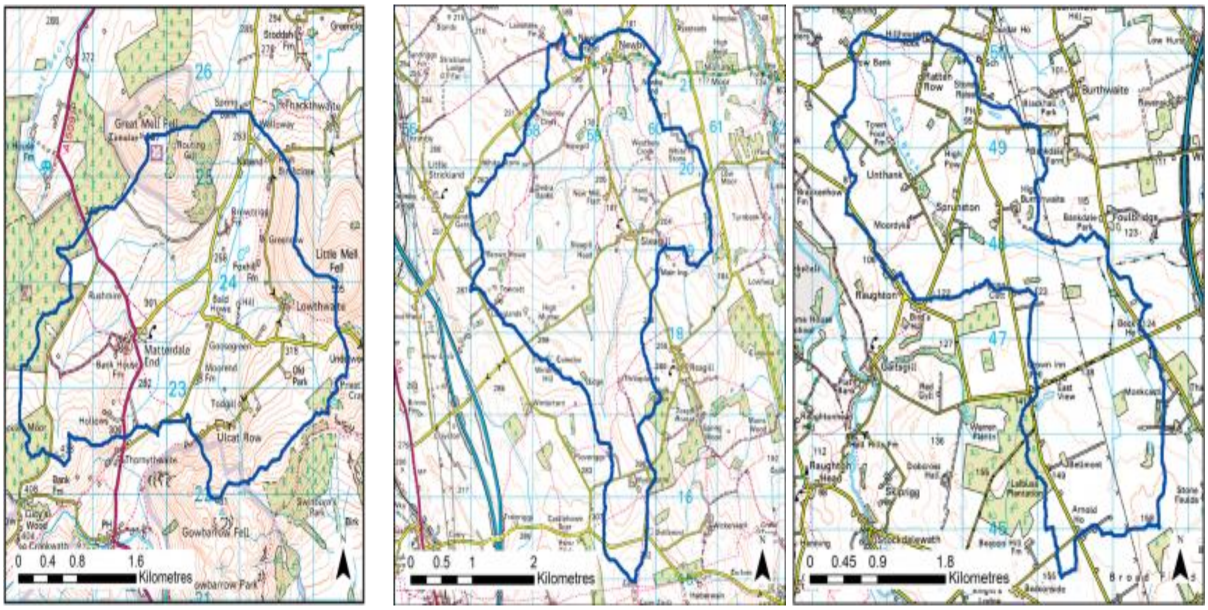


Figure 3.12 Dacre, Morland and Pow maps (EdenDTC, 2011)

technologically sophisticated continuous monitoring (CM) stations (Appendix F) at the outlets of the Eden DTC subcatchments (Pow and Morland) are equipped with a Hack Lange NH4D SC Ammonium Sensor, Hach Lange Nitratax SC Sensor and a Hach Lange PHOSPHAX process photometer, which measures the ammonium, nitrate and phosphate (TP and SRP) content of the river respectively. There is also a multiparameter YSI sonde measuring turbidity, ammonium, conductivity, temperature, pH, chlorophyll and dissolved oxygen content of the river. This study focused on nitrate, phosphate and turbidity from these field instruments. These water quality vaiables are sampled and analysed in-situ and the data are logged at 15 minute time step.

An automatic water sampler (autosampler) and a Time Integrated Mass-flux sampler (TIMs) were also installed (EdenDTC, 2011). The Dacre sub-catchment has every item of equipment except for that which sampled and analysed in-situ for nitrate, TP and TRP of the river water. However, it is also equipped with an autosampler that collects samples that were analysed manually in the laboratory using the standard methods for measuring suspended sediment concentration, nitrate and phosphate. The resulting data represent a reference against which the data collected and analysed in-situ by the continuous monitoring stations were compared. The data were also very useful for making comparisons among sub-catchments.

3.5.3. Data collection

The data from the DTC project have been collected, archived and linked to the file server by the DTC team at Newcastle University, and were accessible for this study for further analysis. Details of the analysis will be discussed in future chapters.

3.5.4. Summary of spatial, hydrological and water quality data used for this study

The spatial datasets used for the catchment characteristics (section 3.2) are obtained from existing spatial datasets summarised below (table 3.3). The flow data are from combination of sources involving the author (CHASM study), the EA, the National River Flow Archive (NRFA) and the EdenDTC database (table 4.1). More details on flow data from CHASM project is in chapter four (see Table). The nutrient data sources are in two classes: the low frequency monitoring (LF) and the high frequency monitoring (HF) datasets. The LF water quality data were primarily obtained from grab sample during the seasonal and spot sample campaigns by the author. The HF water quality data was obtained from the EdenDTC database. The summary of the hydrological and water quality data is in table 3.4.

Data	Source	Format
Elevation	Edina Digimap	Raster and shapefile
Land use	ITE land cover map of Great Britain 2000	Shapefile
Soil classification	Soil map of England and Wales (Thompson and Avis, 1983)	Paper map
	EdenDTC project (www.edendtc.org.uk)	Paper map
Geology	Edina Digimap/ British Geological Survey	Shapefile
HOST	Macaulay Institute (www.macaulay.ac.uk/host/)	Shapefile

Table 3.3 Summary of the spatial datasets

Data	Frequency	Parameters	Source
Nutrient	LF	SS, NO_3, total and soluble reactive P	Author (CHASM study)
	HF	Turbidity, NO_3, total P and total reactive P	EdenDTC database (www.edendtc.org.uk)
Hydrology	HF	Stage data collected from GG, RD, SD, BB and AP. Rainfall data from GG and GM	CHASM gauge stations (collected by the author with the exception of Artegarth station)
	HF	Stage and discharge data for KS, GM, TS and GC	EA and NRFA
	HF	Rainfall and discharge data for Dacre, Morland and Pow	EdenDTC database (www.edendtc.org.uk)

Table 3.4 Summary of flow and water quality datasets

*LF implies low frequency sampling while HF represents high frequency sampling

3.6. Modelling

It is essential to extend the findings beyond the Eden sub-catchment. The TOPCAT-NP model has minimum parameter requirement and yet captures the essential properties and processes in non-linear sub-catchments at different scales. This will be discussed in more detail in Chapter 7 of this thesis.

3.7. Summary

This chapter highlighted the key characteristics of the Eden sub-catchment as it relates to this study. The multi-scale experimental design captures a range of sub-catchment characteristics stretching from 1 to 1373 km^2. There are total of nine sub-catchments under the CHASM project, seven of which are nested giving a basis to investigate the spatial dependency in suspended sediment and nutrient dynamics in the Eden catchment. Near continuous data that were supplied by the DTC team from the three DTC sub-catchments, provide opportunities to identify the processes driving nutrient transport. The sub-catchments are situated at a range of elevations and also contain contrasting land uses. The two projects therefore provided a rare opportunity to gain an insight into the mechanisms of nutrient loss into the River Eden, and the TOPCAT-NP model will later in this Thesis provide a means of generalising the findings, by testing how various management options arising from the understanding gained of the mechanisms of nutrient loss can help tackle the problem(s).

Chapter 4: A Spatial Scale Evaluation of the Nutrient and Suspended Sediment Regime of the Eden Catchment

4.1. Introduction

A reasonable assessment of nutrients and nutrient-associated suspended sediment concentration and export is critical to addressing the problem of nutrient pollution and attendant ecological problems in rivers. Hydrological processes occurring in river basins have the potential to drive the nutrients reaching these rivers. This chapter presents the quantification and results of the hydrological and nutrient variables in spatial scale context using the CHASM study platform. The results of some soil properties that relate to nutrient and sediment concentrations in the river are also presented. Details of the field and laboratory studies for both the soil and water quality variables have been reported in Chapter 3.

4.2. Hydrological Characterisation

The transfer of nutrients from soil to water starting from mobilisation from source to delivery (Eden Demonstration Test Catchment, 2014b) occurs through various hydrological pathways that export nutrients to the river. In this section the characterisation of precipitation and river flows will be considered separately.

4.2.1. Precipitation

During the course of this study, two automatic weather stations (AWS) installed by the CHASM project were in operation at Gais Gill and Great Musgrave. The data from the AWS at Great Musgrave was chosen to describe the precipitation of the Eden catchment because it has data covering the entire study period. The graph of the rainfall data obtained from the Great Musgrave station is presented (figure 4.1a) and covers a period from October 2011 to April 2013 representing the period that the field campaign for the scale related study was carried out. Unlike the Meteorological (Met) Office report, where it was stated that the 2012 summer was the wettest in 100 years (Met Office, 2012) and also confirmed at Morland, an Eden sub-catchment (figure 4.2), the AWS record in Great Musgrave (figure 4.1b) only indicated a marginal increase in flows during that summer when compared with the winter and the spring seasons earlier in 2012. The rainfall and runoff pattern at Morland gauge in the summer was wetter following a long dry spell that occurred in the winter and spring. The rainfall recorded by the AWS in the summer at Great Musgrave might

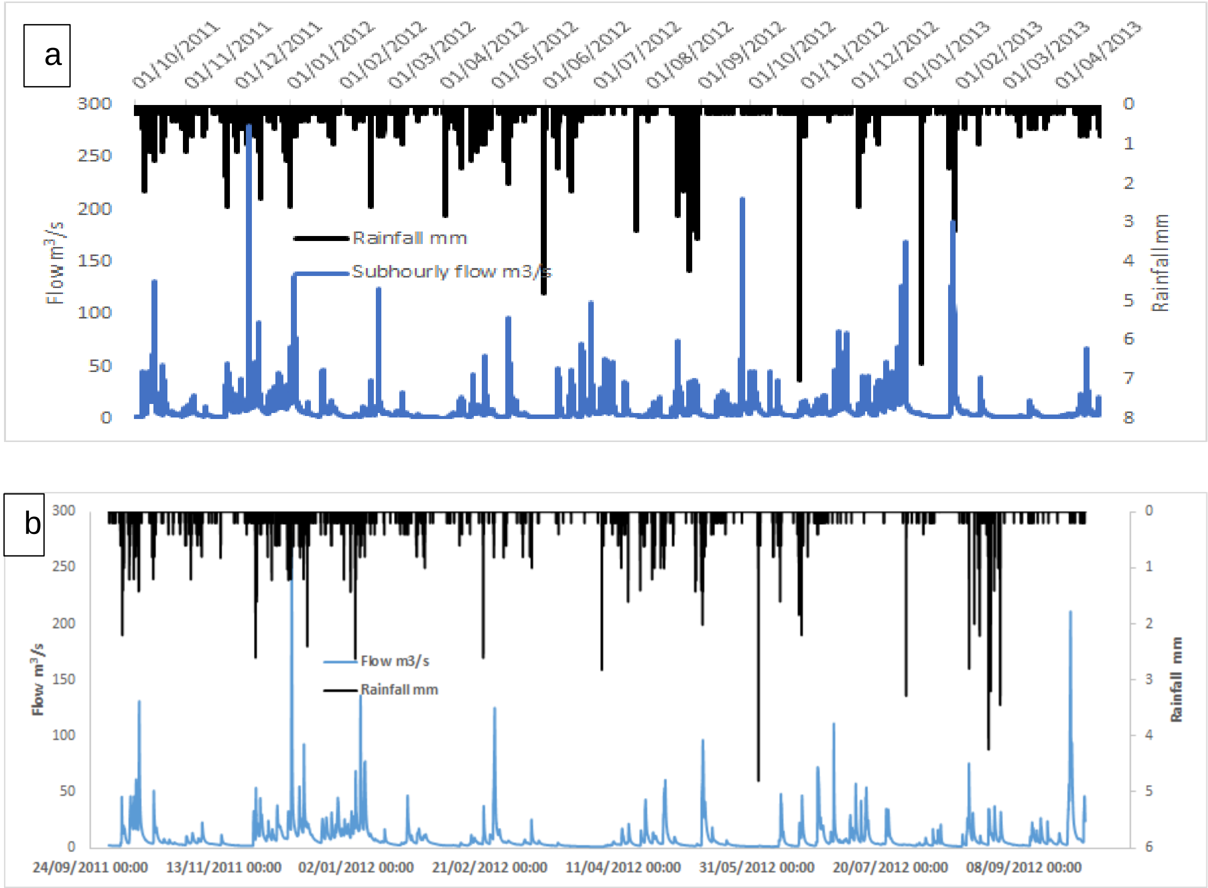


Figure 4.1 Sub-hourly rainfall pattern at Great Musgrave for period covering (a) April 2011-April 2013 and (b) October 2011- September 2012

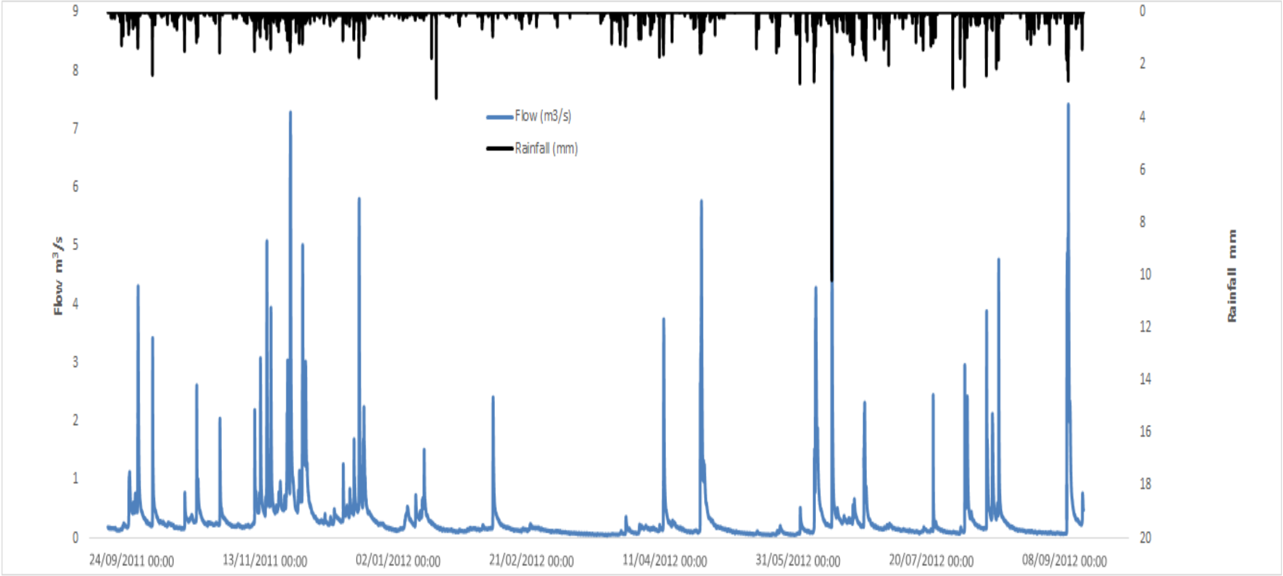


Figure 4.2 Sub-hourly rainfall and flow pattern; Morland subcatchment from October 2011 - September 2012

have been affected by environmental factors such as wind or a momentary failure in the AWS, because the equipment twice recorded error values in June and July that were too high for a measurement at 15 minutes time step and these were removed from the record. The annual rainfall (783.6 mm) recorded by the Great Musgrave station for the year 2012 (when most of the seasonal campaigns for this study was conducted) was drier in comparison to the average SAAR value (1270 mm) for the 1961-1990 period (Barber, 2013). The long dry spell may have been responsible for the lower value. The mean rainfall in the Eden was shown to be linearly related to elevation (Walsh, 2004).

4.2.2. Flow

The gauging stations that generated the stage and flow data are provided by the CHASM project and EA respectively (see table 4.1). The stage data were converted to flow data using rating coefficients (Appendix A). Figure 4.1b and figure 4.2 show the flows for the water year covering October 2011 to September 2012 in the Eden catchment. An important observation is the comparatively unusually dry winter in the 2011 – 2012 water year and it also presents the summer, regarded as the wettest in 100 years (Met Office, 2012). Interestingly the summer seasonal campaigns were carried out during this period. Kirkby Stephen (KS) is chosen as a representative sub-catchment to show the flow duration curve (FDC) and summary statistics for the Eden catchment because its size, land use and other catchment characteristics represent the investigated sub-catchments of different range of sizes. There is also a long record of flows dating back to 1972 (apart from a few years for which data are missing) and this sub-catchment has been used by other researchers who investigated the Eden catchment (Mills, 2009; Barber, 2013). The summary statistics and the FDC comparing the historical data (1972 - 2011) with 2011 and 2012 data, including the periods when the four seasonal campaigns were conducted, are shown (table 4.2**,** figure 4.3). Although a number of spot samples were collected up to April 2013 the FDC for 2013 was not included because the data from the national archive for KS were incomplete (covering only January to September). The data for 2012 were obtained by downscaling the data from Great Musgrave (GM) gauging station (the nearest) because the EA could not supply flow data for the year 2012. KS and GM have similar catchment characteristics and therefore the ratio of areas was used to downscale the flow data for GM. The relationship where the data overlapped between the downscaled flow data and observed data for KS showed a strong linear relationship ($R^2 = 0.96$) leading to a strong confidence in the technique. Wade *et a*l. (2012) also directly used the flow data at Binfield to interpret the hydrochemistry of a nearby station, The Cut at Bray. The details of missing data from some of the gauging stations used for this study will be discussed later. The two years, 2011 and 2012, with mean flow of 3.5 m^3/s and 3.0 m^3/s respectively, were each wetter than the mean flow (2.6 m^3/s) from the long term data.

Catchment	Monitoring equipment	Data type	Provider	Comment
Gais Gill	Diver	Stage	CHASM	stage downloaded and flow calculated by the author
Ravenstonedale	Diver	Stage	CHASM	stage downloaded and flow calculated by the author
Smardale	OTT Thalimedes	Stage	CHASM	stage downloaded and flow calculated by the author
Great Musgrave	Gauge staff, Weir, etc.	Flow	EA	Flow data supplied by EA
Appleby	Gauge staff, Weir, Diver, etc.	Flow	EA, CHASM	Stage for the diver downloaded and flow calculated by the author
Temple Sowerby	Gauge staff, Weir, etc.	Flow	EA	Flow data supplied by EA
Great Corby	Gauge staff, Weir, etc.	Flow	EA	Flow data supplied by EA
Blind Beck	OTT Thalimedes	Stage	CHASM	stage downloaded and flow calculated by the author
Kirkby Stephen	Gauge staff, Weir, etc.	Flow	EA	Flow data supplied by EA

Table 4.1 Stage and flow monitoring equipment in the River Eden and tributaries

Note: CHASM represents Catchment Hydrology and Sustainable Management while EA stands for Environment Agency

Period	Daily flow (m^3/s)				
	Mean flow	Q10	Q50	Q95	Maximum
1972 – 2011	2.6	6.52	1.02	0.17	43.8
2011	3.5	8.3	1.52	0.34	72.1
2012	3.0	7.15	1.60	0.44	35.0

Table 4.2 Flow statistics for the River Eden at Kirkby Stephen (based on mean daily flow)

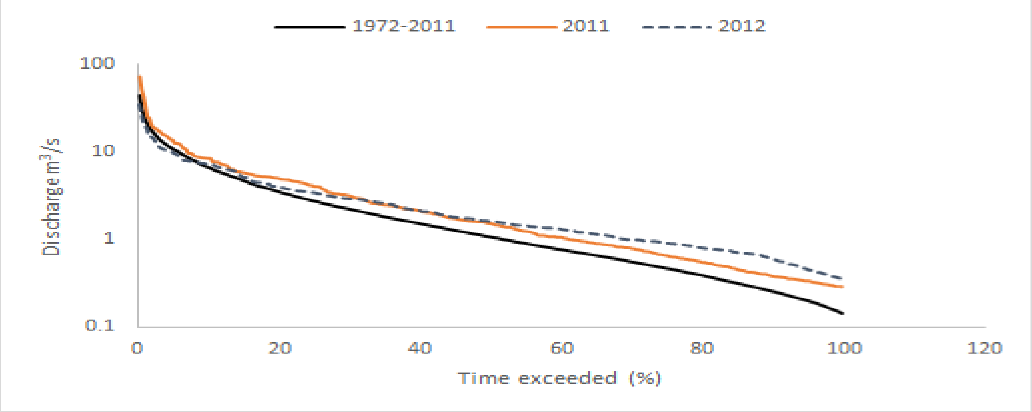


Figure 4.3 River Eden at Kirkby Stephen flow duration curve (based on mean daily flow) comparing the 2011 and 2012 data with data from 1972 – 2011

Dealing with missing flow data

The summarised details of the equipment deployed in all the catchments for the purpose of measuring river flows and the type of data they generate have been shown in (table 4.1). However, there were challenges in the acquisition of data from some gauging stations during the course of this study. The former Diver (stage measuring device) installed at Gais Gill (1.1 km^2) was last downloaded in June 2011 but was found missing in September 2011. A new device was later installed but a new rating curve could not be developed due to the time constraints. A linear regression technique using the overlapping data from the first device and a nearby gauging station at Artlegarth (2.9 km^2) was used to both infill the missing data and also to extend the flow data at Gais Gill (GG) well into the period of stage measurement by the new device at GG. Performing linear regression between the flow data downloaded before the first GG device was lost and the flow data for Artlegarth seems reasonable even though there was some “noise” in the relationship (R^2 = 0.64) (figure 4.4a). A regression equation (R^2 = 0.94) between the ‘extended’ flow data and the new stage data was used to update the flow data for GG every time that the latest device was downloaded (figure 4.4b). This is in agreement with

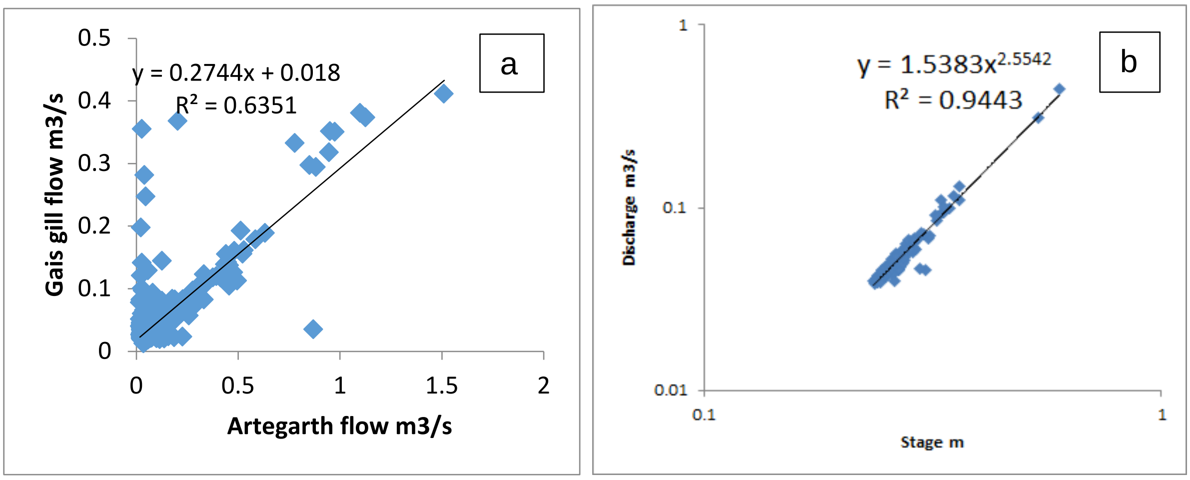


Figure 4.4a-b Regression analyses used to generate flow data for Gais Gill station after the first device was lost in November 2011

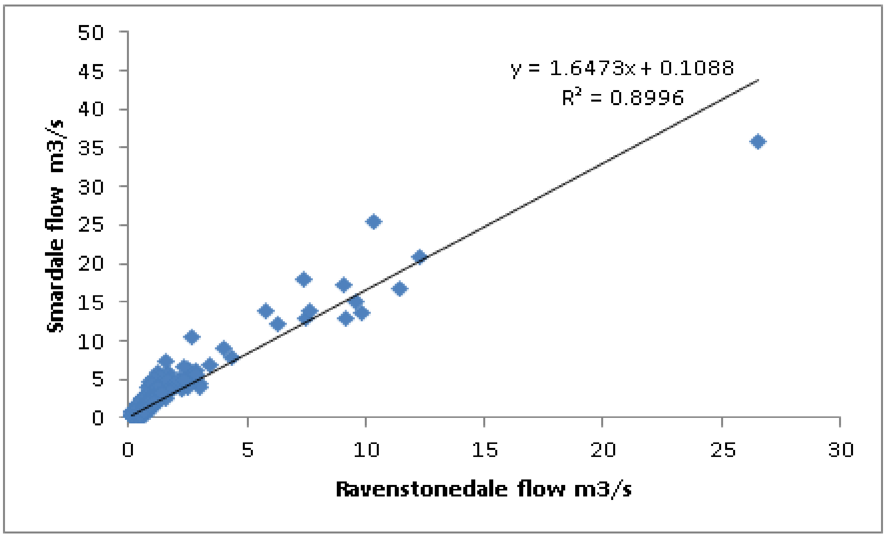


Figure 4.5 Regression analysis used to generate flow data for Smardale station

the approach of Halliday *et al*. (2013) who estimated the flow at the Upper Hafren through a strong linear regression with the flow at the Lower Hafren.

When the OTT Thalimedes (a stage measuring device) at Smardale (37 km^2) was discovered broken on May 2012, a similar regression technique was used to infill the data gap (R^2 = 0.90) using data from this gauging station and another one in close proximity, Ravenstonedale (26 km^2), that shares similar catchment characteristics (figure 4.5). The EA database for Kirkby Stephen (69.4 km^2) was corrupted and the data for 2012 could not be retrieved as at the time of this report. The data from the nearest EA station that shares similar land use and essential catchment characteristics was downscaled (Great Musgrave (223.1 km^2), using the ratio of their areas to generate 2012 data for the Kirkby Stephen gauge. The equation is given by:

$$\frac{Q_{KS}}{Q_{GM}} = \frac{A_{KS}}{A_{GM}} \tag{4.1}$$

Where Q_{KS} and A_{KS} are the daily flow data and catchment area at KS respectively, and Q_{GM} and A_{GM} are the daily flow and catchment area at GM respectively.

The National River Archive has daily flow data for KS from January to September 2013 limiting the downscaling to only 2012. Figure 4.6 shows that there was a strong relationship ($R^2 = 0.96$) between the observed flow data and the downscaled data in KS over the periods the two data sets overlapped, indicating that the use of a downscaling technique at KS was reliable. Of the two types of equipment measuring stage data at Appleby, this study depended primarily on the Diver installed by the CHASM project because it had rating coefficients obtained for the section of the river where it was sited. There were very short data gaps in January 2012 and February 2013. Regression equation ($R^2 = 0.93$) between the stage data from the EA and the CHASM flow data from November 2011 to April 2013 was used to fill those gaps (figure 4.7).

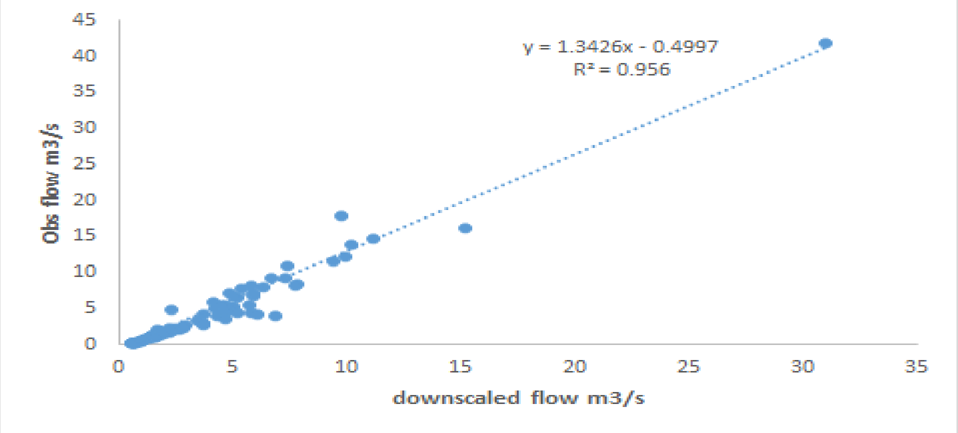


Figure 4.6 Relationship between the observed flow and downscaled flow at Kirkby Stephen from the period when the two data sets overlapped

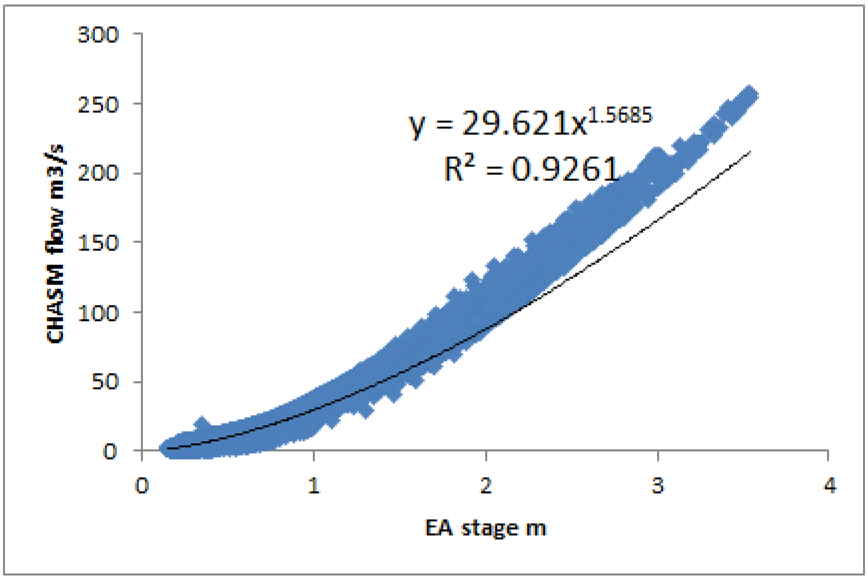


Figure 4.7 Regression analysis between the CHASM flow data and the EA stage data at Appleby

4.3. Nutrient and sediment concentrations

The adequate management of nutrients towards the achievement of good water quality requires an understanding of the distribution and dynamics of nutrients and sediment in a catchment. The processes governing nutrient export vary within a catchment, and water quality monitoring to evaluate non-point pollution sources must be such that this variability is taken into account. Water samples taken at the catchment outlet are believed to represent the catchment behaviour. All the data used for this study were collected at the outlets of the catchment near the EA, CHASM and DTC gauging stations. Important details about the data collection from the gauging stations have been discussed in the previous sections. Previously the soil and water sampling and laboratory analyses have been reported in Chapter 3.

4.3.1. The water quality variables and flow

The relationship between flow and the water quality variables at Kirkby Stephen is shown in figure 4.8. In almost all the seasons and for the annual plots the concentration of phosphorus fractions (total and reactive phosphorus) and suspended sediment were positively associated with flow. Nitrate concentration on the other hand was often negatively associated with flow. Occasionally nitrate exhibited a ‘dual pattern’. This is the case when at a given sampling station or study location, a nutrient exhibit relationship that have both positive and negative gradient

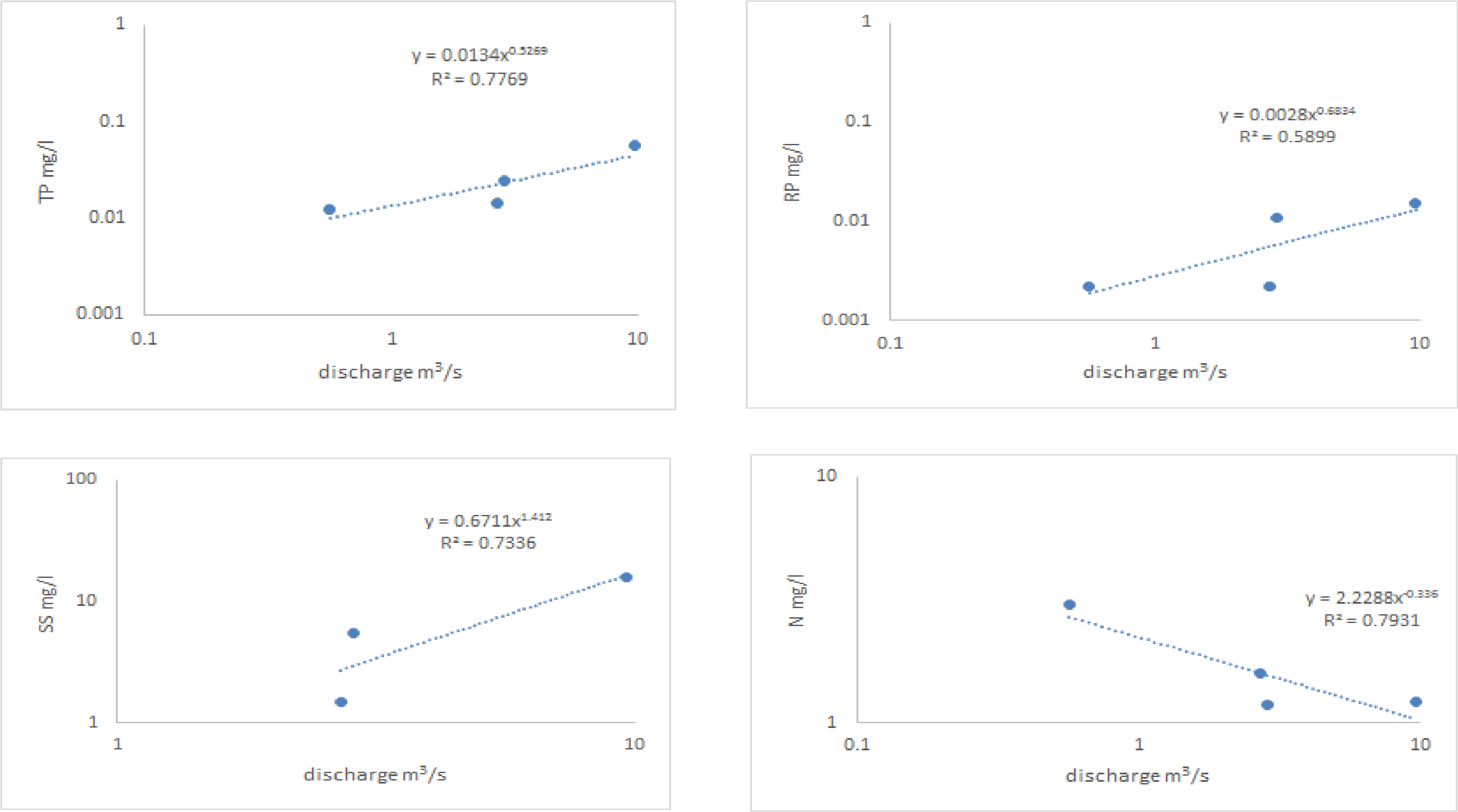


Figure 4.8 Relationships of TP, RP, SS and N with flow at Kirkby Stephen in autumn 2011 (one of the SS data point in autumn returns zero value and was therefore excluded so as to permit the graphing of the log-transformed data)

depending on flow. For instance, in the River Eden at Temple Sowerby (TS, 616 km^2), nitrate decreased at relatively lower flows and later increased with flow (figure 4.9). Smardale and Great Corby were the other catchments that showed a slight increase in nitrate at higher flow (Appendix B).

One of the inferences that could be drawn from contaminant flow relationship is their source(s). A river dominated by constant nutrients inputs will form a dilution curve with negative gradient as flow increases. Examples of such sources (point sources) are sewage treatment water works (STWs) and septic tank systems (STSs, view as multiple point sources under some circumstances). Groundwater, as nutrient source, also display dilution curve. Conversely, a river contaminant concentration/load controlled by rain-driven inputs will have a positive gradient of such contaminant with increasing flow. Sources (i.e. diffuse sources) that can be inferred include agricultural and septic tank inputs and within-channel mobilisation (Wood *et al.* 2005; Jordan *et al.*, 2007; Halliday *et al.*, 2015). Kirkby Stephen and most of the CHASM study sites show positive gradients when TP, RP and SS are related with flow indicating that they are likely sourced from agricultural inputs and through in-channel mobilisation whereas nitrate with negative gradients is from groundwater source (EA, 2013) and to a lesser extent STWs and STSs (due to low population density in the Eden). Temple Sowerby stands as an example of sub-catchments in the Eden that combined both point and diffuse sources.

It should be noted that the strength of the power law relationships of all the variables regressed with flow varied with location and season (table 4.3). The relationship was improved downstream (at the larger sub-catchments) compared to upstream, and in autumn 2011. It is known that flow increases downstream and autumn 2011 was reported to have high flows (see section 4.2.2), a pointer to the role that hydrology plays in nutrient concentrations in this catchment. This result also underscores the importance of collecting a good number of samples at high flows.

Sources of uncertainties

Although efforts were made to collect samples during seasons with high flows, constraints posed by the logistics that facilitated immediate visits shortly after rainfall events meant that most of the samples were collected during the falling limb of the hydrograph. Apart from a number of visits made during periods of known high flows, SS data collected earlier in the Eden catchment (Mills, 2009) that cover a wider range of flows were merged with the data collected during this investigation.

Besides, the WQP data from the DTC collected at a high resolution from the continuous monitoring (bankside) equipment captured the full range of flows and will compensate for the sampling constraints. These data also support and foster a further understanding of the nutrient transfer processes in the Eden catchment. The details of the study conducted using the DTC data are reported in the next chapter.

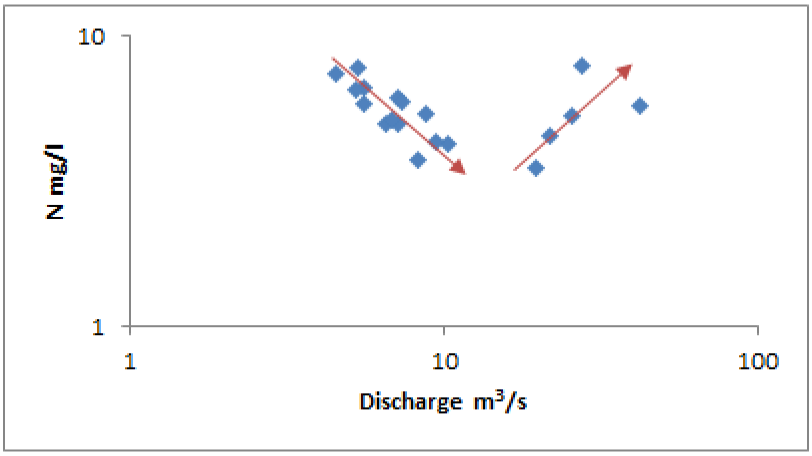


Figure 4.9 The dual relationship of nitrate with flow at Temple Sowerby for the 2011 – 2012 water year (i.e. the period of the seasonal campaign)

Station/area (km^2)	**WQV**	**R^2**				
		Autumn	**Winter**	**Spring**	**Summer**	**Annual**
Gais Gill (1.1)	TP	**0.768**	0.182	**0.479**	0.046	**0.049**
	RP	**0.573***	0.756*	**0.512**	0.931	**0.011**
	SS	**0.475***	**0.566***	0.495	0.531	**0.04**
	N	-	-	-	-	**0.243**
Ravenstonedale (26)	TP	**0.857**	**0.194**	**0.269**	**0.719**	**0.241**
	RP	**0.980**	**0.296**	**0.30**	**0.377**	**0.285**
	SS	**0.712**	**0.287**	**0.448**	**0.912**	**0.455**
	N	0.439	**0.520**	**0.014**	**0.017**	0.073
Smardale (37)	TP	**0.977**	**0.049**	**0.532**	**0.001**	**0.074**
	RP	**0.79**	**0.266**	**0.625***	**0.001**	**0.094**
	SS	**0.807**	**0.112**	**0.00005**	**0.124**	**0.543**
	N	0.98	**0.944**	**0.018**	0.726	0.067
Great Musgrave (223.1)	TP	**0.686**	**0.107**	**0.002**	**0.018**	**0.111**
	RP	**0.595**	**0.096**	**0.122**	0.412	**0.003**
	SS	**0.928**	0.006	0.499	**0.186**	**0.709**
	N	0.924	0.941	0.058	0.712	0.511
Appleby (334)	TP	**0.823**	**0.002**	**0.163**	**0.591**	**0.476**

Station/area (km^2)	**WQV**	**R^2**				
		Autumn	**Winter**	**Spring**	**Summer**	**Annual**
	RP	**0.922**	0.025	**0.133**	**0.048**	**0.013**
	SS	**0.858**	0.341	**0.008**	**0.495**	**0.638**
	N	0.968	0.938	0.773	0.761	0.611
Temple Sowerby (616)	TP	**0.209**	**0.752**	**0.97**	**0.926**	**0.463**
	RP	**0.012**	0.672	**0.945**	0.23	**0.233**
	SS	**0.8**	**0.193**	0.454	**0.592**	**0.752**
	N	0.56	0.968	0.941	0.609	0.377
Great Corby (1373)	TP	**0.312**	**0.316**	**0.741**	**0.258**	**0.147**
	RP	**0.008**	**0.577**	**0.642**	0.077	**0.069**
	SS	**0.866**	**0.359**	**0.704**	**0.478**	**0.691**
	N	0.375	0.769	0.935	0.943	0.531
Blind Beck (9.2)	TP	**0.122**	**0.514**	0.001	0.024	**0.111**
	RP	**0.0004**	**0.094**	**0.064**	**0.137**	**0.076**
	SS	**0.19**	**0.135**	**0.016**	0.617	**0.051**
	N	0.627	0.990	0.640	0.162	0.228
Kirkby Stephen (69.4)	TP	**0.777**	**0.973**	0.509	0.046	**0.014**
	RP	**0.59**	**0.7**	0.55	0.303	0.029
	SS	**0.734***	0.129*	**0.181**	**0.341**	**0.722**
	N	0.793	0.318	0.239	0.698	0.25

Table 4.3 Annual and seasonal R-square values of the relationship between flow and the Water quality variables

Note: Graphs having a R^2-value in bold have positive slope. * indicates that one of the data points in that season has reported a zero concentration (i.e. below the detection limit), WQV represents Water Quality Variables, TP, RP, SS and N represent total phosphorus, reactive phosphorus, suspended sediment and nitrate respectively. With the exception of Gais Gill, Blind Beck and Appleby where their data was not found, annual SS was merged with the SS data collected in the same catchment by Mills (2009).

4.3.2. Seasonality in the concentrations of the water contaminants

Figure 4.10 depicts the graphs showing a seasonal comparison amongst the contaminants and represents the means of the four visits in each season. Interestingly, the unusual flow recorded in the water year from September 2011 to August 2012 (see section 4.2.2) appears to influence the nutrient concentration in the River Eden. There were high concentrations of TP and SS in the unusually wet autumn although more instances of higher TP concentrations were recorded in the 'record wet' summer. The concentration of RP was clearly highest in summer and this was closely followed by the concentration in the spring. During the relatively dry

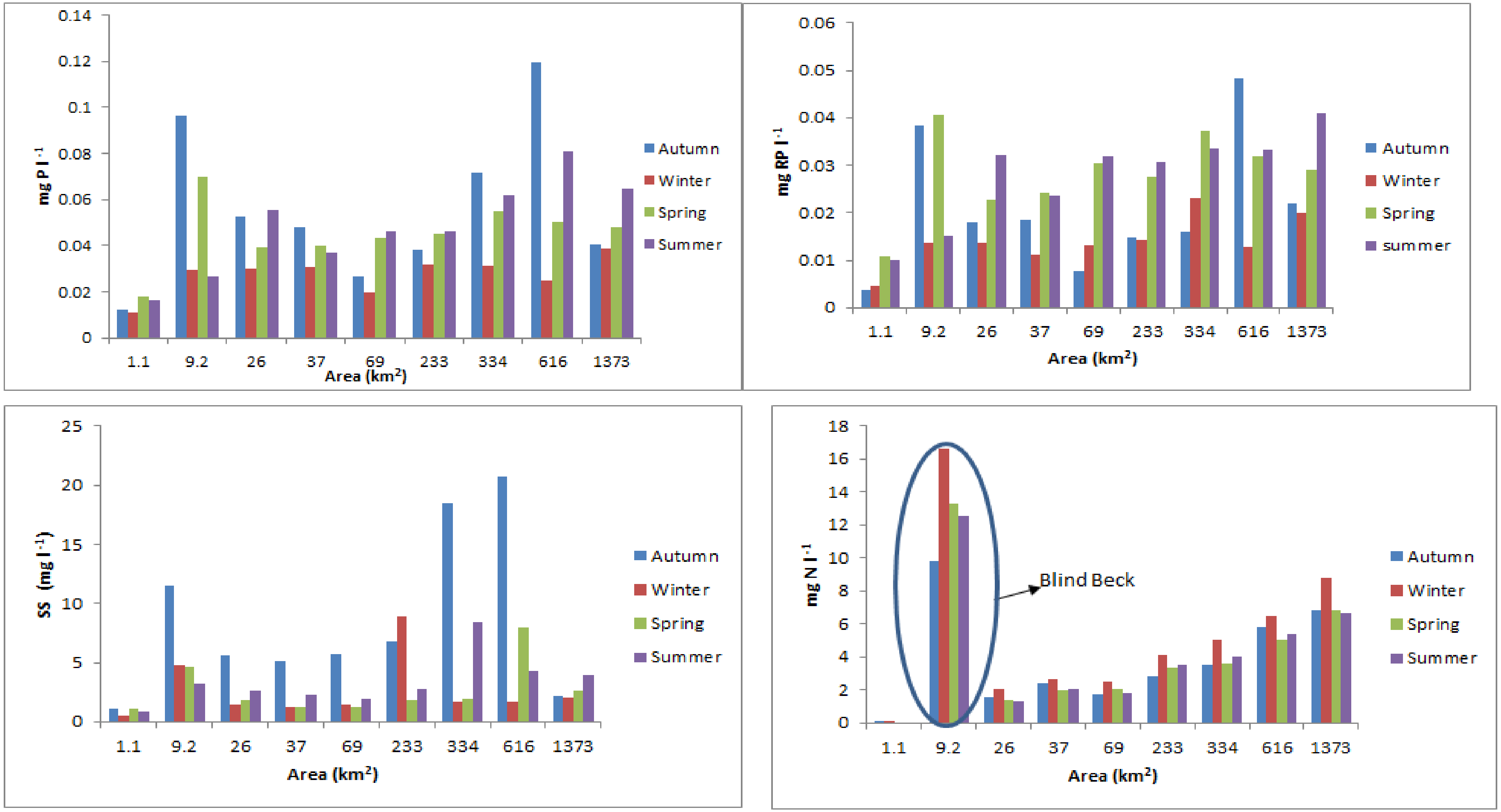


Figure 4.10 Seasonal nutrient concentrations in the Eden catchment during the seasonal campaign as a function of catchment area

winter SS and TP concentrations were generally lowest compared to other seasons. The result was mixed with the RP concentrations. It should be noted that the winter study took place late in the season, a drier period in the winter, due to logistical constraints. The drop in TP and SS concentrations at GC was probably due to a lower presence of poorly drained soil (and associated surface run off) compared with TS (See Section 4.3.4) and also the influence of ‘clean’ River Eamont coming from Lake Ullswater that is a tributary to River Eden at Great Corby. Contrastingly, nitrate was highest in the unusually dry winter and lower in the other seasons. The tendency of nitrate to increase at low flows has been described as a dilution effect (Quinn *et al*. 2007). Apart from the variability in flow, the variability in the weather conditions appeared to influence nitrate concentration in the headwaters.

Impact of weather conditions on algal growth and nitrate concentration in the headwater sub-catchment

The variations in nitrate concentrations at Gais Gill (GG) between the cold and warm periods are shown in table 4.4. Nitrate concentrations dropped to zero (i.e. below detection limit) during the warmer periods especially in spring and summer. This depletion was associated with a period when the algal growth flourished (based on visual assessment) (figure 4.11), and presumably stimulated in-stream biochemical processes leading to the assimilation of the nitrate for the cell growth of algae. Seasonal cycles with concentration minimum occurring in the summer and coinciding with the period of low flow and high temperature was also observed in the Upper Hafren catchment in Plynlimon, Wales (Halliday *et al.*, 2013). The minimum concentration was attributed to biological uptakes which peak in the summer. This is due to less scouring/flushing, more residence time as a result of low flow and high temperature; conditions which favour algal bloom. Thus, seasonality not only controlled the nutrient concentrations in the river through flow but also through the impact of the associated changes in temperature, which moderated the ecological and physical processes in the river. Beyond the temporal variability in the concentration of the water quality variables there was also some spatial variability.

Date	**N (mgL^{-1} NO_3-N)**	**Flow (m3/s)**
01/11/2011	0	0.081
03/11/2011	0	0.065
21/11/2011	0.0795	0.039
24/11/2011	0	0.117
16/12/2011	0.2095	0.049
06/03/2012	0.121	0.057
14/03/2012	0.075	0.05
19/03/2012	0	0.05
21/03/2012	0	0.049
02/05/2012	0	0.049
09/05/2012	0	0.046
16/05/2012	0	0.06
21/05/2012	0	0.05
25/06/2012	0	0.073
23/07/2012	0	0.06
26/07/2012	0	0.061
31/07/2012	0	0.056
06/08/2012	0	0.066
19/09/2012	0	0.064
10/10/2012	0	0.05
07/11/2012	0	0.052
20/12/2012	0	0.105
14/01/2013	0.262	0.04
30/01/2013	0.156	0.143
27/02/2013	0.218	0.097
26/03/2013	Snow	Snow
10/04/2013	0.223	0.096
26/04/2013	0	0.126

Table 4.4 Variations in nitrate concentration in cold and warm weather at Gais Gill

Figure 4.11 Variation in algal growth at Gais Gill in (a) cold (27/02/2013) and (b) warm weather (31/05/2012)

4.3.3. The pattern of nutrient and sediment concentrations in the nested Eden catchment and land use

The nested network of the Eden catchment was explored to check the spatial variability of the parameters in the river. Of the nine sub-catchments selected under the CHASM project for this study, two were outside the nest: Blind Beck (BB, 9.2 Km^2) and Kirkby Stephen (KS, 69.4 km^2). These were taken out of figure 4.10 in order to obtain a continuum (of catchments) and this is presented in figure 4.12a. The phosphorus fractions (TP and RP) and SS concentrations share similar patterns. Although there was an increase in the concentration of these three parameters downstream when compared to the headwaters the spatial pattern was indistinct. On the other hand the nitrate concentration clearly increased and showed a distinct spatial pattern downstream.

A closer consideration of figure 4.10 shows that Blind Beck (9.2 km^2), a relatively small catchment, clearly and consistently had the highest concentrations of nitrate (18.6 mg l^{-1} NO_3-N was recorded on 21/11/2011 during the autumn campaign) and other variables measured here were amongst the highest values of all sites. A study conducted in the catchment in 2008, (Barber, 2008), indicated that Blind Beck (BB) has high nutrient contents because of intensive agricultural activities in the catchment. Changes in dominant processes and land management (e.g. biological uptakes, agricultural inputs, etc.) can be inferred as part of the important factors determining variation in stream concentrations among catchments. These processes or management seems to have a spatial pattern that can be linked to catchment characteristics within the nested catchment system of the River Eden (see the sub-sections below). A change in dominant processes has been reported between two sub-catchments in Plylinmon Wales. The stream concentration of nitrate in the Upper Hafren dominated by moorland was influenced by biological uptakes whereas at the forested Lower Hafren, the uptake effect was masked by a combination of advection, dispersion and soil processes (Halliday *et al*. 2013)

As an alternative explanation, therefore, the spatial scale dependency in nutrient content in the River Eden might have been related to the intensity of land use and some of the other catchment characteristics which increase downstream as shown in Chapter 3 (table 3.2).

4.3.4. Relationships between catchment characteristics and land area

Figure 4.12a presents a broad representation or a proxy of the relationship between catchment characteristics and WQP, captured as area. The analysis of GIS using existing datasets made it possible to relate some of the catchment characteristics with area as shown in figure 4.12b. The negative power law relationship ($R^2 = 0.90$) of catchment mean elevation with area implies that larger catchment are at lower elevation in the nested system studied. When the non-nested sub-catchments were included (i.e. BB and KS), the relationship weakens ($R^2 = 0.16$). Blind Beck, though occupied a smaller area (9.2 km^2) has the lowest mean elevation (220 m), an indication that the relationship of catchment area with mean elevation is not that straight forward. Further, Kirkby Stephen (69 km^2, 385 m) despite having larger catchment area than RD 26 (km^2, 351 m) and SD (37 km^2, 331 m), is at higher mean elevation. However, within the nested system in the Eden catchment, the catchment area can be regarded as an indirect representation of the mean elevation.

A catchment characteristic that is closely related to elevation is geology. Mills (2009) indicated that geology dictates the topography which in itself includes elevation amongst others. In the Eden, argillaceous rocks (mudstone and shale), that are more resistance to erodibility, predominantly underlain uppermost region. At the intermediate zone is the limestone while sandstone is at the lowland basin.

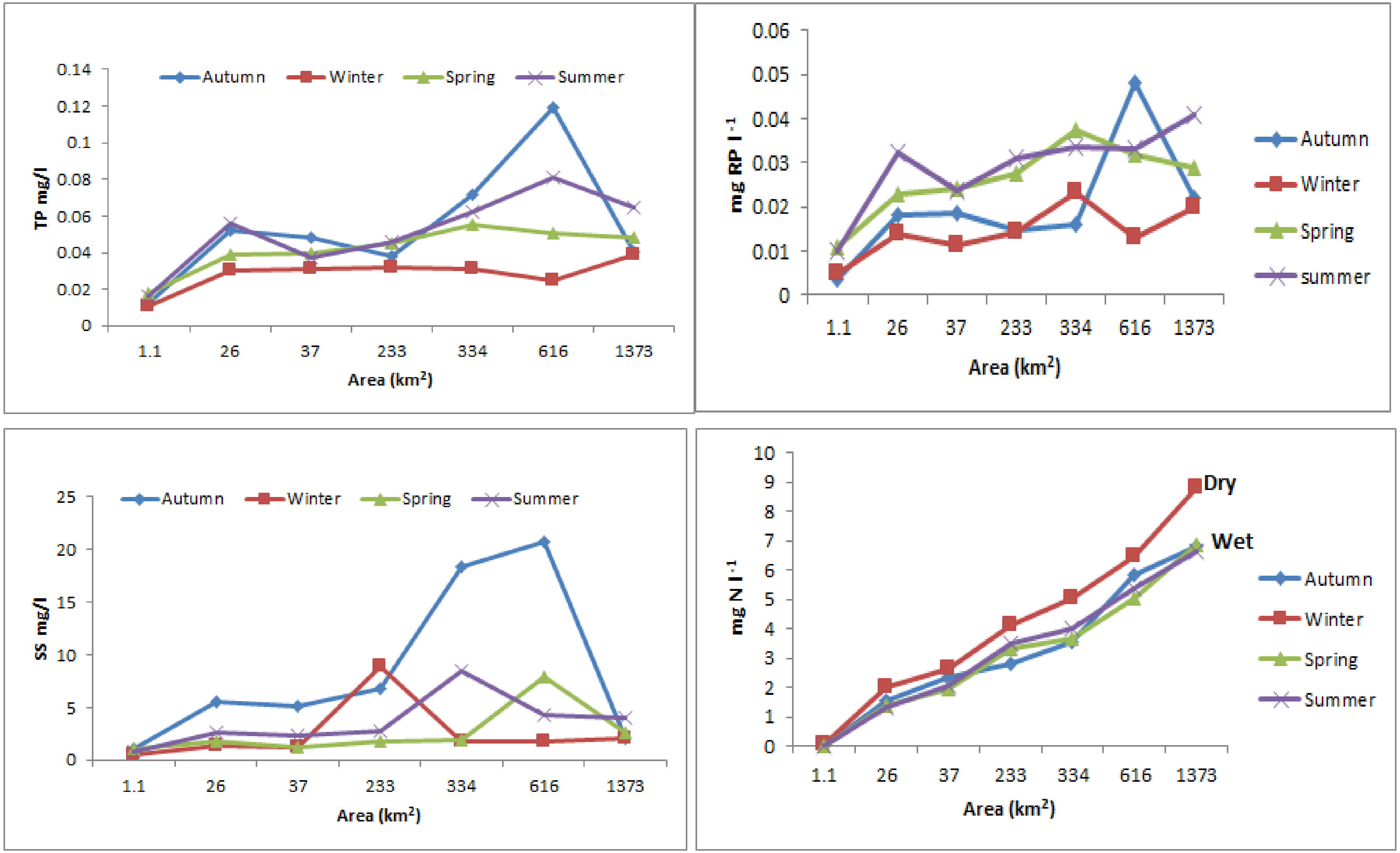


Figure 4.12a Spatial pattern of P, SS, RP and N along the Eden catchment nested system

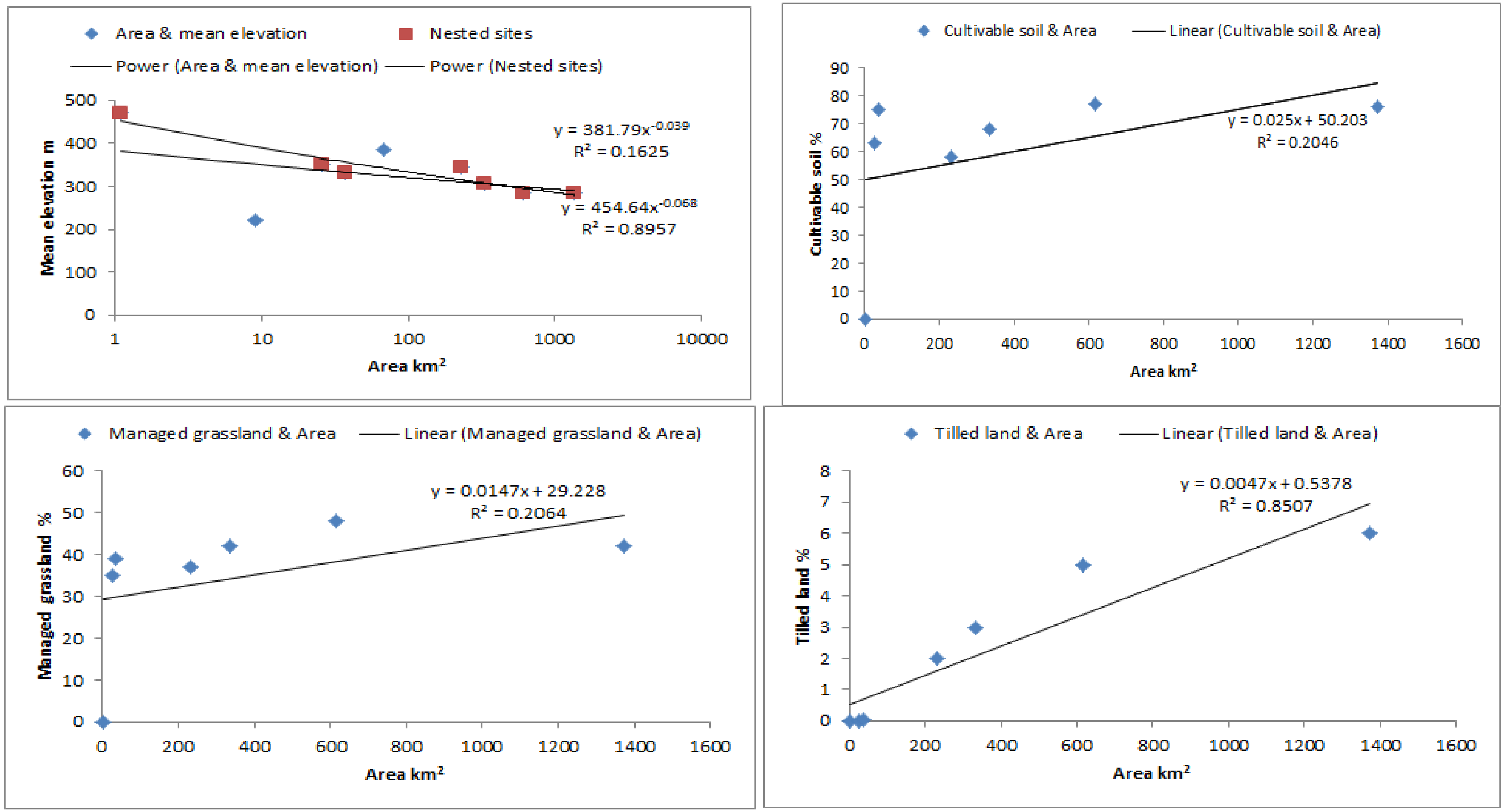


Figure 4.12b Relationships between some Eden catchment characteristics and catchment area

The Hydrology Of Soil Type (HOST) was also related to the area by isolating and pooling together free drain soil and poorly drain, slightly seasonal waterlogged soil, from other HOST classes (figure 4.12b). For this study, these two HOST classes were represented as cultivable soil partly because of their agricultural potential and also for ease of reference. The relationship between the HOST and catchment area appear to be non-linear but could not be fitted to power law as done with elevation because the existing HOST datasets indicated that the smallest subcatchments, located at the uppermost area of the Eden catchment, GG, is 100% peat. That is, it is has no cultivable soil (0%) and therefore could not be fitted to power law but was fitted to linear relationship. Although weak ($R^2 = 0.20$), there is positive linear relationship between the cultivable soil and the catchment area. Two domains are observable on the graph which appears to be the reason for the weak linear relationship: the ‘tributary domain’ and the main ‘River Eden domain’.

The tributary domain consists of GG (1.1 km^2), RD (26 km^2) and SD (37 km^2) having cultivable soil with 0, 63 and 75% respectively of which free drain component are 0, 35 and 56% respectively. The main River Eden domain, within the nested system, starts with GM (233 km^2), follow by AP (334 km^2), TS (616 km^2) and ends with GC (1373 km^2). In the HOST classification, cultivable soil accounts for 58, 68, 77 and 76% respectively while the free drain components are 37, 38, 35 and 45% respectively. It implies that SD in the tributary domain has higher cultivable soil than larger catchment such as GM and AP in the main River Eden domain. Further SD has the highest free drain soil (56%) whereas TS has the highest poorly drain seasonal waterlogged soil (42%). This is expected to be linked to both soil water (tile drainage) and fertility management (fertilizer and manure application) and should have implication in stream nutrient and SS concentration and yield.

To be more specific on land use, two of the classes chosen as representative of agricultural land use intensity were percentage of managed grass land and tilled land (figure 4.12b). Both land use were fitted to a linear graph for the same reasons stated under cultivable soil. Like cultivable soil, the linear relationship ($R^2 = 0.21$) between managed grassland and area was not strong. There are also two domains described above, except that the percentage managed grassland in SD is only greater than that of GM in the main River Eden domain. Another similarity with cultivable soil is the drop in percentage managed grassland at GC compared to smaller TS. It suggests that the managed grassland depends on the cultivable soil in the Eden catchment and the two should have similar impact on the water quality of the River Eden.

Tilled land has a stronger relationship (R^2 = 0.85) with the catchment area compared with managed grassland (figure 4.12b). It increases up to the catchment outlet at GC in a way similar to nitrate-area relationship (figure 4.12a) and may well be the dominant driver of the nitrate pattern in the River Eden. The downstream increase in managed grassland and tilled land compared to headwater further underpin the influence of land use on stream nutrient concentration. The similarity, in pattern, between managed grassland and cultivable soil in the Eden suggests the dependence of land use and the associated grazing livestock system on soil quality in the Eden. A soil study that compared stream nutrient concentrations between two catchments having contrasting land use intensity (and associated percentage of cultivable soil) is reported in section 4.3.6.

4.3.5. Relationships between the water quality variables and some catchments characteristics

The relationship between nutrients and SS concentrations, and elevation is shown in figure 4.13a. The negative relationship between these WQV and elevation suggests that elevation is not directly required to produce high stream concentrations of TP, RP, SS and N. The ease of cultivation at lower slope explains the reason that land use intensity increases relative to area, unlike elevation, as earlier reported. It implies that less manure and fertilizer input, and less soil exposure to forces of erosion is expected at higher elevation; hence, the negative relationship. The strength of the relationship is in this order: N (R^2 = 0.81) > RP (R^2 = 0.78) > TP (R^2 = 0.74) > SS (R^2 = 0.35). The stronger relationship among the nutrients compared with SS is a pointer to the fact that fertility management increases with the intensity of agricultural activities downstream.

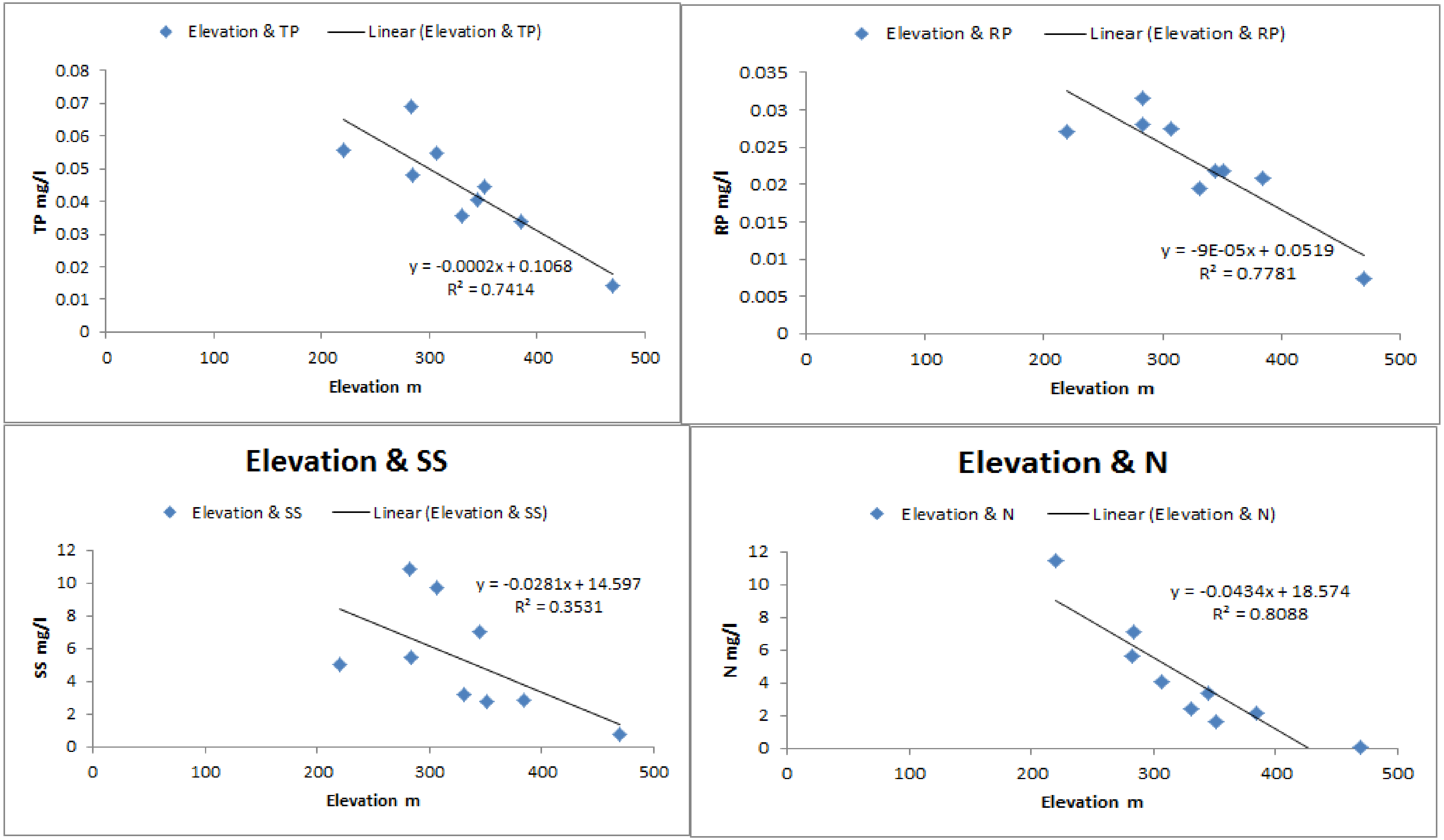


Figure 4.13a Relationships between nutrients, suspended sediment, and elevation

The scatter in SS relationship with elevation suggests that apart from soil exposure and perturbation due to land preparation etc. within the terrestrial catchment, other factors within and in the neighbourhood of the aquatic catchment may be contributing to soil loss or stream SS concentration. Mills (2009) conducted a field survey in the Eden catchment and identified some forms of sediment input within and in the immediate environment of the aquatic component of the catchment. These include bank erosion, livestock poaching, valley side scars, debris flow and in-channel sediment storage that can be re-worked during the next flood or high flow event.

The predominant pathways of transport of water quality variables/parameters vary and this can be influenced by soil type. Therefore the two HOST classes (poorly drain seasonal waterlogged soil and free drain soil) and cultivable soil were plotted against the nutrients and suspended sediment (figure 4.13b). Total P, RP & SS have remarkable relationship (R^2 = 0.74, 0.66 and 0.61 respectively) with poorly drain soil but their relationships with free drain soil are relatively weaker (R^2 = 0.30, 0.37 and 0.05 respectively; alternatively, SS relationship appears negatively slope as indicated by the orange line). Poorly drained soils are often clayey and enhances run off because of poor infiltration capacity. Run off leads to erosion, and P and suspended sediment are predominantly lost through this process. The scatter in the graph is probably due to in-channel and river bank sources such as re-suspension of sediment, P desorption etc. Less P is loss through leaching, a process that is enhanced in a free drain soil, and the weak relationship between free drain soil and SS is an indication that SS is rarely transported by infiltration process.

Unlike P and SS, nitrate had a stronger linear relationship (R^2 = 0.63) with free drain soil but weaker relationship (R^2 = 0.19) with poorly drain seasonal waterlogged soil. The comparatively stronger relationship with free drain soil is due to transport pathway that is enhanced by high infiltration capacity. This translates to high leaching which is a predominant means of nitrate transport. The scatter in this relations and/or the fraction of nitrate loss accounted for, by the relationship with poorly drain soil may have been due to tile drain (Gall *et al.*, 2015) installed in this soil, groundwater source and nitrate washed off via overland flow or runoff during the period of high storm.

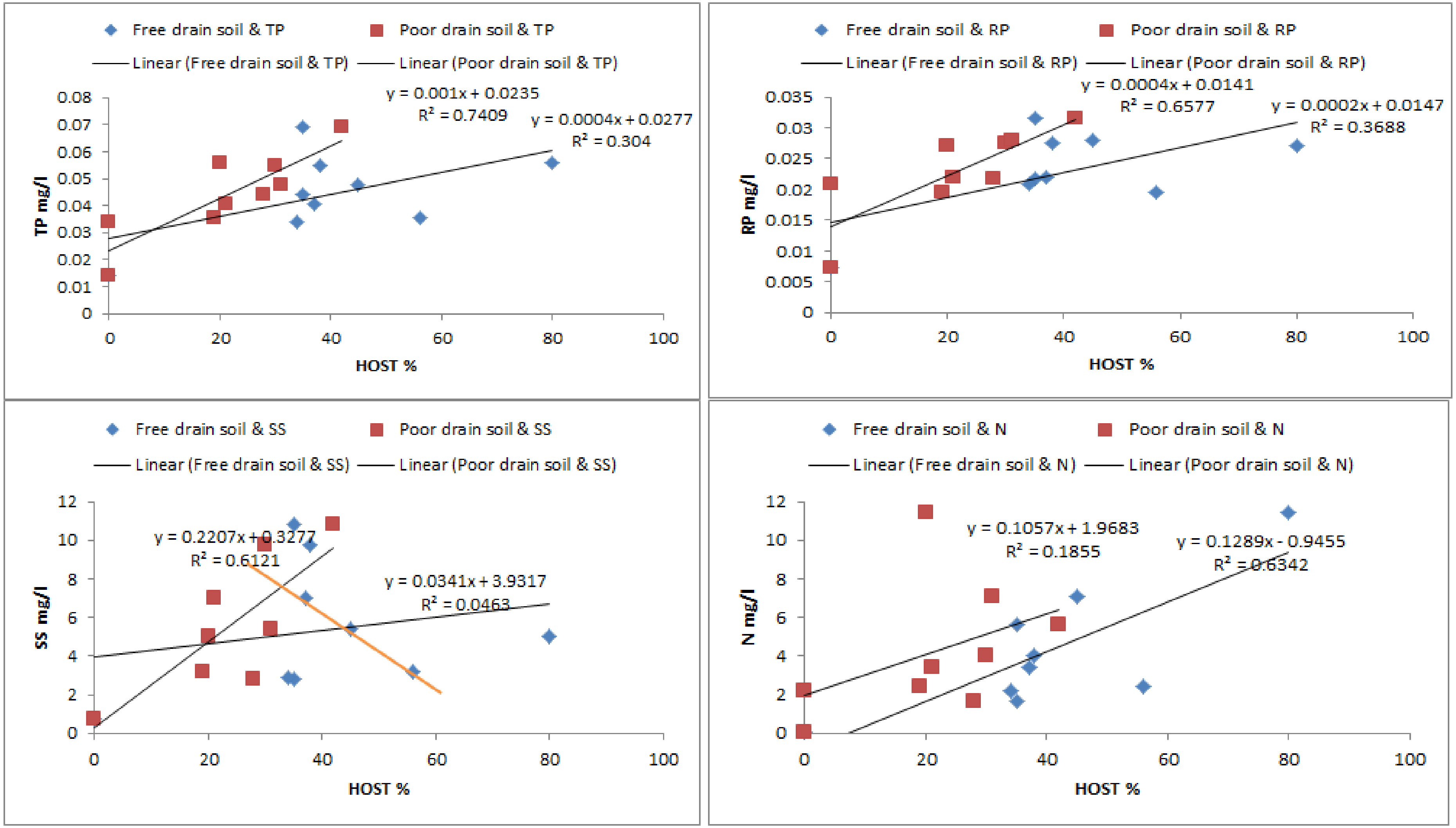


Figure 4.13b Relationships between nutrients, suspended sediment and some HOST classes

The nutrients and sediment was also compared with the two representatives of land use noted earlier, that is, managed grassland and tilled land (figure 4.13c and d). Total P, RP, SS and nitrate were positively related to managed grassland (R^2 = 0.79, 0.88, 0.51 and 0.90 respectively, all linear except nitrate that was exponential) but negatively related to unmanaged grassland (R^2 = 0.78, 0.87, 0.56 and 0.73 respectively, all linear although nitrate value increases to 0.82 when fitted to exponential curve) which suggests that intensity of land use increased the loss of these nutrients and sediment from the catchment whereas their stream concentration did not depend on unmanaged grassland. Apart from erosion process arising from land preparation, trampling and poaching associated with predominantly livestock system, as is the case with the Eden, which result in SS and associated P loss. Fertility management also drives the nutrient loss.

When TP, RP, SS and nitrate was regressed with tilled land, the linear relationships (R^2 = 0.51, 0.59, 0.33 and 0.80 respectively), was positive. A closer consideration of the strength of the relationship shows that nitrate was by far the highest unlike what obtains under managed grassland. The reason is probably due to the absence or comparatively minimal influence of poaching; trampling and P-rich animal droppings of livestock on tilled land which would have influenced stream SS and associated P concentrations. The fact that SS is comparatively weaker on both managed grassland and tilled land further supports the probability of considerable stream/river bank and in-channel contributions.

Urban land use is assumed to be an index of point sources arising from sewage treatment waterworks (STWs) and septic tank systems (STSs). Figure 4.13e depicts the relationship of TP, RP, SS and nitrate (R^2 = 0.26, 0.47, 0.19 and 0.56) with percentage of urban land use. The generally weak to marginal relationships is a reflection of low population density resulting in relatively low contribution from the urban sources in the Eden catchment. The stronger relationship with the more soluble RP and the soluble nitrate suggests STWs and STSs sources for the two nutrients. There could also be groundwater sources due to drilling activities (for the STSs and boreholes) in the catchment. It seems possible that drilled pits may facilitate quicker percolation of nutrient laden soil water to groundwater.

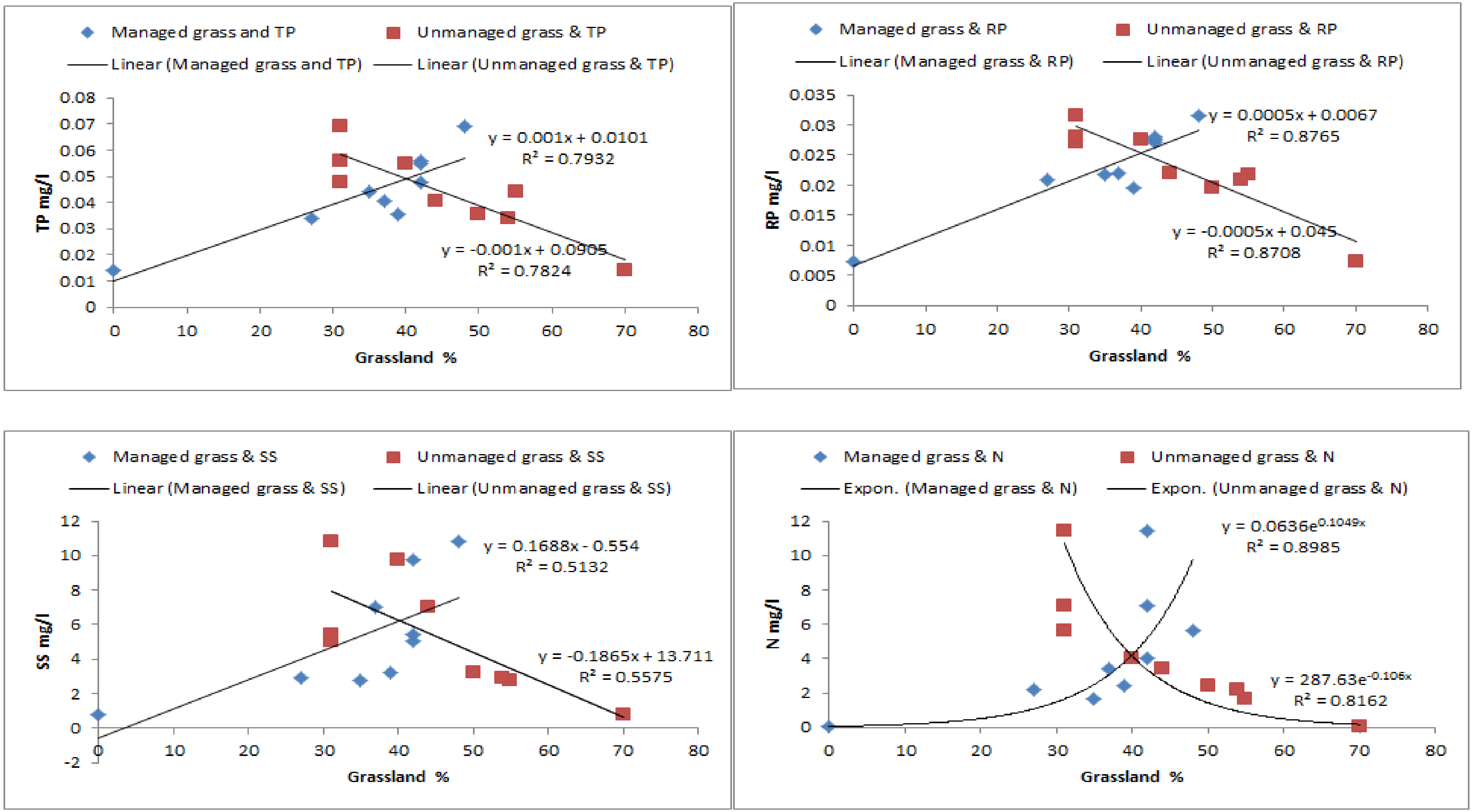


Figure 4.13c Relationships between nutrients, suspended sediment and grassland

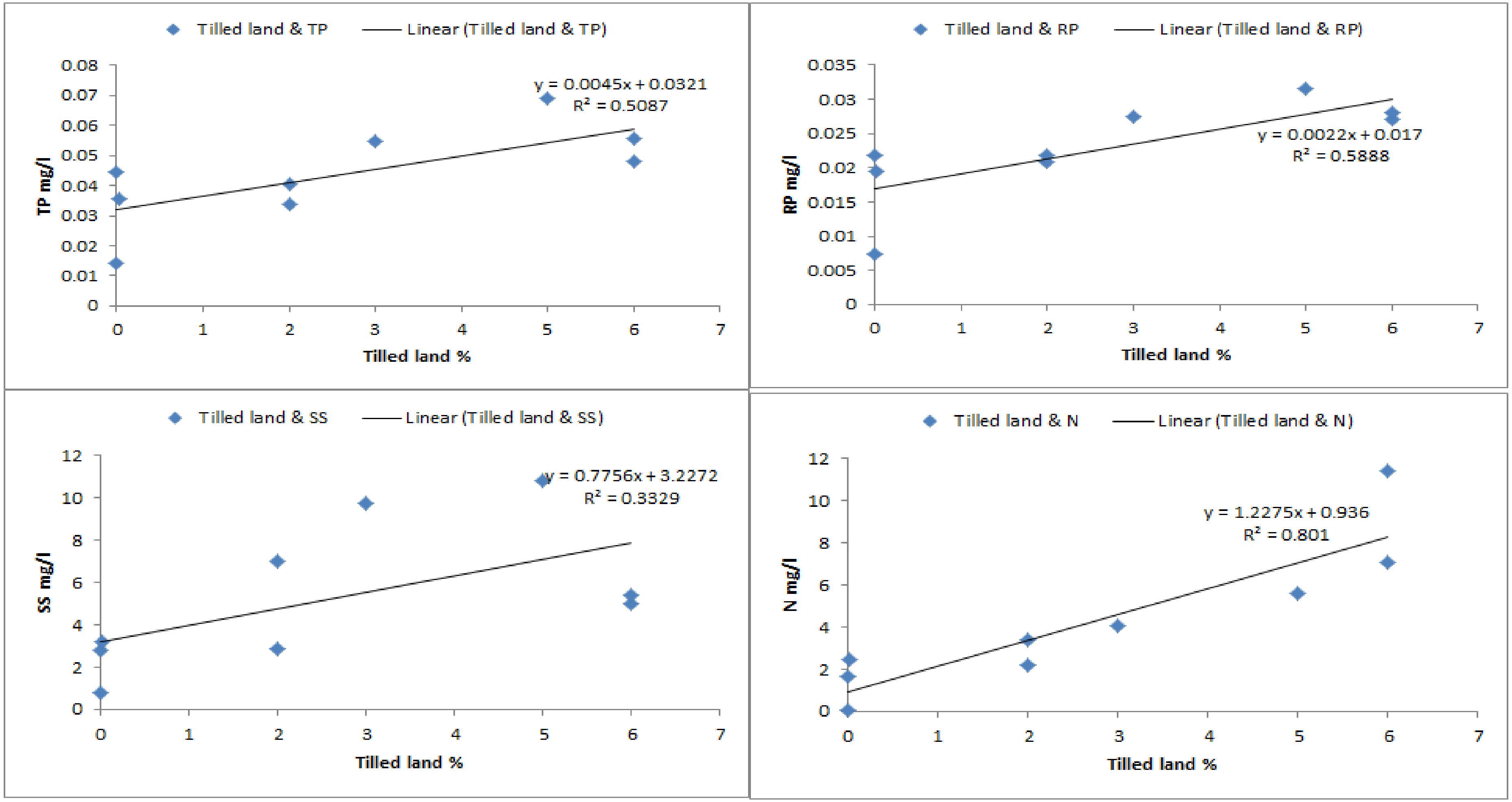


Figure 4.13d Relationship between nutrients, suspended sediment and tilled land

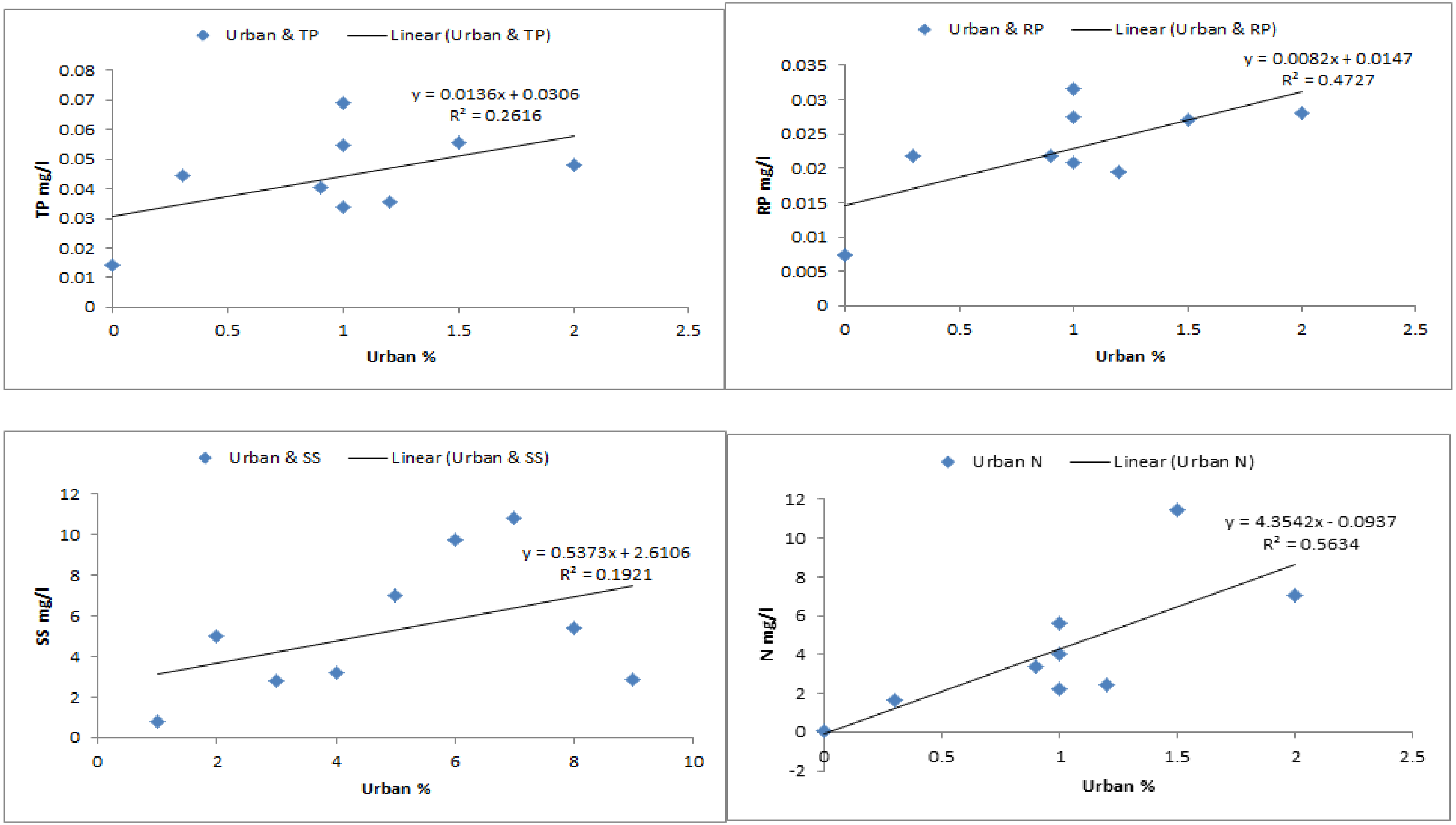


Figure 4.13e Relationship between nutrients, suspended sediment and urban land use

Thus, hydrology, climate, in-stream biochemical processes land use and other catchment characteristics (including soils) are factors that play an important role in the nutrient and sediment transport of the River Eden. Riparian soil, being at the receiving end of the terrestrial catchment and is expected to be finer in particle size (hence more reactive) was compared with stream nutrients and sediment concentrations in this study.

4.3.6. Comparison of soil data with the nutrient and sediment concentrations in the Eden

Apart from the importance of the location of riparian soil, logistics and time constraints are other reasons the study is limited to this zone. In addition to playing a critical role in moisture storage, soil also stores nutrients. This section presents the relationship between some soil properties and the water quality variables estimated in the selected catchments: Gais Gill (GG) and Blind Beck (BB). Figure 4.14a – c compares soil labile P (water extractible P), bicarbonate P, soil nitrogen (soil N) and soil organic matter (SOM) in the top soil at GG and BB. Except for SOM in the warmer weather (spring and summer), SOM, soil P fractions and soil N were higher at BB. The only exception in soil N relationships occurred in spring. Increased soil perturbation due to increase in agricultural activities in BB, a catchment known to be high in farming intensity, was capable of creating a favourable environment for microbial activities. For instance, BB is entirely covered by cultivable soil (100%; i.e. 80% free drain soil and 20% poorly drained seasonal waterlogged soil) (figure 4.14d). The land use consists of managed grassland (42%), unmanaged grassland (31%), tilled land (6%) and urban (1.5%) (table 3.2). Therefore, the agricultural activities at BB and increased temperature during the spring and summer should trigger increased decomposition of organic material (SOM accumulation) and mineralisation by microbes. The mineralised SOM was then taken up by plant in the cropping season and the uptake effect on mineralisation of SOM appears to mask the accumulation effect leading to its depletion. Although soil N is known to be closely related to SOM, however, a slightly higher value at BB during the summer (unlike the SOM) may have been due to the application of organic manure and fertilizer.

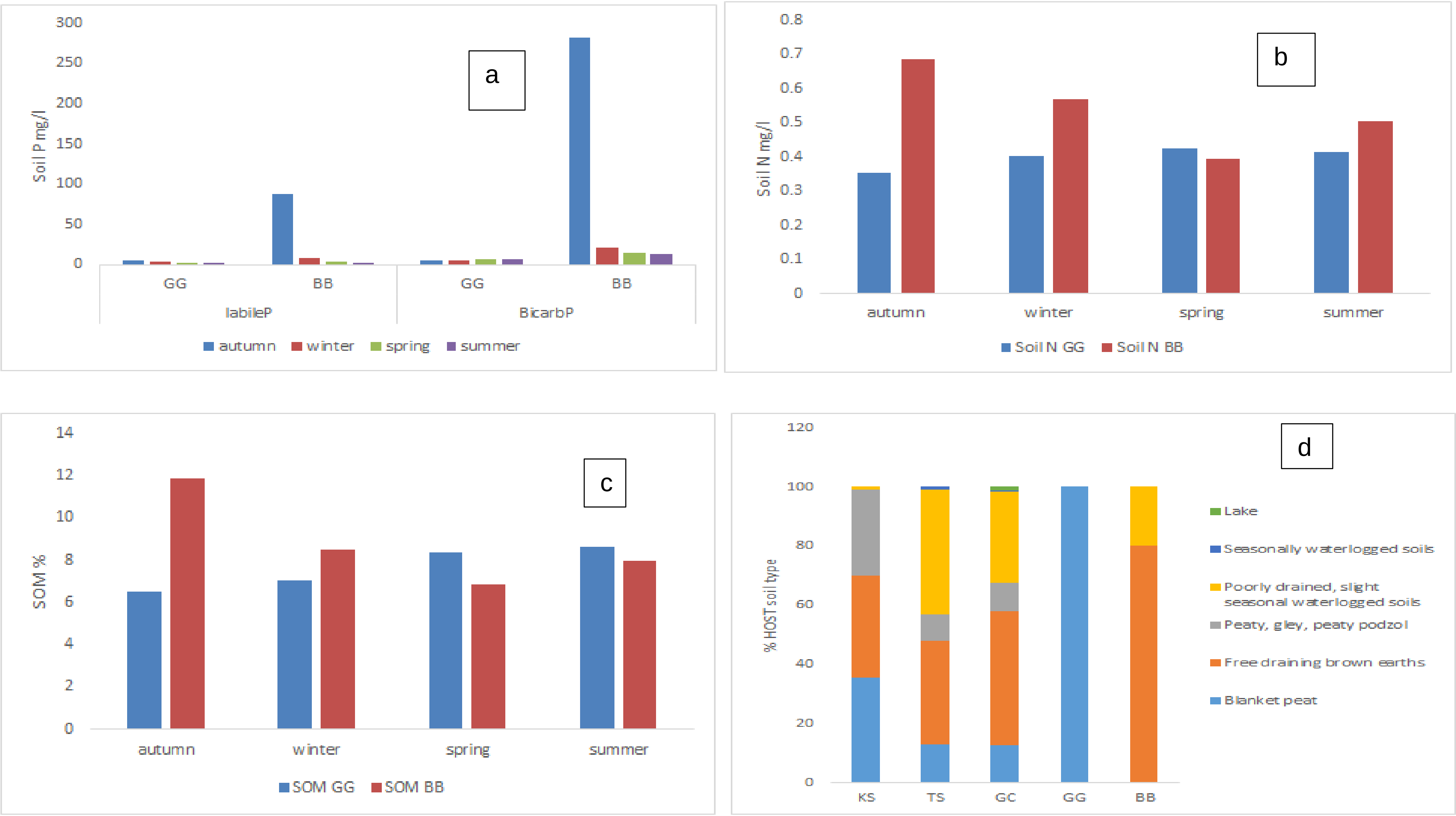


Figure 4.14 a-d (1) A comparison of some soil properties between GG and BB and (2) Spatial distribution of HOST soil types in the Eden catchment

A slight increase in Bicarbonate P, soil N and SOM at GG indicates the predominance of accumulation effect due to microbial decomposition unlike BB. Gais Gill (GG) stream is pristine, the soil is a peat (100%, see table 3.2 and figure 4.14) and the land use is primarily unmanaged grassland (70%) and the existing dataset indicates that there is neither managed grassland nor tilled land (see table 3.2). The distribution of the soil properties in the soil profile may have played an important role in the soil-water nutrient transfer process.

Figure 4.14d reveals the soil distribution of some Eden sub-catchments from upland Kirkby Stephen (KS, 69 km^2) to the lowland Temple Sowerby (TS, 616 km^2) and Great Corby (GC 1373 km^2). It also compares these features between Gais Gill (1.1 km^2) and Blind Beck (9.2 km^2). Gais Gills and Blind Beck has been discussed in the previous paragraph the soil distribution from KS to GC further underpins the importance of soil on land use and water quality in the Eden. It is clear that KS has the highest percentage of peat and peaty soil while the two sub-catchments lowland of the Eden have more poorly drained and free draining brown earths. Since peaty soils can only be subjected to light grazing upland soil has less intensive agricultural operations compared to lowland soils. In the lowland sub-catchments TS (616 km^2) has more poorly drained and waterlogged soils than GC (1373 km^2) and hence is prone to more erosion (or infiltration excess runoff) which is probably the reason the SS and TP concentrations were higher in TS than GC despite GC being larger. The HOST soil types for the other sub-catchments of the scale- related CHASM study are in table 3.2 in chapter three.

The Pearson correlation chart in table 4.5 indicates that there was no significant correlation ($p<0.05$) in P between the top- and sub- soils in BB whereas there was a strong negative (significant; $p<0.01$) correlation in P at both depths in GG. This implies that there were high values of P in the soil profile as a whole in BB that was available for stream transfer. The strong, positive correlations between both the labile P and bicarbonate P in the soil on one hand and the TP ($p<0.01$) and RP ($p<0.05$) in the stream in BB on the other hand, support this argument. Thus, it appears that some interaction between the soil and agricultural land use is implicated in the transfer of P in BB.

	Gais Gill				Blind Beck			
	labileP	**Bicarb.P**	**Soil N**	**SOM**	**labileP**	**Bicarb.P**	**Soil N**	**SOM**
River TP	-0.102 0.810	-0.027 0.949	0.060 0.887	0.033 0.938	0.951 0.000	0.985 0.000	0.594 0.121	0.584 0.128
River RP	-0.519 0.187	0.016 0.971	0.103 0.807	0.124 0.770	0.765 0.027	0.816 0.013	0.343 0.405	0.368 0.370
River N	0.274 0.512	-0.036 0.933	-0.006 0.989	-0.060 0.888	-0.905 0.002	-0.942 0.000	-0.485 0.223	-0.500 0.207
Depth	-0.568 0.142	-0.986 0.000	-0.983 0.000	-0.964 0.000	-0.170 0.688	-0.054 0.899	-0.728 0.041	-0.774 0.024

Table 4.5 A Pearson correlation among soil properties at GG and BB

4.4. Evaluating sediment and nutrient loads and specific yields

The regulatory agencies (e.g. EA) depend on estimates of water quality export when issuing licenses and when monitoring the river for consent compliance. The nutrient load is obtained from the product of concentration of the parameter of interest with flow and is integrated over time to compute loads, which in turn can be divided by catchment area to give specific yields. The results of the load analysis of phosphorus, suspended sediment and nitrate are the focus of this section.

4.4.1. Choice of method and limitations

The estimation of catchment loads is plagued with uncertainties arising from the frequency of sampling, nature of the catchment and the estimation methodology employed (Webb *et al.*, 1997; Johnes, 2007; Cassidy and Jordan, 2011). The accuracy is highest at sub hourly, near-continuous or (obviously) continuous sampling frequencies; this is difficult to achieve in large nested catchments because of funding constraint. Catchments with high base flow index are more likely to have accurate load estimates than the flashy type in the absence of continuous monitoring equipment for water quality assessment. Although all the methods underestimate the loads of the WQP, the estimation methods that incorporate extrapolation methods by means of a simple rating relationship were reported to give the highest accuracy in estimates of suspended sediment loads in some British rivers (Webb *et al.*, 1997).

A synchronous grab sampling approach was used across the nine CHASM catchments as described in Chapter 3. Since it was neither sub hourly nor continuous therefore load estimates for these sub-catchments contained some level of uncertainties. The sub hourly data from the DTC sub-catchments (also in the Eden) provided a benchmark from which the processes observed under the CHASM monitoring could be validated. Besides two different methods of estimation were employed to provide an idea of the patterns of load of SS, P and N under the CHASM monitoring; one of which is based on the rating relationship.

4.4.2. The development of sediment and nutrient rating curve for load calculation

The extrapolation method employed combined rating and flow duration (FDC) curves together (Julien, 1998). The rating relationship is a power law function simplifies as:

$$C = aQ^b \qquad (4.2)$$

where C is the concentration, Q is the flow, a and b are empirical constants. However, in practice, the commonly reported technique involves log transformation (Cooke *et al.*, 2005) of the C and Q followed by a least squares regression (Phillips *et al.*, 1999; Asselman, 2000). It means that the log-transformed C and Q data that are plotted are related as:

$$\log_{10} C = a + b \log_{10} Q \qquad (4.3)$$

A back-transformation of this C results in a modified form of the simple model shown in equation 4.2. Thus, the equation predicting C is given by:

$$C = 10^a Q^b \qquad (4.4)$$

The FDC was constructed for the water year when all the seasonal studies were carried out. The flow, as used by Julien (1998), was calculated from the midpoint (see table 4.6) of the flow duration intervals extracted from the FDC for each of the chosen sub-catchments. The rating coefficients obtained for the sub-catchments as described in section 4.3.1 were used along with the flows (from flow duration curves) to generate the concentrations that were used to estimate the loads.

The R^2 values for the nutrient and SS rating equations of the Eden sub-catchments and the calculation of the annual loads using this technique for Great Musgrave, as an example, are shown in table 4.3 and table 4.6 respectively. The sub-catchments whose R^2 values were too low were omitted.

Time interval (%)	Interval midpoint (%)	Inter-val ΔP (%)	Flow (Q) (m^3/s)	Concentration (mg/l)	Q * $\Delta P/100$ (m^3/s)	Sediment load Qs * ($\Delta P/100$)*CF (tons/year)
0.00-0.02	0.01	0.02	273	188.1	0.0546	324.83
0.02-0.1	0.06	0.08	223	153.5	0.1784	866.1
0.1-0.5	0.3	0.4	136.1	93.42	0.5442	1608
0.5-1.5	1	1	73.45	50.28	0.7345	1168
1.5-5.0	3.25	3.5	43.2	29.49	1.512	1410
5.0 -15	10	10	22.95	15.62	2.295	1134
15-25	20	10	12.47	8.461	1.247	333.7
25-35	30	10	8.25	5.586	0.825	145.8
35-45	40	10	5.975	4.039	0.5975	76.33
45-55	50	10	4.63	3.126	0.463	45.77
55-65	60	10	3.69	2.488	0.369	29.04
65-75	70	10	2.92	1.967	0.292	18.16
75-85	80	10	2.365	1.591	0.2365	11.90
85-95	90	10	1.74	1.169	0.174	6.433
95-98.5	96.75	3.5	1.29	0.8654	0.04515	1.236
Total						7179

Table 4.6 Annual load for Great Musgrave using flow duration-rating curves method
Note: CF is a value used to convert from m^3 s^{-1} to tons yr^{-1}

Apart from the omitted sub-catchments, variables such as P load were also excluded as total P load estimation was only feasible for two of the sub-catchments (Appleby, 334 km^2 and Temple Sowerby, 616 km^2) based the R^2 values. Because the FDC method requires rating curves that were not well defined in some sub-catchments for high flows, resulting in a calculated load uncertainty; therefore, it is essential to explore another technique that is not limited by the strength of the relationship between C and Q.

Approximate method

The approximate method is the alternative technique used in this study to calculate loads, is the mean of the export/load calculated as the product of the sample concentration and the flow at the sample time, multiplied by a factor accounting for the duration of the record (Cassidy and Jordan, 2011). It is expressed as:

$$Annualload = K\frac{\sum(C_i * Q_i)}{n} \qquad (4.5)$$

where K is the duration factor accounting for a year of loads, C_i represents the concentration , Q the flow and n the number, of data points of the ith nutrient (or SS).

Table 4.7 shows an example of the calculated loads and yields using the approximate method for Great Musgrave. To calculate the loads, suspended sediment concentrations (SSC, mg/l) adjusted to SSC (mg/m^3) was multiplied by the flow (m^3/s) to give instantaneous load in milligram per second. The mean of instantaneous load was converted to annual load in tonnes per year by a conversion factor K which is 0.0316 in this case. In almost all the catchments chosen for the suspended sediment load estimation the annual loads estimated using the approximate method were lower than from the first method (i.e. an under estimation) but a Pearson correlation (r) of the load calculated by the two methods is 0.849 (p-value is 0.032) implying that these two methods are positively correlated and the relationship is significant ($P < 0.05$). Unlike the suspended sediment analysis the corresponding nitrate loads from the two methods were closer in value (table 4.8). It means that the approximate method provides an alternative to the more accurate FDC-rating curve approach in estimating the spatial pattern of the loads in the Eden catchment.

4.4.3. Calculation of specific yield

The specific yield (export) is obtained by dividing the estimated nutrient and sediment load of a catchment by the area of the catchment (table 4.7).

4.4.4. The pattern of loads and specific yields of nutrients and sediments in the nested Eden catchment

In this section the focus is to present the spatial scale dependency in the load of the water quality variables and their specific yield. Figure 4.15 depicts the nitrate and suspended sediment (SS) loads evaluated using the FDC-rating method. The graph depicting nitrate is only feasible from Great Musgrave (233 km^2) to Great Corby (1373 km^2) where there were comparatively higher R^2 values (see table 4.3). The approximate method provides an estimate of the entire contaminant load for all the sub-catchments (figure 4.16). In a clear departure from what was obtained in the relationship of nutrients and SS concentrations to catchment area, their loads into the River Eden clearly increase downstream of the River Eden (figure 4.16). The spatial scale patterns of exports of nitrate and SS from the two methods were similar (figure 4.15, figure 4.16 and table 4.8). The TP and RP exports were not compared because the FDC could not be used, since the rating curves were not well-defined for high flows for most of the sub-catchments (explained above).

Date	SSC (mg/l)	Flow (m^3/s)	Instant. Load (mg/s)	Instant. Yield (mg/s/km^2)
01/11/2011	5.25	12.00	63000.0	270.39
03/11/2011	2.25	8.03	18067.5	77.54
21/11/2011	0.75	1.89	1417.5	6.08
24/11/2011	18.75	23.1	433125.0	1858.91
16/12/2011	3.50	9.81	34335.0	147.36
06/03/2012	1.83	3.81	6985.0	29.98
14/03/2012	1.17	2.34	2730.0	11.72
19/03/2012	31.67	2.14	67766.7	290.84
21/03/2012	0.83	1.83	1525.0	6.55
02/05/2012	1.67	3.08	5133.3	22.03
09/05/2012	1.67	2.27	3783.3	16.24
16/05/2012	1.00	4.27	4270.0	18.33
21/05/2012	2.83	2.67	7565.0	32.47
25/06/2012	4.58	8.03	36804.2	157.96
23/07/2012	2.17	2.84	6153.3	26.41
26/07/2012	1.33	2.67	3560.0	15.28
31/07/2012	4.17	2.74	11416.7	49.00
06/08/2012	3.42	3.99	13632.5	58.51
19/09/2012	3.00	3.87	11610.0	49.83
10/10/2012	1.33	3.21	4280.0	18.37
07/11/2012	1.83	4.23	7755.0	33.28
20/12/2012	62.50	48.90	3056250.0	13116.95
14/01/2013	3.33	2.95	9833.3	42.20
30/01/2013	12.00	26.90	322800.0	1385.41
27/02/2013	3.50	1.87	6545.0	28.09
26/03/2013	2.08	2.05	4270.8	18.33
10/04/2013	1.17	2.62	3056.7	13.12
26/04/2013	1.75	5.75	10062.5	43.19
Mean			148490.5	637.30
Annual Load (tonnes/yr)			4695.6	
Annual Yield (tonnes/yr/km^2)				20.15

Table 4.7 Calculated annual load and yields for Great Musgrave

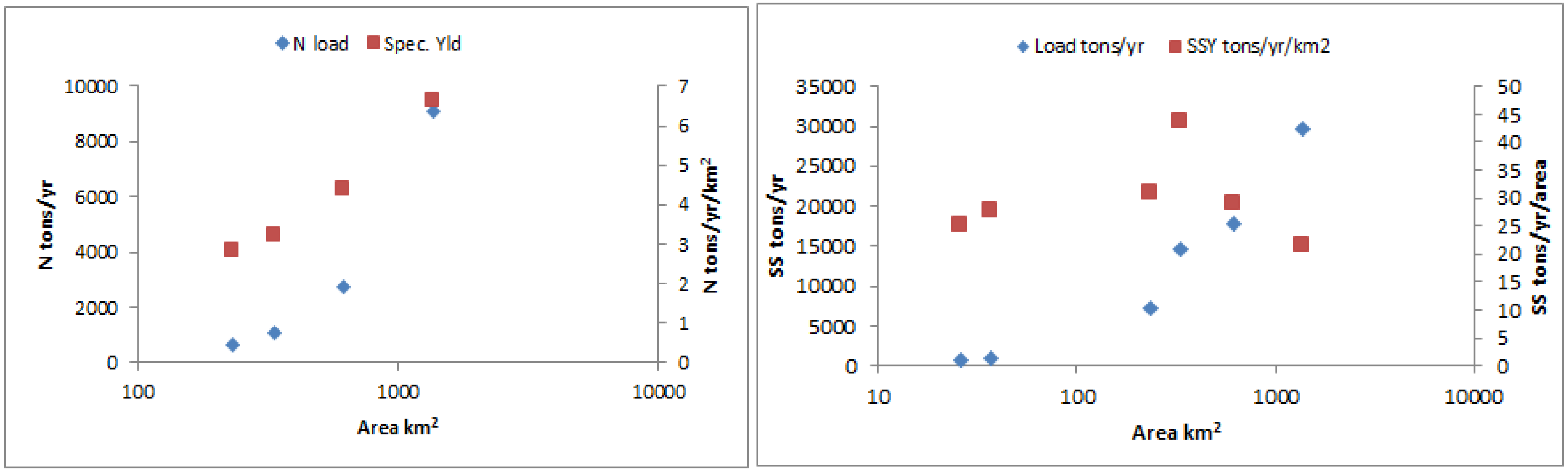


Figure 4.15 Spatial pattern in nitrate and SS, loads and yields in the River Eden using the FDC-rating technique.

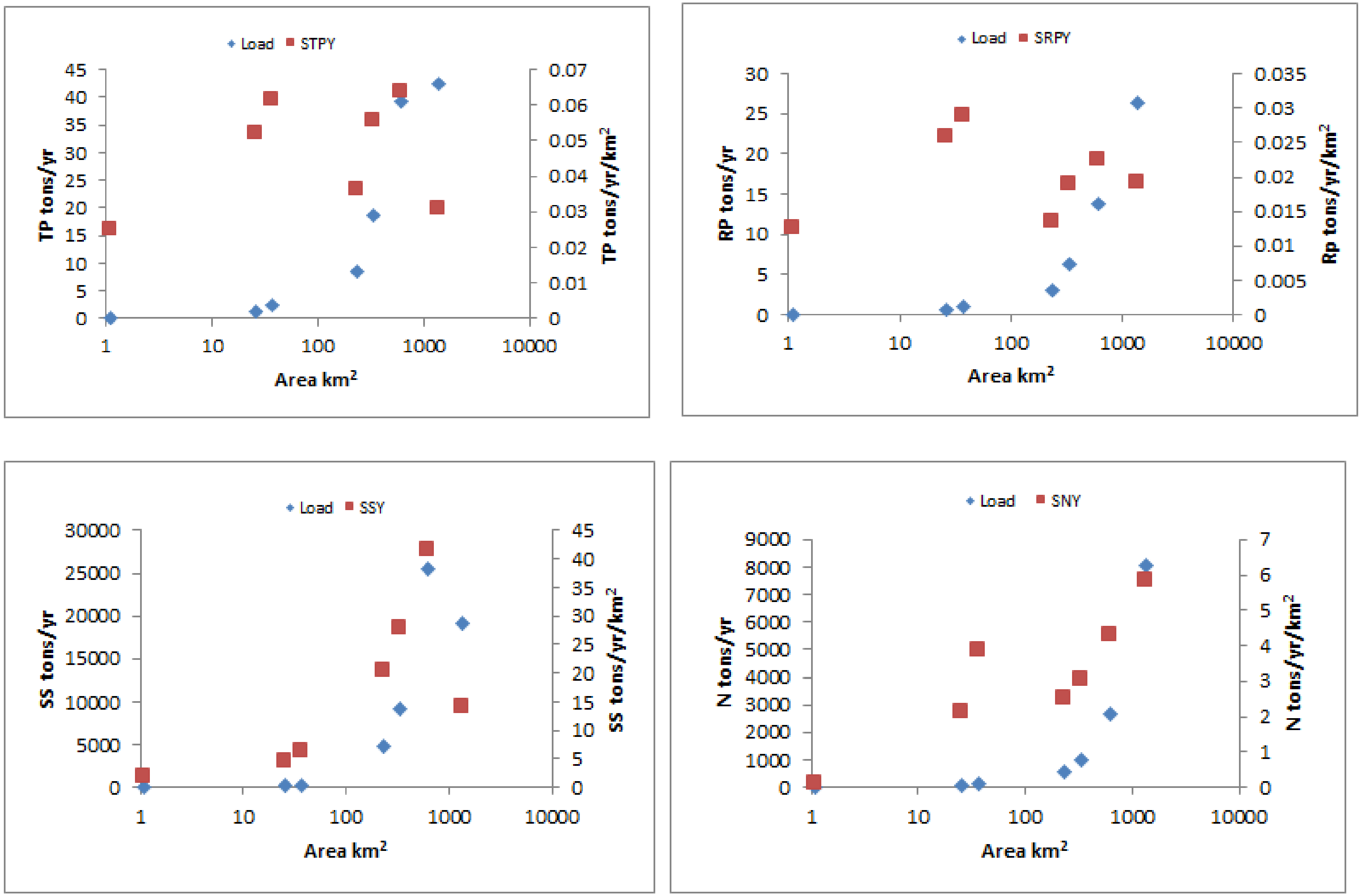


Figure 4.16 Loads and specific yields of TP, RP, SS and nitrate in the River Eden using the Approximate method.

Location Area (km^2)	**Sediment Load tonnes/yr**		**Location Area (km^2)**	**Nitrate Load tonnes/yr**	
	FDC-rating	Approx.		FDC-rating	Approx.
26	650.0364	119.4186	n/a	n/a	n/a
37	1027.302	238.3398	n/a	n/a	n/a
233	7179.081	4726.261	233	660.8736	583.6383
334	14605.61	9257.501	334	1074.554	1018.111
616	17871.29	25523.55	616	2709.496	2655.715
1373	29604.79	19223.69	1373	9112.911	8032.377

Table 4.8 Comparison between the FDC-rating and approximate methods for estimating nitrate and SS loads in the River Eden

The load estimation methods depend on flow, therefore an increase in flow downstream increases the nutrient loads into the river.

The specific yields for nitrate (SNY) and SS (SSY) showed a clearer spatial trend as the catchment area increases. However, there was a decline in SSY at Great Corby (GC). In addition to soil erosion, the increasing trend in SS may be due to in-channel sources, bank erosion, valley side scar etc. (see Section 4.3.3). The decline at GC was probably due to a comparatively less percentage area of land with poorly drained, seasonal waterlogged soil in GC compared with Temple Sowerby (see table 3.2 and Section 4.3.3). This soil type encourages surface runoff which an important transport pathway for SS and associated P. There is also sediment-free water from River Eamont, that comes from a large Lake Ullswater, which is a tributary to the portion of River Eden that flows through GC. Although there was an increase in the specific yields of total phosphorus (STPY) and reactive phosphorus (SRPY) downstream when compared with the headwater sub-catchments their spatial pattern downstream was not distinct. However, it appears to follow the ‘two-domain’ pattern of cultivable soil and managed grassland that was discussed in Section 4.3.3. All the nutrients increased up to a catchment area of 37 km^2 (i.e. Smardale) that forms the first domain, the ‘tributary domain’. The second domain, ‘main Eden’ began from catchment area of about 233 km^2 (i.e. Great Musgrave) and increased to catchment area 616 km^2 (i.e. Temple Sowerby, with the exception of nitrate) before dropping at Great Corby. Therefore, soil type, that in turn influences land use (e.g.

managed grassland) and associated fertility management, is probably another factor playing a critical role in nutrient transfer in the Eden.

4.5. Summary

This chapter has quantified some of the important catchment characteristics and processes that are associated with nutrient transfer and export in the Eden catchment. The period of record, hydrological event and flows were highlighted and the relationships between hydrology and other catchment characteristics; such as soil, elevation, climate and in-stream processes, and water quality were demonstrated. The sediment and phosphorus rating curves were found to have a positive gradient whereas nitrate rating curve were found to have a tendency to be negative and under certain conditions were a combination of both. There was a downstream increase in SS, phosphorus and nitrate concentrations observed relative to the headwaters. The pattern was linked to soil type and land use (managed grassland). The reductions in SS and phosphorus concentrations in Great Corby relative to Temple Sowerby were linked to soil types. Nitrate concentrations showed the most distinct increasing trend downstream and also depend on land use (particularly tilled land) and soil type (free drain soil). Specific yields were calculated using the FDC and the approximate methods because of the constraint posed by the rating curve uncertainties at high flow. Nitrate and SS yields exhibited a clearer spatial increase compared to the phosphorus fractions. Blind Beck (BB), a sub-catchment downstream of the headwaters, provided an example of how land use influences contaminant concentrations in the Eden catchment. The BB case study when supported with a downstream increase in arable land has shown that the spatial increase in water quality determinands moving downstream was probably related to the land use intensity. Thus the two key dominant factors influencing nutrient and sediment transport identified from the spatial scale study platform (CHASM) are land use and hydrological processes. The land use depends on soil type. Some of the challenges with missing data due to equipment failure were addressed by downscaling or by the use of extrapolation techniques (regression analysis). The uncertainties associated with estimation of some of the water quality determinands were stated whilst efforts made to minimise these were reported. For instance minimising the data limitations (when using grab samples to explain nutrient transfer) requires the use of field equipment that can guarantee either frequent sampling or preferably near-continuous water quality data instead of infrequent grabs. The next chapter incorporates near-continuous water quality data from the DTC to investigate further the hydrological processes and in particular the impacts of contrasting land use on nutrient losses in the Eden catchment.

Chapter 5: Evaluating the Nutrient and Suspended Sediment Regime of the Demonstration Test Sub-catchment

5.1. Introduction

For a more reliable understanding of the processes governing nutrient transfer in a sub-catchment, the previous chapter recognises the advantage of using data acquired through continuous or near-continuous measurement over data obtained from grab samples. The Demonstration Test Catchment (DTC) project was set up by the Department for Environment, Food and Rural Affairs to achieve this. This chapter therefore evaluates impact of hydrological processes and variation in land use on nutrient export into the River Eden by using high resolution data from the DTC project. The target is to gain insight into the processes underlying the pollution problem and potentially how to manage them. The three sub-sub-catchments (hereafter refer to as catchments) considered are Dacre Beck (Dacre), Morland Beck (Morland) and the Pow; these have different elevation ranges and contain different intensity of stocking densities and other farming activities.

5.2. Hydrological Characterisation

Precipitation data were measured using tipping bucket rain gauges and precipitation sensors attached to automatic weather stations in each catchment, the flow data were acquired through the combination of Schlumberger mini-diver used to measure water level and Sontek/YSI Argonaut SW (Shallow Water) velocimeter that measures velocity of flow in 2-D (see section 3.5.6 for a list of the Eden DTC equipment). These are located at the sub-catchment outlets.

5.2.1. Precipitation and flow

The precipitation in the period comprising September 2011 to September 2012 is captured in figure 5.1. The three catchments showed similar precipitation and flow patterns. An initial wet early autumn was followed by a dry period before another wet period in late autumn that extended to early January. The larger part of the winter to summer was a relatively long dry spell. The summer was exceptionally wet. Climatic conditions were thus unusually dry then wet, as reported in Chapter 4.

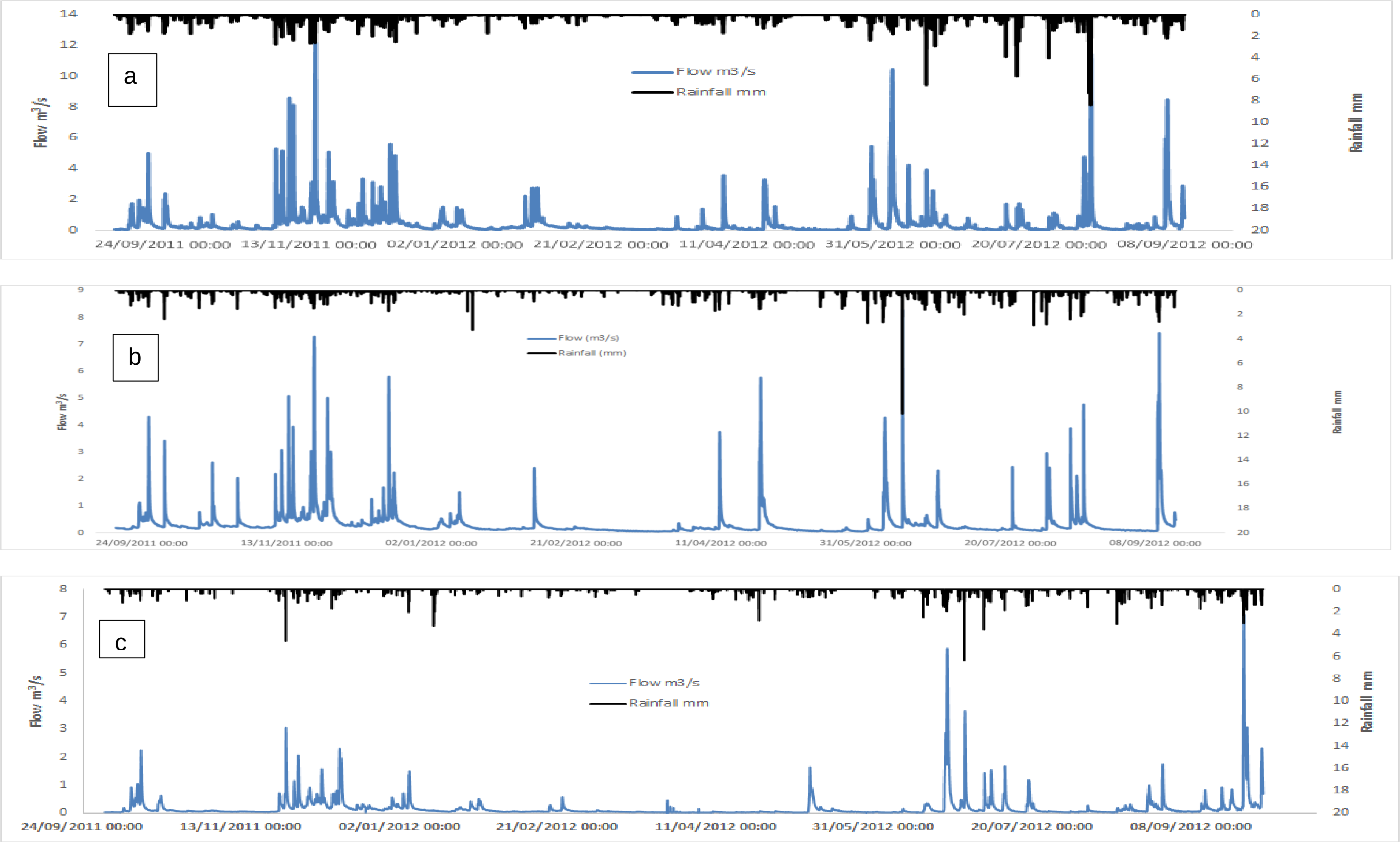


Figure 5.1 Sub-hourly rainfall and flow for (a) Dacre and (b) Morland (c) Pow from September 2011 – September 2012

The graphs also show that the Dacre catchment was the wettest followed by Morland while the Pow was the driest. This is further described in table 5.1 which summarises the precipitation, flow and elevation characteristics of the DTC catchments. The rainfall and flow in these catchments increase with elevation agreeing with Walsh (2004).

Catchments	SAAR (mm)	Annual precipitation (mm)	Mean flow (m^3/s)	Max. elevation (m)
Dacre	1587	1974.3	0.475	537
Morland	1165	1184.0	0.280	392
Pow	856	1014.0	0.166	155

Table 5.1 Hydrological summary and elevation of Dacre, Morland and Pow

5.3. Nutrient and sediment concentrations, and turbidity

Water quality samples taken at each of the catchment outlets are considered in this section. There are two sets of data. The first set was obtained using sophisticated bankside environmental monitoring equipment (subsequently referred to as continuous monitoring equipment – "CM") capable of collecting and analysing nitrate, phosphate and turbidity in samples, in-situ, at 15 minutes sampling frequency. The second set was collected using an autosampler and the samples were analysed using conventional laboratory methods to measure nutrient or sediment concentration. These samples were analysed in the Environment Agency laboratories as part of the Eden DTC project and have been quality assured by the EA. It is against this second dataset that the former was checked. These two datasets provided by the Eden DTC project were used in this chapter. Other work done to make the data fit for the purpose reported here will be mentioned. In this chapter, the results will be used to draw comparisons and contrasts between the catchments. The links between the DTC catchments and the processes driving their environmental parameters, and the observations from the CHASM sub-catchments will be highlighted.

5.3.1. Comparison of concentration data from the autosampler and the CM equipment

Concentration data, corresponding in date and time (January – September 2012) to that obtained from the autosampler (ISCO), were extracted from the time series obtained using the continuous monitoring (CM) equipment and the box plot is displayed in figure 5.2 (also see appendix C) and the mean and median shown in table 5.2. For the total P and total RP, the mean and median were similar underpinning the correctness of the CM data. However, there were outliers in the concentration of TP and TRP in both the autosampler and the CM data. The outliers notwithstanding, the similarity in statistics confirm the accuracy in the CM data. Nitrate (N) concentrations obtained from the CM data are slightly higher than the autosampler N values and may be due to the presence of outliers in the nitrate concentration data. The CM equipment does not measure SS but measures turbidity which has been widely considered as a proxy for SS, but the two cannot be compared being different environmental parameters. In addition to the rating relationship of the environmental parameters with flow, the relationships between turbidity and SS, and the other environmental parameters are considered in subsequent sections.

	AutosamplerTP (mg/l)	**CM TP (mg/l)**	**Autosampler TRP (mg/l)**	**CM TRP (mg/l)**	**Autosampler N (mg/l)**	**CM N (mg/l)**
Mean	0.1877	0.1783	0.0768	0.0801	7.271	9.877
Median	0.1480	0.1370	0.0592	0.0609	7.514	9.478

Table 5.2 Comparison between mean and median hourly concentration of the contaminants generated by the autosampler and the CM equipment at Morland

5.3.2. The water quality variables and flow

The three DTC sub-catchments are similar in size and the pattern or slope of the rating relationships between N, P and SS and either flow or turbidity are also similar though the strength of the relationships (R^2-values) differ. Therefore Morland was chosen to represent the DTC sub-catchments in this section (see Appendix C for Dacre and Pow) and the summary of the R^2-values for Dacre and Morland will be provided for comparison. There are two sets of graphs showing flow plotted against concentration; one set is from the autosampler data while the other set is from the CM data. Another two sets show turbidity plotted against concentration with one of the sets representing concentration obtained from the autosampler and the other for concentration data obtained from the CM equipment. The CM data collected at 15 minute time resolution were converted to hourly data. The CM data captured the

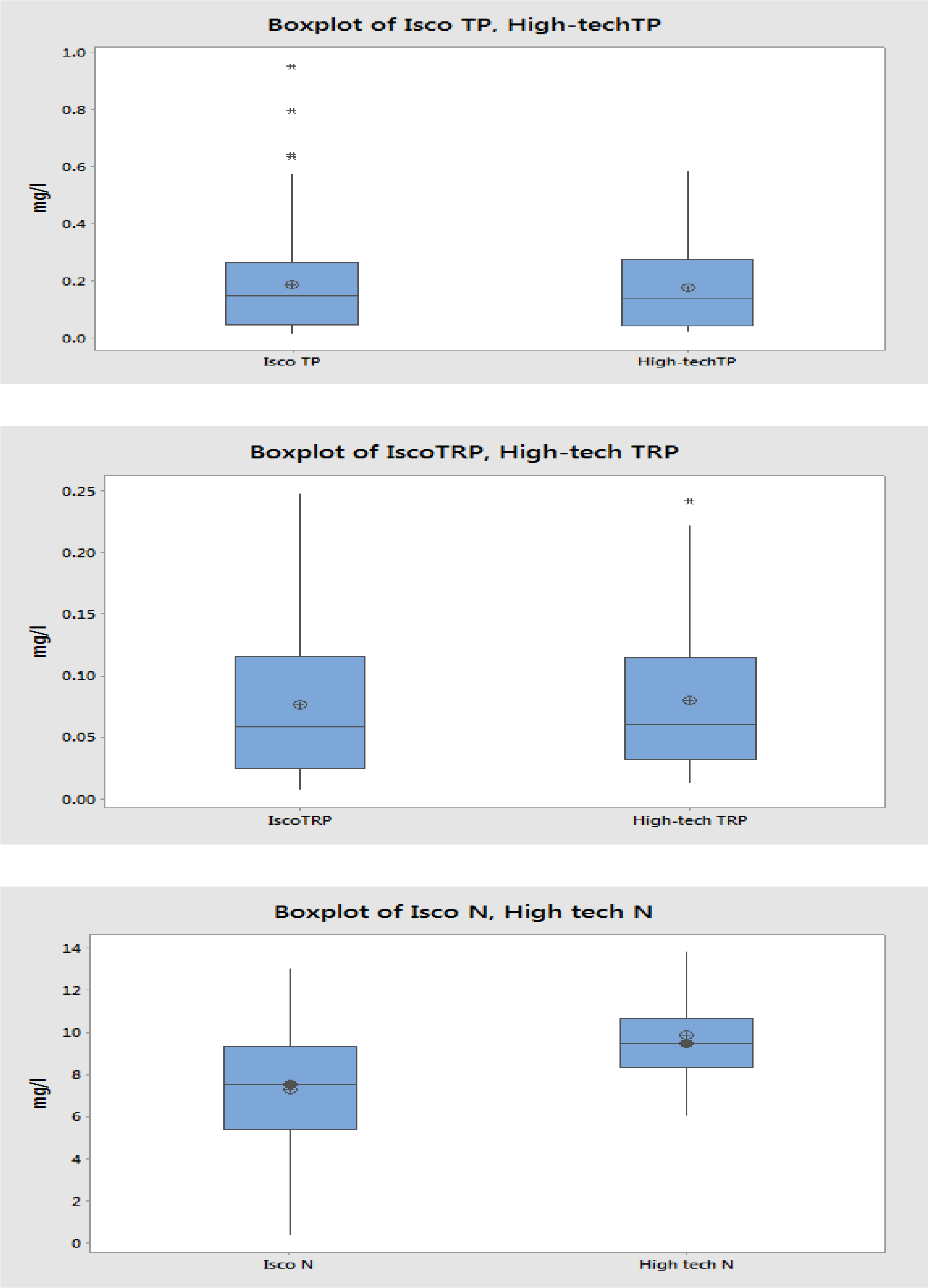


Figure 5.2 Box plot comparing the contaminant concentrations from the two measuring equipment at Morland

WQP concentrations for the whole spectrum of flow, thus eliminating the uncertainties associated with using rating relationship.

Flow and WQPs

Figure 5.3 depicts the first set of graphs, for this subsection, showing the plot of flow against the corresponding concentration data obtained from samples collected using the autosampler. Essentially, TP, TRP, SS and N graphs resemble those rating relationship shown under the CHASM data. Like the CHASM graphs, TP, TRP and SS show a positive gradient relative to flow while N has an inverse relationship. The positive gradient suggests diffuse sources (agricultural input and land management, tile drain, livestock poaching, bank erosion, bed suspension etc.). Negative slope shown by N suggests point source (sewage treatments waterworks, STWs,) and/or groundwater source (Wood *et al.*, 2005; Jordan *et al.*, 2007). Septic tank systems (STSs) can contribute to diffuse pollution (Palmer-Felgate et al., 2010; Wither *et al.*, 2011, 2012) and can operate as multiple point sources (Jarvie *et al.*, 2010, Wither *et al.*, 2012). Therefore both the nutrients can come from the STSs. However, contributions from STSs and STWs in the Eden are limited due to low population density. N also shows a slight change in slope at higher flows which appears to be the reason for the low R^2 value and implies that it came from both point and diffuse sources. It is similar in the other two DTC sub-catchments. The complex relationship of N with flow, whereby slope switched at higher flow, is in accord with what was observed in some CHASM sub-catchments (e.g. Temple Sowerby).

For the second set of graphs where the data obtained from the CM water quality equipment was plotted, the relationship of the concentration with flow is similar to that shown by the plot using samples from the autosampler analysed for TP, TRP and SS. However, the R^2-value is not as strong which can be linked to presence of outliers as shown on the curve. Nitrate showed a near constant response relative to flow (figure 5.4). This is in phase with findings of others who partly or fully observed constant nitrate response in River Enborne (Bowes *et al.*, 2015) and in The Cut (Halliday *et al.*, 2015). The problem of weaker relationship may have been partly due to a complex relationship with flow and the presence of outliers (to be discussed later).

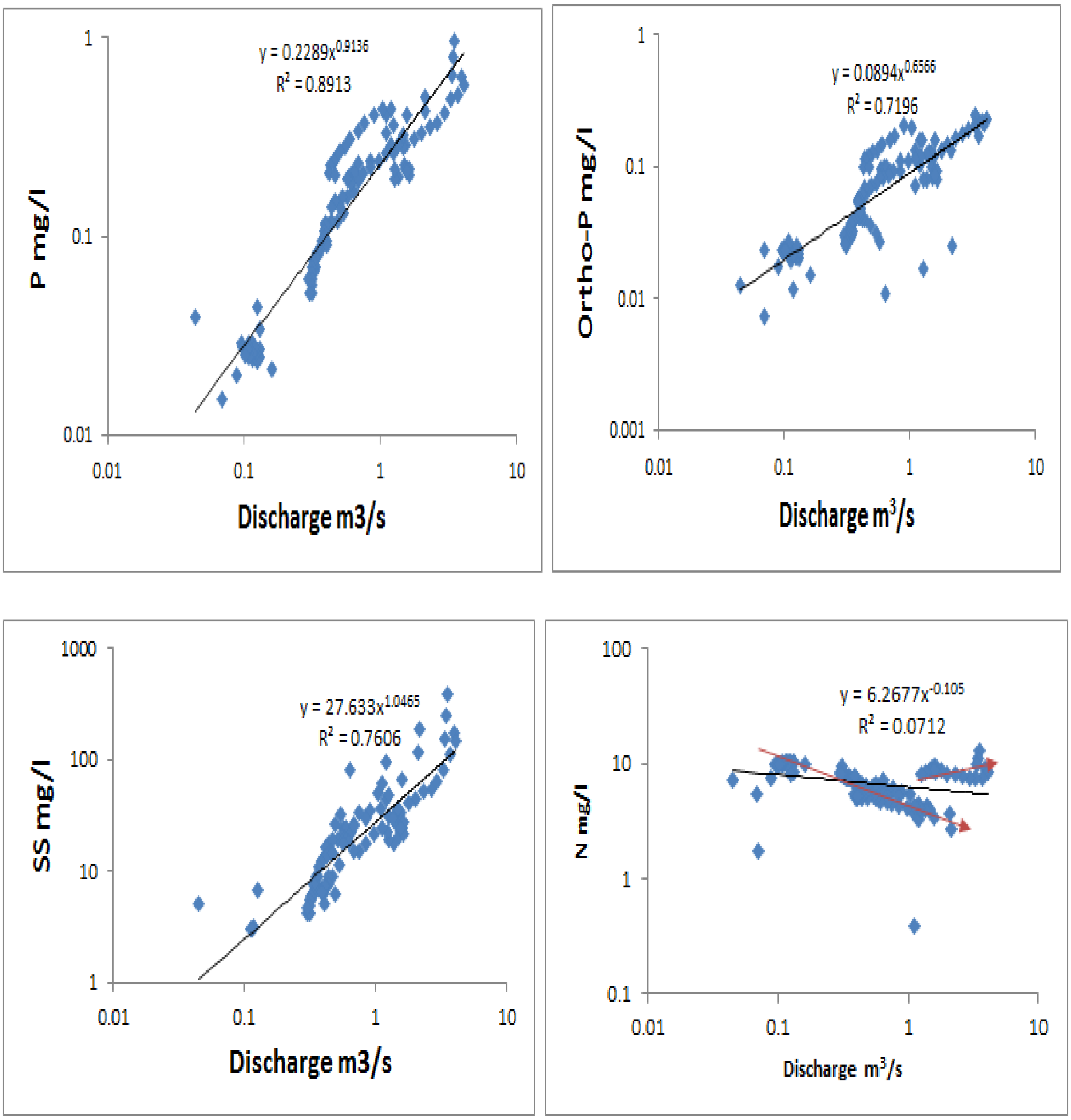


Figure 5.2 Scatter plots of hourly flow against P, TRP (Ortho-P), SS and N at Morland from samples collected using the autosampler

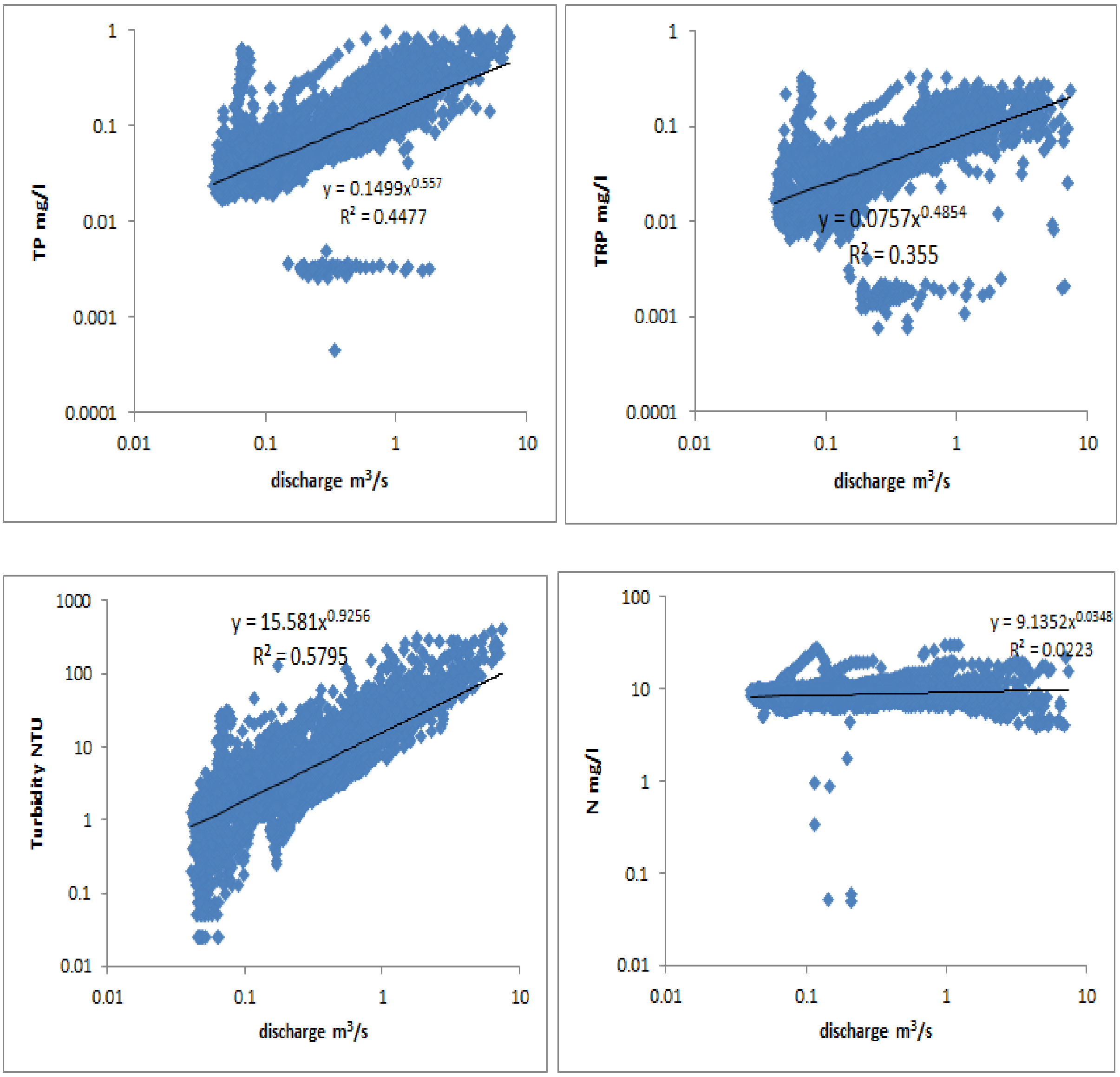


Figure 5.3 Scatter plots of hourly flow against P, TRP (Ortho-P), turbidity and N at Morland using the CM equipment

Turbidity and WQPs

Turbidity, being a measure of the transparency of water (Ziegler, 2002), has been reported as a good surrogate for SS under certain conditions and has the advantage of near continuous monitoring and a turbidity probe can be acquired at a reasonably cheap price. With the availability of the data from all the three DTC catchments, made available by the Eden DTC project, the plots of turbidity with flow (as done with the other water quality variables, figure 5.4), and turbidity against SS and nutrients obtained from the autosampler were produced (figure 5.5 – 5.6).

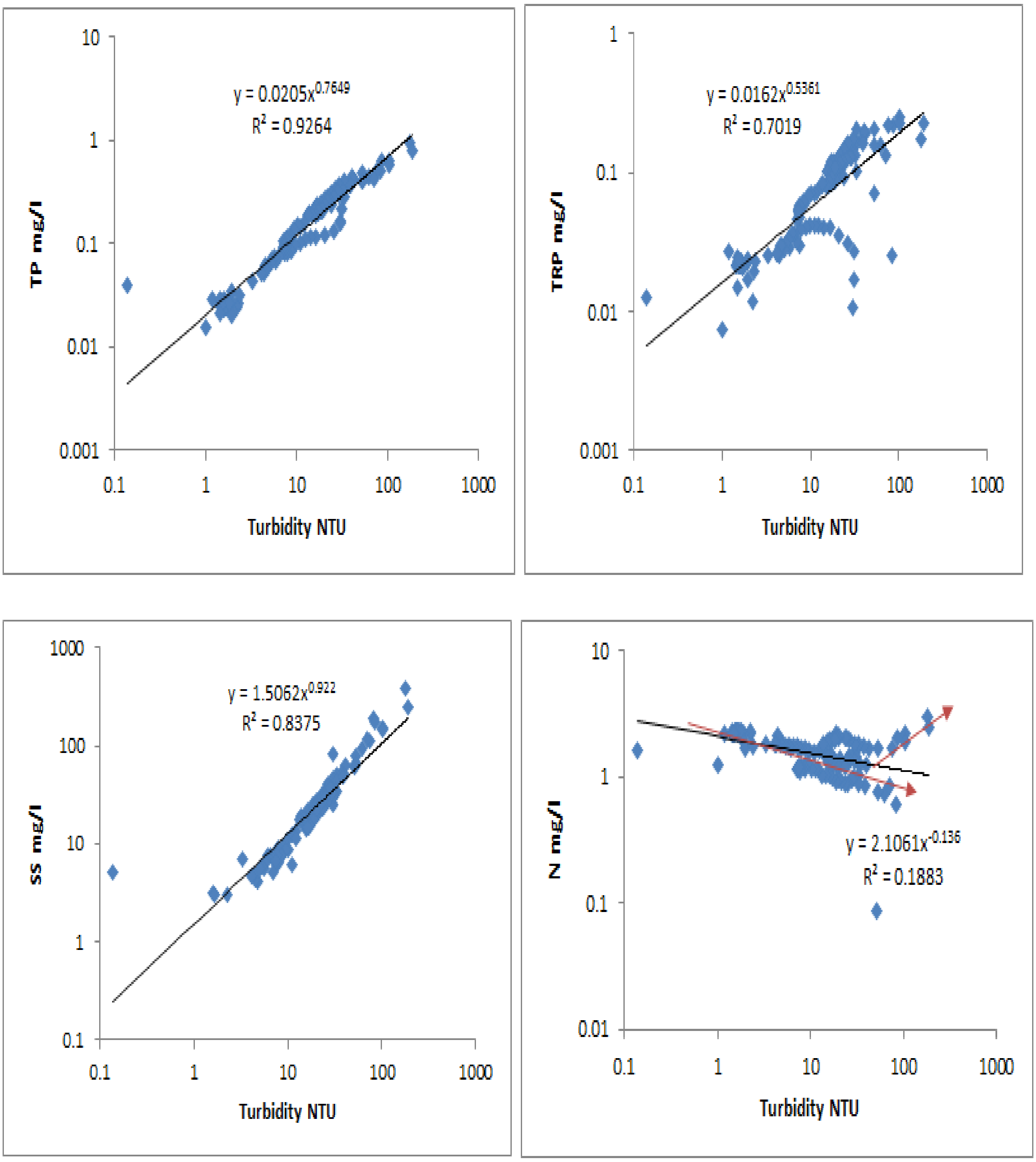


Figure 5.4 Scatter plots of hourly turbidity against P, TRP (Ortho-P), SS and N at Morland based on the autosampler sampling date

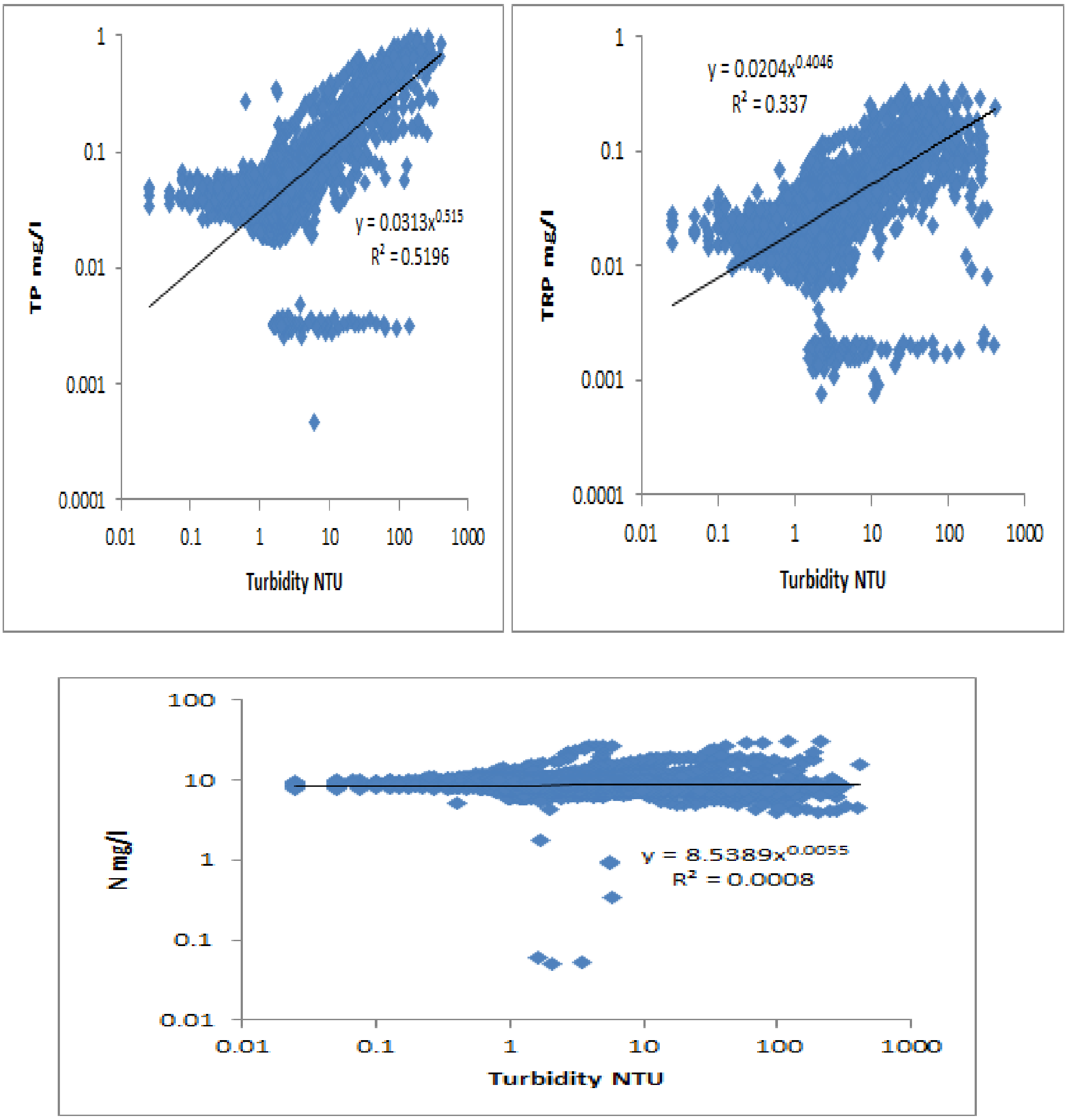


Figure 5.5 Scatter plots of hourly turbidity against P, TRP (Ortho-P), and N at Morland using the CM equipment

With these data and their graphs (figure 5.5 and figure 5.6), it is now possible to consider whether turbidity can act as surrogate for nitrate and phosphates. Similar to what was performed with the rating relationship using flow data, there are two sets of graphs based on the two types of field equipment used in the DTC project to generate a high resolution dataset describing the rating relationship of turbidity with TP, TRP and N. The slopes of the graphs were similar to what was obtained with flow data. Thus, it is possible to generate two sets of annual data for the WQP. The first are the data from the rating relationship with both the flow or turbidity data and the second are the annual data measured by the CM equipment all year round. For SS, however, it is only the former that applies because the CM equipment did not measure SS. A summary of the R^2-value for flow and turbidity rating is given in table 5.3.

A	**Morland**		**Dacre**	
	Turbidity	**Flow**	**Turbidity**	**Flow**
N	0.188	0.071	0.273	0.228
TP	0.926	0.891	0.595	0.398
TRP	0.702	0.720	0.397	0.377
SS	0.838	0.761	0.605	0.508

B	**Morland**		**Dacre**
	Turbidity	**Flow**	**N/A**
N	0.0008	0.0223	N/A
TP	0.5196	0.4477	N/A
TRP	0.337	0.355	N/A
SS	N/A	N/A	N/A
Turbidity	N/A	0.5795	N/A

Table 5.3 R^2 values for rating relationship between the environmental parameters and turbidity and flow using data obtained from (a) the autosampler and (b) CM equipment respectively.

Note: The continuous monitoring equipment cannot measure SS concentrations in both catchments. There were also no continuous N and P data recorded at Dacre.

Interrelationship among the WQPs

The correlations between the four environmental parameters were also tested and the results including the Pearson correlation (r) and p-value are shown in table 5.4. Concentrations of SS, TP and TRP were positively correlated but N was negatively correlated. This indicates that N is predominantly loss through different flow pathway (subsurface or groundwater via infiltration/percolation) and processes (leaching and without sorption to soil matrix) (Gall *et al.* 2015). It probably also has a considerable contribution from other source that is not so common with P such as groundwater (see EA 2003, report on source of N load in the Eden). With a correlation value of 0.996 between TP and SS, it implied that any pattern shown in the TP measured from the CM data relative to flow for instance, could be an alternative that describes the expected pattern of SS were it to be measured by a near-continuously measuring instrument.

	Autosampler N	**Autosampler TRP**	**Autosampler TP**
Autosampler TRP	-0.849		
Autosampler TP	-0.745	0.983	
Autosampler SS	-0.690	0.963	0.996

Table 5.4 Pearson correlation between the WQPs in Morland
Note: $p<0.001$

Sources of uncertainties

The uncertainties and caveats associated with data obtained by extrapolating using regression techniques have been raised in Chapter 4. These primarily arose due to the difficulty in collecting enough samples at high flow. Both the autosampler and the CM equipment (particularly the latter) were able to sample the stream across the entire spectrum of flow data. That is not to say that the data obtained from these two sets of equipment do not have some degree of errors. For instance, there are instances when the data from the autosampler at Dacre, obtained through the Eden DTC had some error values. This affected nitrate and SS in particular. Apart from the error values seen in the CM data (though negligible because it involved less than 5% of the whole dataset), there were outliers (figure 5.7) which could have been responsible for the weaker rating relationships observed with these data. Despite these errors associated with the Eden DTC data, the key issue of capturing data at high flows was addressed and the data are reliable in explaining the processes driving nutrients transport. Minor difference in N response notwithstanding, an agreement between the observations made under the CHASM and the DTC

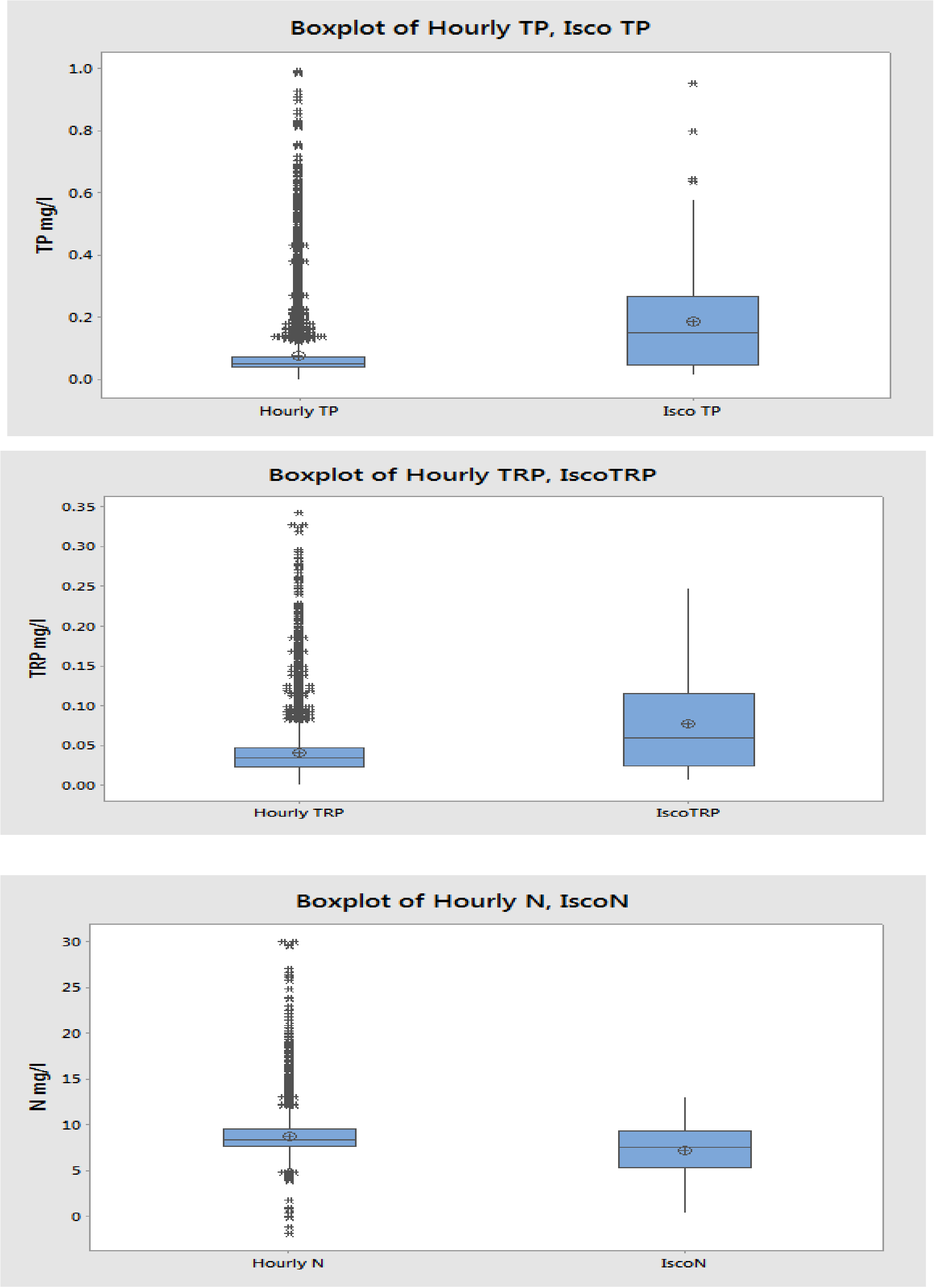


Figure 5.6 Comparison of the outliers of hourly TP, TRP and N data from the CM data (Hourly) with those from an autosampler

studies can help draw conclusion on processes controlling the spatio-temporal pattern in nutrient transport in the Eden catchment.

5.3.3. Seasonality in the concentrations of the water quality variables

The concentrations of P, nitrate and SS across the seasons is as plotted in figure 5.8 and figure 5.9a-b. Figure 5.7 compares the distribution of the nutrients in two of the Eden DTC catchments with different degrees of agricultural land use. The two catchments showed the same seasonal nutrient patterns hence justifying the decision to use Morland as the representative catchment as discussed previously. The figure is based on the rating relationship (Concentration vs. flow) from the data obtained from the autosampler.

With this approach, it is possible to have a full year of data for SS. This is because equipment for the direct measurement of SS do not (currently) exist among the bankside (CM) equipment. The median concentrations of P (as TP and TRP) and SS, as seen in the chart, for mid to late winter and spring, when there was long dry spell, were the lowest. The highest median concentration of N was shown in spring. If this result is to be explained by a dilution effect it raises a question regarding the winter concentration seeing that the two are both characterised by long dry spells; although early winter (December 2011 to early January 2012) was wet (see figure 5.1). Compared to a relatively wetter autumn and summer, it is expected that winter should be closest in concentration to spring. To verify this, graphs of the water quality determinands were plotted for Morland using the data from the bankside equipment (CM data) (figure 5.9a-b).

The P data and the SS (represented by turbidity in figure 5.9b), shown in figure 5.8 were in agreement with figure 5.9a-b, but the seasonal N pattern differed. The graph plotted using the high resolution CM data shows that the concentration of N was the lowest in the spring but highest in summer unlike the pattern displayed from the concentration data using the autosampler rating relationship (concentration vs. flow). The case of N highlights the shortcoming in using extrapolated data from regression model (i.e. a rating relationship). This may arise because regression model for N was based on the assumption that N is often negatively related to flow unlike P and SS whereas the signal from the CM measurements show complex N response.

.

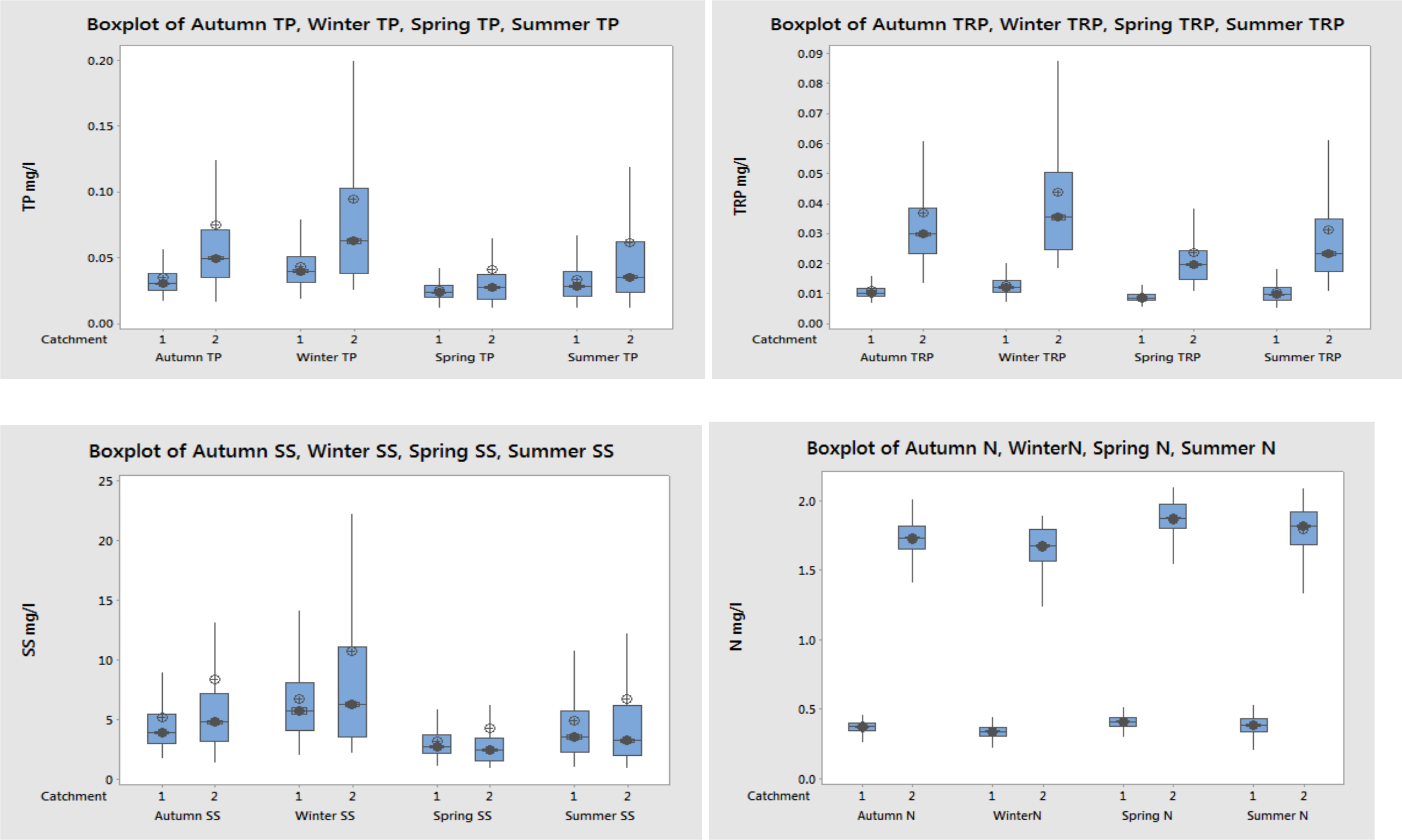


Figure 5.7 Seasonal comparison of TP, TRP, SS and NO_3-N hourly concentrations in Dacre (subcatchment 1) and Morland (subcatchment 2) using ISCO autosampler for the period covering a water year (2011 – 2012)

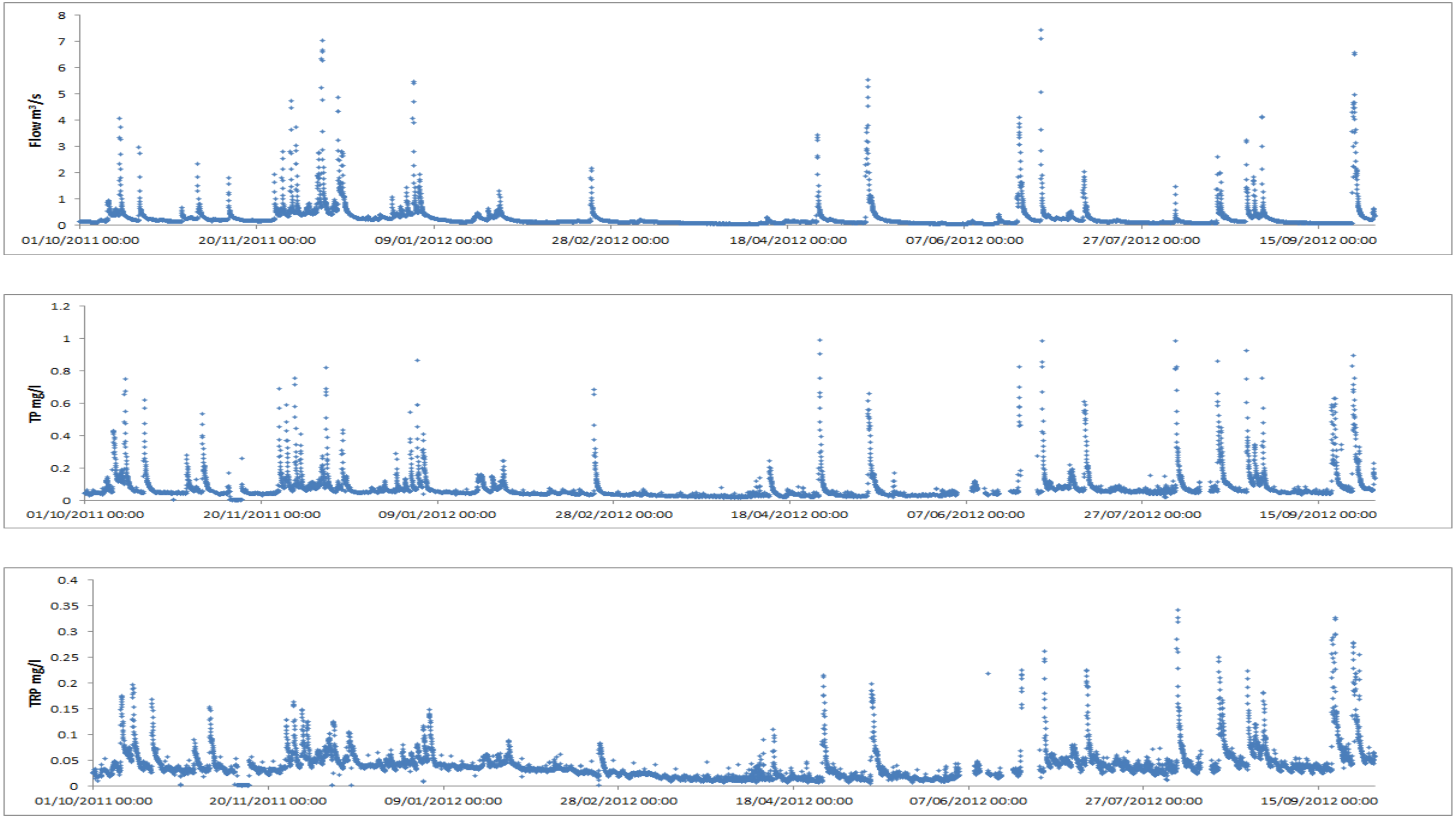


Figure 5.9a Hourly flow, TP and TRP time series recorded at Morland within the Eden catchment, northeast England in 2011-2012 water year

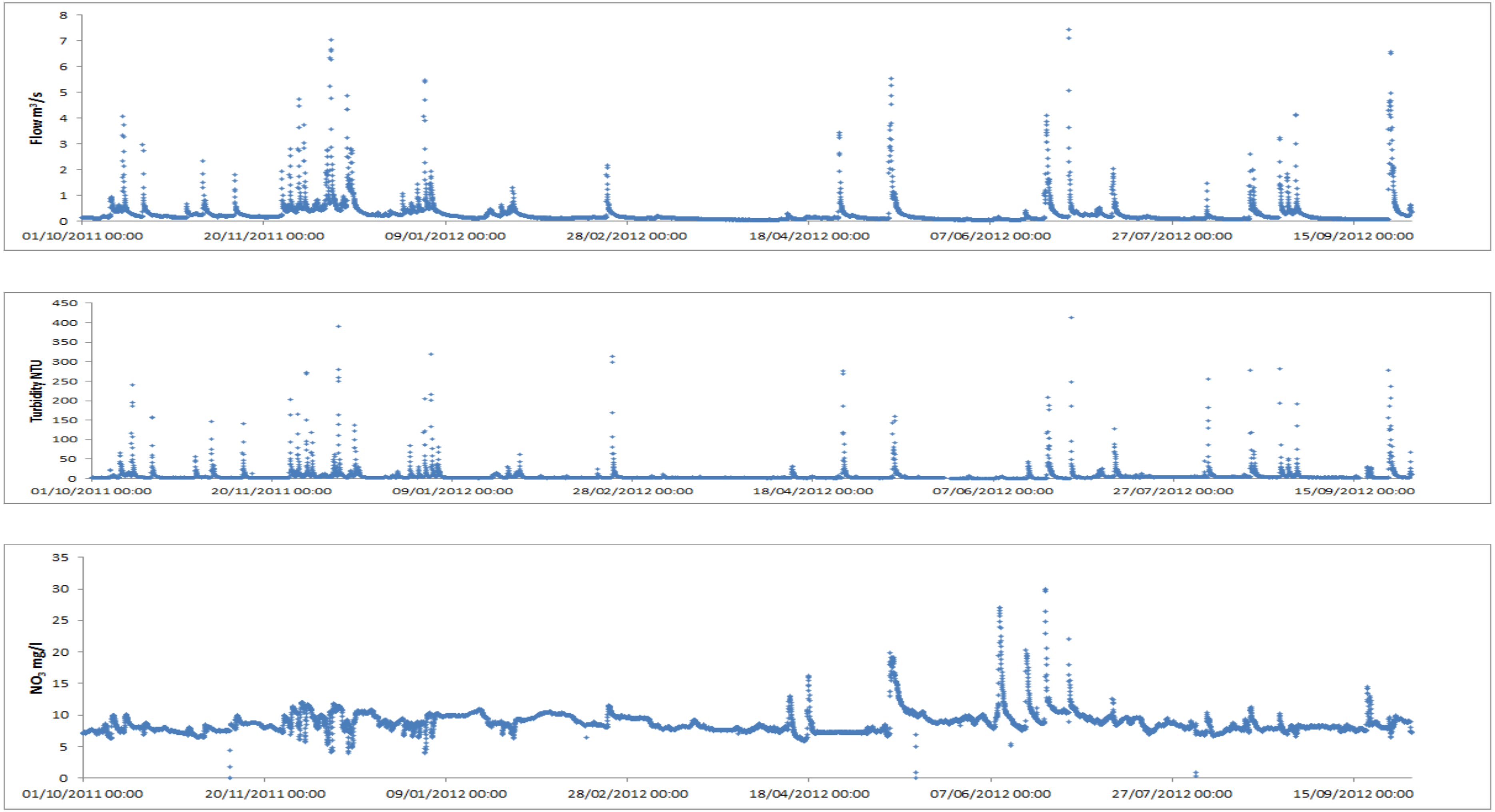


Figure 5.9b Hourly flow, turbidity and NO_3 time series recorded in Morland within the Eden catchment, northeast England in 2011-2012 water year

It was a dilution effect during autumn and winter storms (point source and/or groundwater source, Bowes *et al.*, 2015) but the N concentration increases with flow (diffuse source e.g. agricultural input, tile drain, livestock poaching) during the peculiar wet summer of 2012.The wet summer followed a long dry spell earlier in 2012 and may have flushed out N accumulated during the dry period (see Reynolds and Edwards, 1995; Halliday *et al.*, 2013) and also viewed as weather–induced variation in surface water quality (Rozemeijer and Broers, 2007, Wriedt et al., 2007). Similar complexity was observed in Temple Sowerby (see figure 4.9) when there was a switch in N concentration in autumn. Autumnal flushing following the cropping season has been reported in literatures (e.g. Quinn, 2007). Since the autosampler did not cover the entire season unlike the continuous monitoring data, it may also be that the fraction of the season omitted had a significant influence on the N distribution between winter and spring.

Another highlight of the graph (figure 5.9a-b) is the stream nutrient concentration in April 2012 (and also in early June for N). There were nutrient spikes when there was little or no storm. This suggests either flushing due to cleaning from farm building/hardstandings or slurry application. It is a typical practice to apply fertilizer or manure in the spring and summer. The predominance of almost constant N concentration suggests groundwater source (Jarvie *et al*., 2008) and there has been report of considerable contribution of groundwater to N load in the Eden catchment (EA, 2003).

5.3.4. The pattern of nutrients and sediment concentrations in response to different land use and other catchment characteristics

Earlier in Section 5.2 and table 5.1, the maximum elevation of Dacre, Morland and the Pow are presented. Dacre has the highest elevation, followed by Morland while the Pow is the lowest. The order is reversed in term of intensity of agricultural activities. Dacre contains the least while the Pow is the most intense. Dacre catchment is predominantly underlain by siliceous sandstone while the others are predominantly underlain by calcareous bedrock. Thus, Morland, one of the catchments having a lower mean elevation, is compared with Dacre to show the effect of land use on nutrient and sediment concentrations.

Table 5.5 a-c, compares the maximum concentration between Dacre and Morland. The first table compares the CM data with data from autosamplers before a rating is applied. The flow summary for the CM data is hourly and annual while that of the autosamplers is instantaneous. The next presents the data when rating was applied

a	**CM Morland**		**Autosampler Morland**		**CM Dacre**		**Autosampler Dacre**	
	Min (mg/l)	**Max (mg/l)**	**Min (mg/l)**	**Max (mg/l)**	**Min (mg/l)**	**Max (mg/l)**	**Min (mg/l)**	**Max (mg/l)**
N	0.0504	30	0.086	2.95	-	-	0.192	0.556
TRP	0.0008	0.342	0.007	0.248	-	-	0.003	0.065
TP	0.0005	0.991	0.015	0.951	-	-	0.01	0.406
SS	-	-	3	386	-	-	3.07	122
Flow	0.040 m^3/s	7.43 m^3/s	0.044 m^3/s	4.11 m^3/s	0.028 m^3/s	13.6 m^3/s	0.048 m^3/s	7.69 m^3/s

b	**CM Morland**		**Autosampler Morland**		**CM Dacre**		**Autosampler Dacre**	
	Min (mg/l)	**Max (mg/l)**	**Min (mg/l)**	**Max (mg/l)**	**Min (mg/l)**	**Max (mg/l)**	**Min (mg/l)**	**Max (mg/l)**
N	0.0504	30	1.1	2.1	-	-	0.198	0.538
TRP	0.0008	0.342	0.011	0.333	-	-	0.005	0.033
TP	0.0005	0.991	0.012	1.43	-	-	0.012	0.173
SS	-	-	0.962	225	-	-	1.01	46.7
Flow	0.040 m^3/s	7.43 m^3/s	0.040 m^3/s	7.43 m^3/s	0.028 m^3/s	13.6 m^3/s	0.028 m^3/s	13.6 m^3/s

C	**Morland catchment**	**Dacre catchment**
	Max. concentration (mg/l)	**Max. concentration (mg/l)**
N	2.95	0.556
TRP	0.248	0.065
TP	0.951	0.406
SS	386	122
Flow	4.1 m^3/s	7.7 m^3/s

Table 5.5 a – c Comparison of concentrations of WQPs using data obtained from both the autosamplers and the CM devices

Note: (a) Morland and Dacre hourly data covering the period in 2012 when the two sets of equipment were in operation before rating curve was constructed (b) Hourly data after a rating was applied to the autosampler data in 2011/2012 water year. Only N was generated using N-turbidity relationship (R^2 = 0.19) because the relationship with flow was too weak (R^2 value = 0.07) (c) Hourly data covering the period the autosampler was in operation in both catchments in 2012.

to the autosamplers data and the flow for both are hourly and annual. The third is a summary of the maximum values extracted from the first. It is apparent that Dacre with less agricultural activities (42% managed grassland, 0% tilled land) and at higher elevation has lower stream nutrient and sediment concentrations in comparison to Morland (84% managed grassland, 3% tilled land) with higher agricultural activities but at a lower elevation (table 5.6). The higher percentage of managed grassland and tilled land in Morland despite having high poorly drain seasonal waterlogged soil (84%) suggests high density of tile drain and justifies the concept of combining free drain and poorly drained soil as cultivable soil. Like CHASM catchments discussed in chapter four, higher percentage of cultivable soil in Morland, therefore, is associated with increase land use and higher nutrient export compared with Dacre. Generally, tile drain increase nutrient and sediment stream concentrations and particularly increase nitrate when installed at high density (Gall *et al.*, 2015). T-tests were also used to analyse the differences in TP, TRP, SS and N between the two catchments and it was found that the concentrations of all these environmental parameters were significantly higher ($P<0.05$) in Morland.

	Free drain (%)	**Poorly drain (%)**	**Cultiv-able soil (%)**	**Managed grassland (%)**	**Unmana-ged grassland (%)**	**Tilled land (%)**	**Urban (%)**	**Mean elevation (m)**
Dacre	18	53	71	42	38	0	0	505
Morland	16	84	100	84	9	3	0.6	234

Table 5.6 Comparison of the catchment characteristics in Morland and Dacre

5.3.5 Storm events data and period of dry spell

In order to advance the understanding gained so far on the processes influencing nutrients and sediment in the Eden catchment a graphical analysis of the CM data taken during hydrological events selected from both the wet and the prolong dry period from autumn 2011 to autumn 2012 were carried out using Morland as the representative catchment (figure 5.10 – figure 5.14). Figure 5.10 – figure 5.12 provides an overview of nutrients and turbidity dynamics in the wet period and is quite revealing in several ways. First, figure 5.10, presents the most common

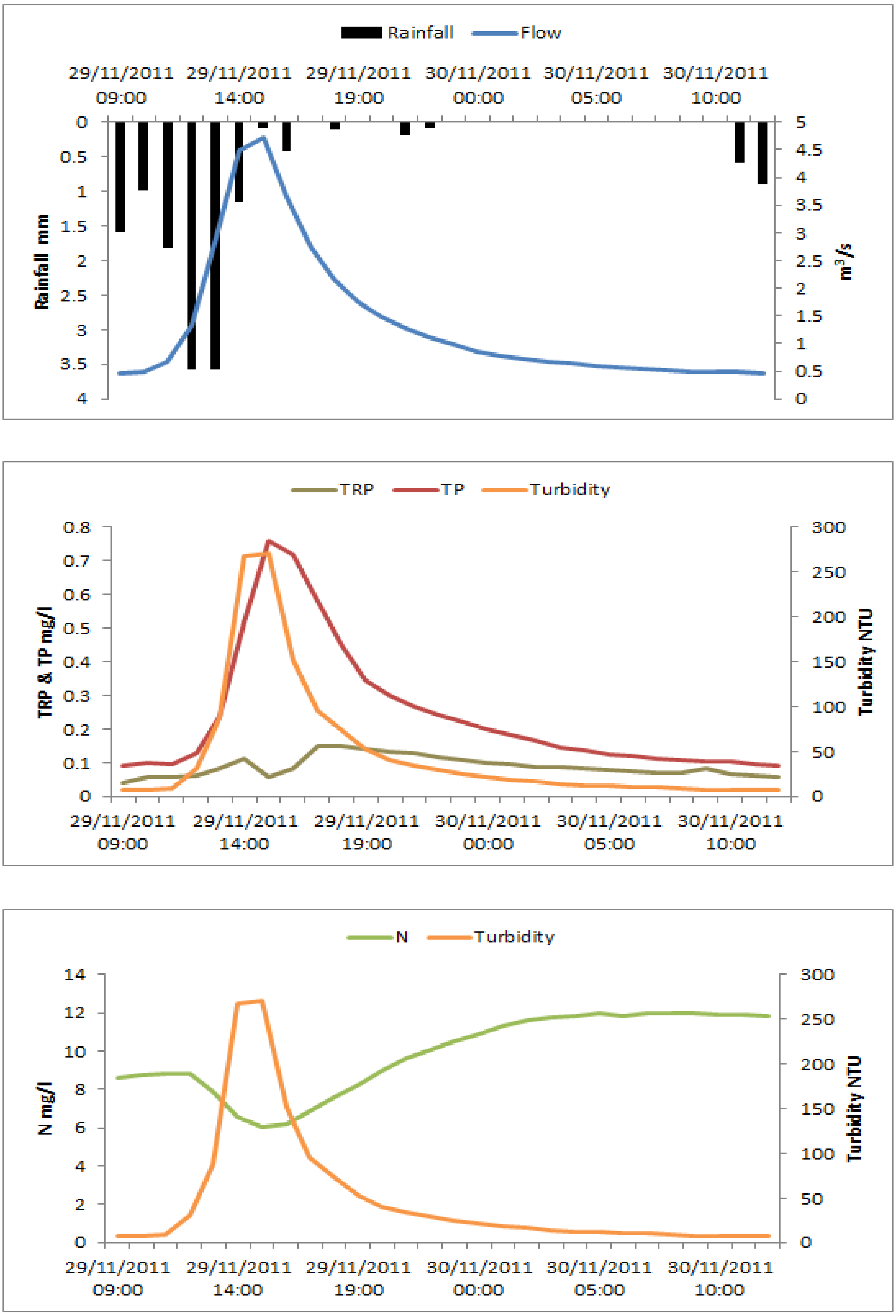


Figure 5.10 Hourly precipitation, flow, nutrients and turbidity contents of Morland in the wet period following an event on 29/11/2011.

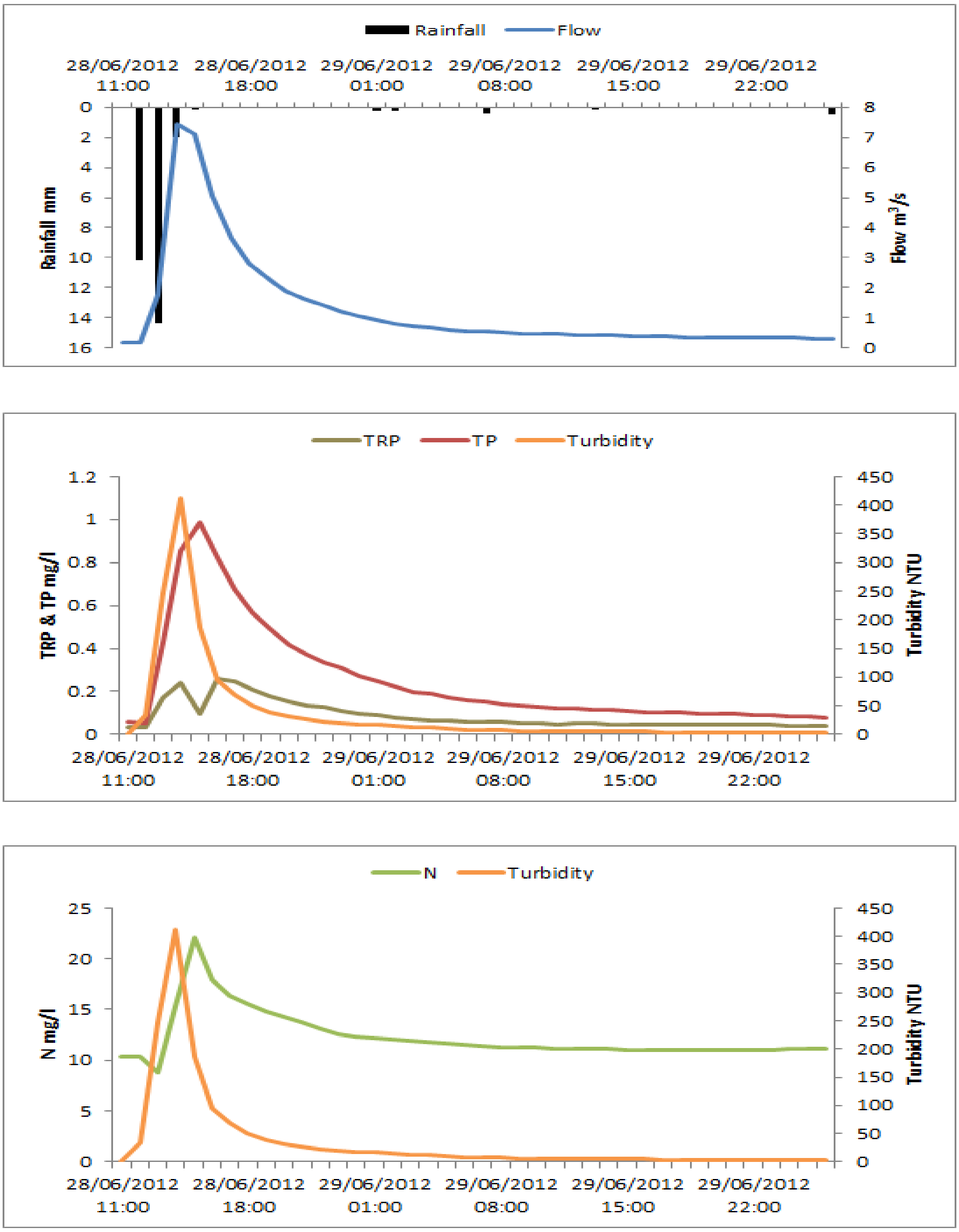


Figure 5.11 Hourly precipitation, flow, nutrients and turbidity contents of Morland in the wet period following an event on 28/06/2012

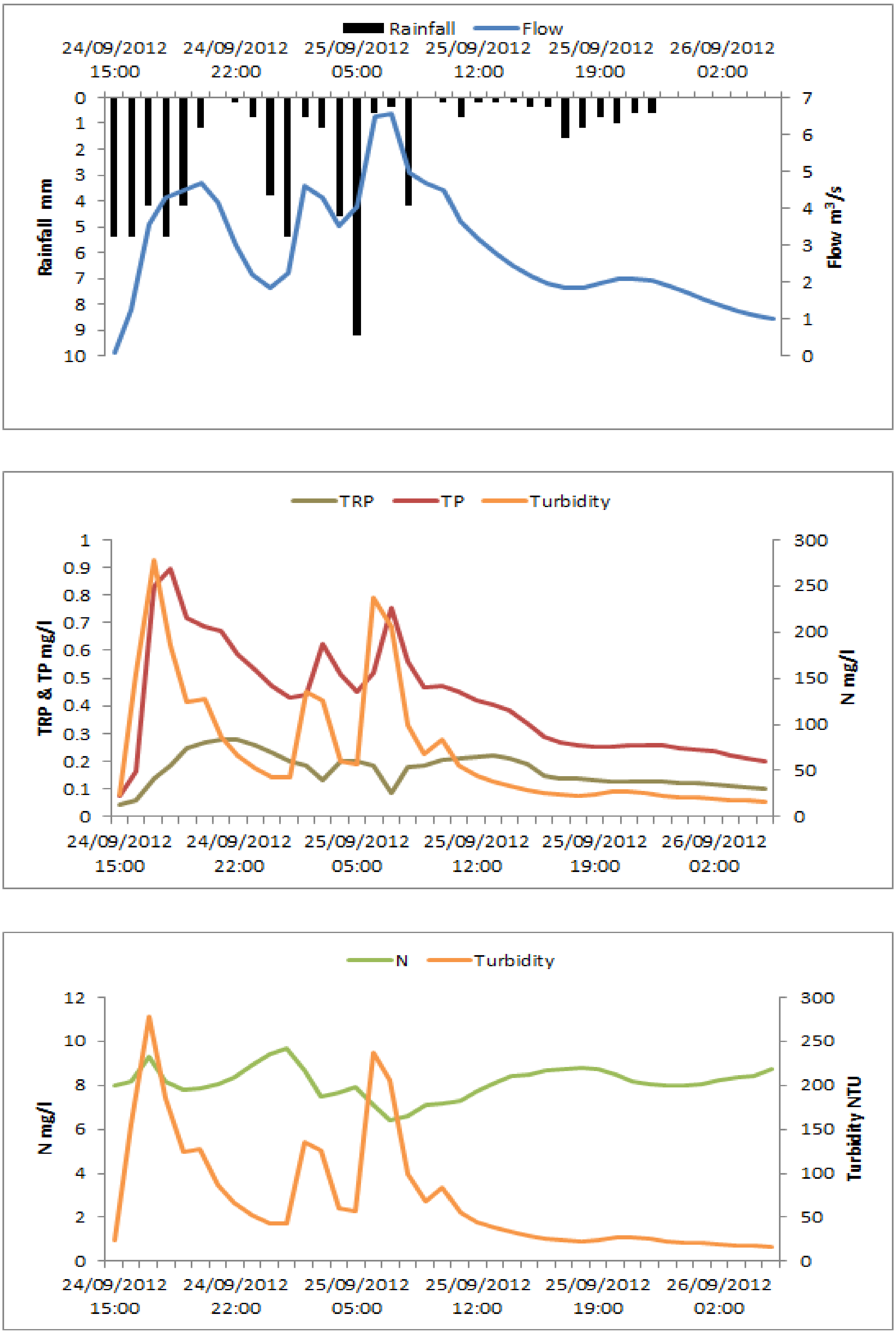


Figure 5.12 Hourly multi-peak precipitation, flow, nutrients and turbidity contents of Morland in the wet period following an event on 25/09/2012.

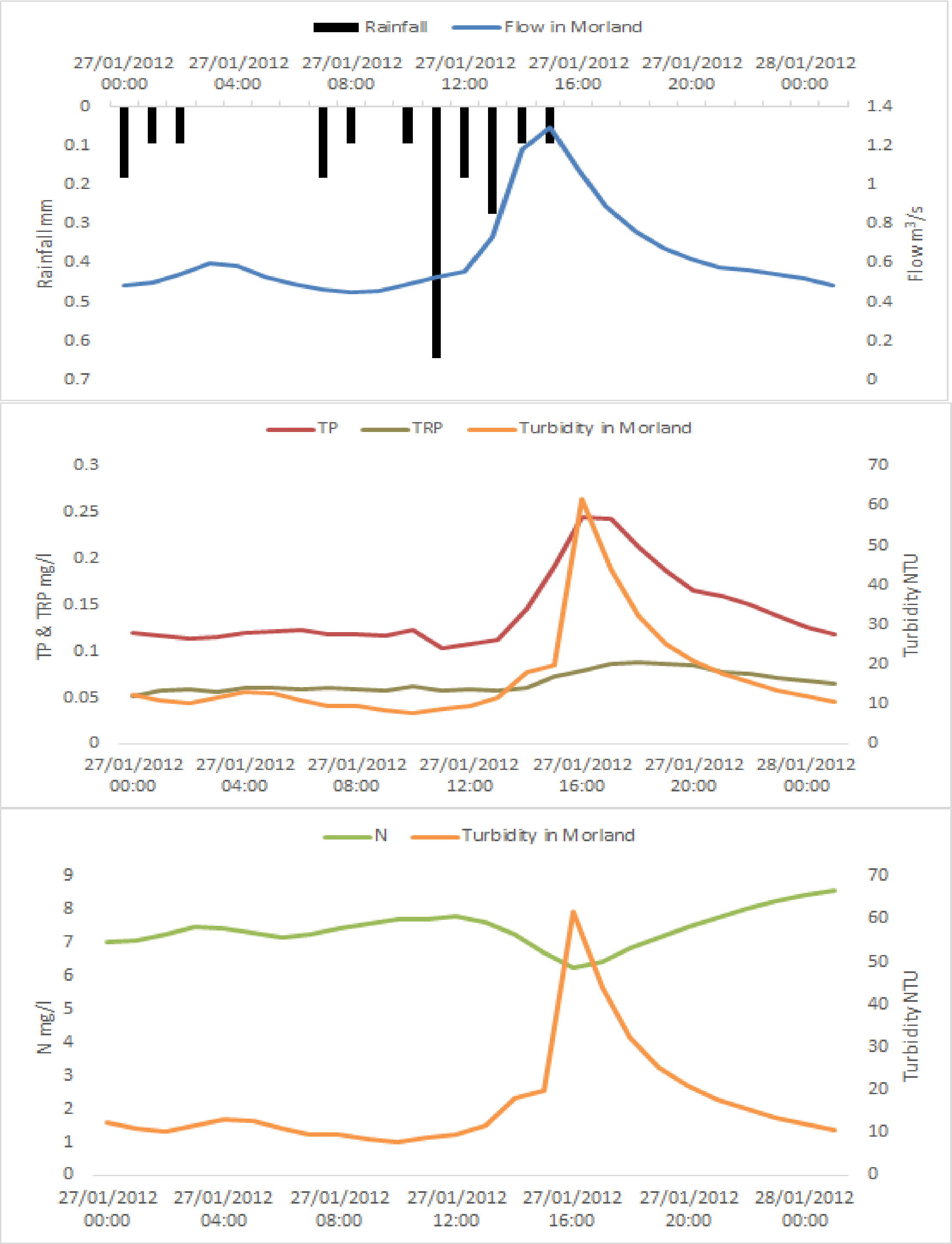


Figure 5.13 Hourly precipitation, flow, nutrients and turbidity contents of Morland in the dry period following an event on 27/01/2012

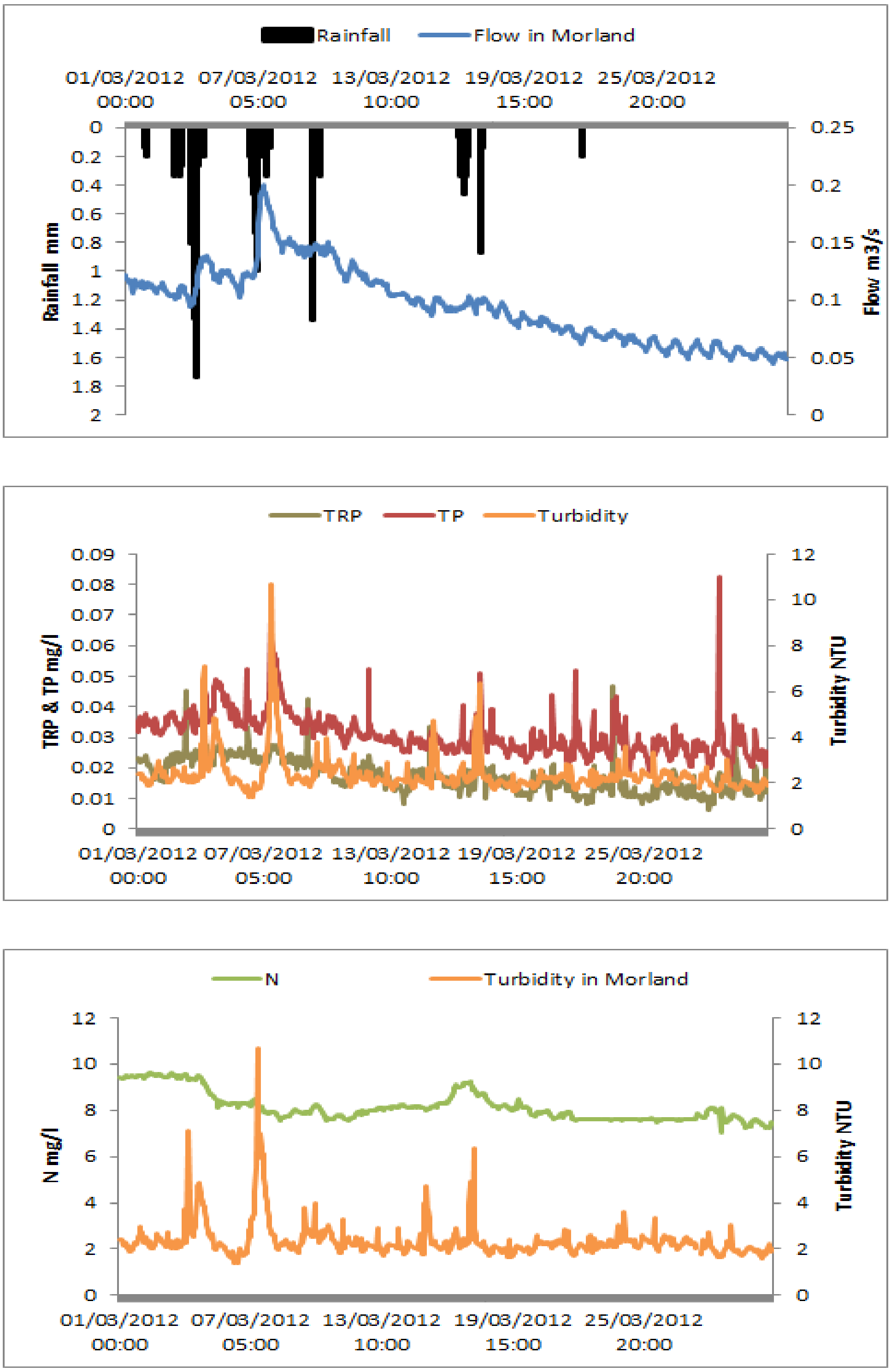


Figure 5.14 Hourly precipitation, flow, nutrients and turbidity contents of Morland during a dry period, March 2012.

scenarios in which TP, turbidity (a surrogate of SS) increased with flow while nitrate decreased with flow, TRP appeared to combine the two relationships. Turbidity often matches flow peak which suggests channel or near channel source (Wade *et al*., 2012). TP narrowly lagged turbidity and it may be that TP has other components that are farther away coming through a quick flow pathway that narrowly missed bed suspension such as field/tile drain (Rozemeijer *et al.*, 2010). TRP initially rose with flow (in-channel or near channel source) then dipped at flow peaks (dilution of component coming from a constant/point source), then another peak (arrival from agricultural diffuse source) before receding with flow. In figure 5.11, another scenario is set out, in which nitrate increased with flow just like TP and also lagged the flow peak unlike turbidity. During this storm event (28/06/2012, i.e. the wet summer), it appears TP and N might have been influenced by a source that narrowly lagged the in-channel source. This could be diffuse agricultural source transported through field drain. Figure 5.12 illustrates a case when there were multiple peaks in flow. TP and turbidity remained consistent in their relationship with flow, TRP increased with flow but without a sharp peak while nitrate appeared to follow the most common scenarios, the negative gradient or dilution effect, except at higher flow when it increased with flow.

Turning now to the nutrient dynamics in the dry period, all the other water quality determinands with the exception of N responded to the low magnitude events by increasing as the low flow increased (figure 5.13 and figure 5.14). It is apparent from Figure 5.14 covering March 2012, that when it was dry the N was constant at low flows. This accords with Bowes *et al*. (2015) who observed complex N signals including constant N in River Enborne in response to different weather conditions. It may also be viewed as a situation whereby a nitrate source at low flow is not receiving a storm event that was large enough to cause dilution. Earlier in this chapter, groundwater source has also been linked to constant stream N concentration. To address the question regarding the response of nutrients, particularly N, to flow dynamics, a flow duration curve (FDC) was developed and all the water quality determinands were sorted based on flows and plotted (figure 5.15). TP, TRP and turbidity appeared to follow the trend shown by the FDC except for a certain period, between 80-90% exceedance, when what appears to look like period of nutrient

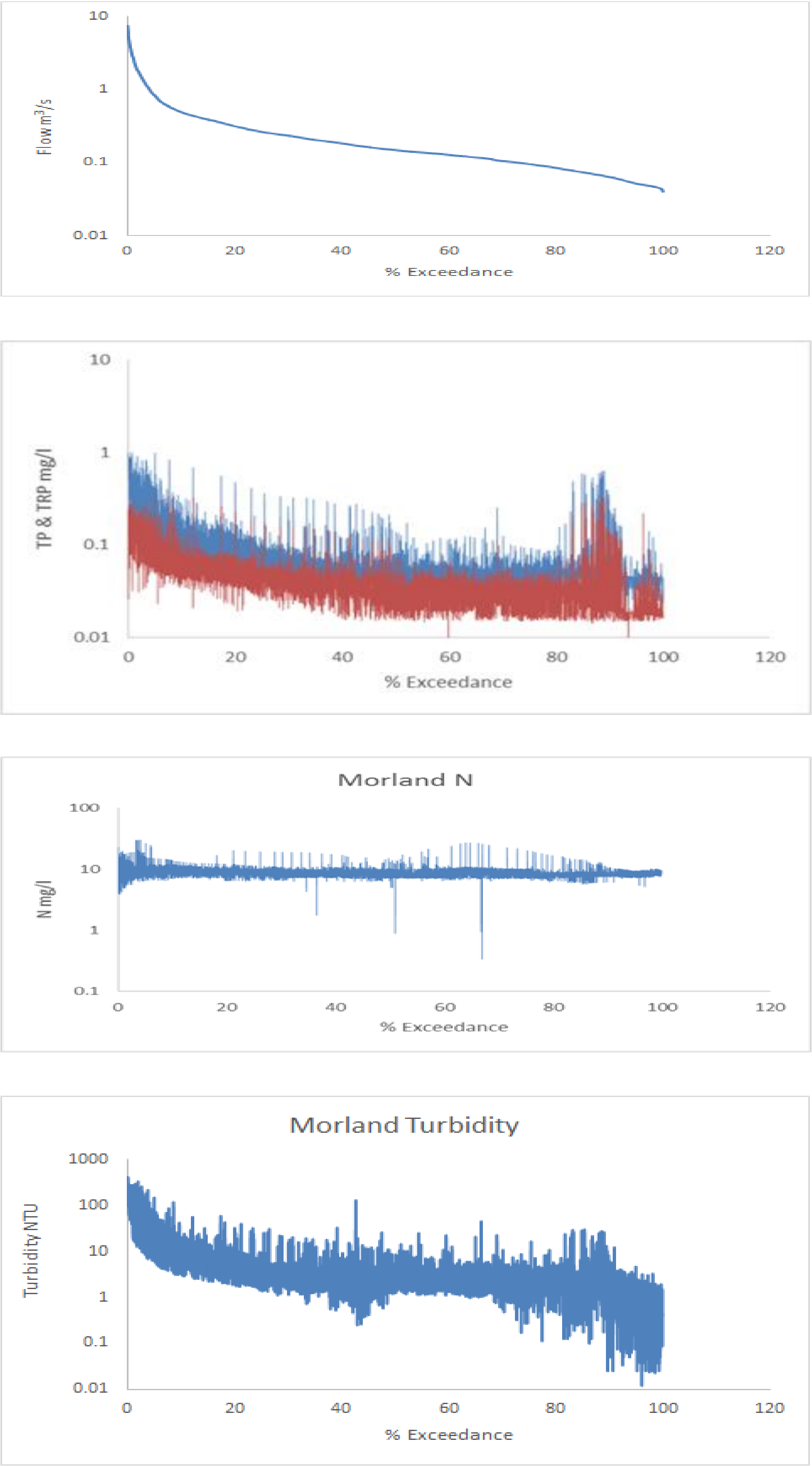


Figure 5.15 Morland flow duration curve and corresponding responses of TP & TRP, N and turbidity from 01/10/2011-30/09/2012

wash off or incidental losses occurred. Nitrate increased for a short period at peak flows but levelled off for most of the lower flow region on the FDC though there were periods showing wash-off events (between 10 - 80% exceedance). The next highlight of the exceedance plot is the flow zones when the environmental permissible threshold/limit (Drinking Water Directive etc.) for some of these parameters were breached. These flow types fall within the high flow zone and in some periods in the mid flow zone.

5.4. Evaluating sediment and nutrient exports and specific yields

Two methods deployed in the calculation of load (approximate and FDC-rating method) and the methods for calculating yield have been described in the previous chapter. The third method which is an estimate of annual load based on integration of the hourly data is presented along with the approximate method in this section This method was made possible due to the opportunity that the near continuous water quality monitoring equipment provided.

5.4.1. Calculation of the annual load and yields

The concentration data from samples collected using the autosamper were subjected to approximate method and annual load was obtained as described in the chapter four. The second technique used in this chapter employed both the hourly concentration data generated from the autosampler data using a rating equation (Appendix C) and the hourly data obtained from the near continuous monitoring equipment (CM). The product of the hourly concentration (mg l^{-1}) and hourly flow (in $m^3 s^{-1}$) and a conversion factor (CF = 0.0036) gives the hourly load. The factor was derived to convert the units to tonnes per hour. The simple addition of all hourly loads in a year gave the annual load. The annual yield was estimated by dividing the load by area followed by the integration of the hourly estimate over the year.

5.4.2. The comparison of loads and specific yields of nutrients and sediment in response to some DTC catchments characteristics

To assess the role of the interactions between land use, elevation and geology on nutrient export, the estimated annual loads and yields for Dacre and Morland were compared as shown in table 5.7 and table 5.8. The differences in the values obtained from different load estimation methods have been addressed in the previous chapter. Except for N, it is worthy of note that the rating method gave

	Morland tonnes/yr			Dacre tonnes/yr		
	Approximate	**Annual Autosampler (rating)**	**Annual CM**	**Approx.**	**Annual Autosampler (rating)**	**Annual CM**
N	42.2	13.7	80.5	8.96	4.67	N/A
TRP	3.44	0.743	0.636	0.356	0.224	N/A
TP	9.24	2.20	1.72	1.49	0.925	N/A
SS	2350	296	N/A	279	176	N/A

Table 5.7 Comparison of annual loads of WQPs from Dacre and Morland using the approximate method (autosampler data) and integration of hourly estimate of the CM data

	Morland tonnes/yr/km^2			Dacre tonnes/yr/km^2		
	Approx	**Annual Autosampler**	**Annual CM**	**Approx**	**Annual Autosampler**	**Annual CM**
N	4.29	1.37	8.05	0.900	0.467	N/A
TRP	0.344	0.0743	0.0636	0.0356	0.0224	N/A
TP	0.924	0.220	0.172	0.149	0.0925	N/A
SS	235	29.6	N/A	27.9	17.6	N/A

Table 5.8 Nutrient yields from the DTC catchments calculated using the Autosampler and CM data

values that were close to CM. The problem with nitrate is down to the weak relationship it has with flow as earlier mentioned. This underpins the reliability of the rating method, as a reasonable substitute; in the absence of fund to supports the bank side monitoring technique, provided the rating relationship is not too weak. Across the various estimation technique deployed, it is apparent that Dacre which is predominantly situated on siliceous bedrock, having a higher mean elevation but a lower agricultural intensity, has a lower export of all nutrients and SS compared to Morland that is predominantly underlain by calcareous bedrock, having a lower mean elevation but a higher agricultural intensity. This supports the interrelationship between elevation and land use in the Eden, as observed among the CHASM sub-catchments, where agricultural land use which intensifies at lower elevation resulted in a higher export of nutrients and sediment from the basin into the river. Having described the impact of hydrological processes and land use in the Eden catchment on water quality, the seasonal patterns in nutrient loads and yields can also play an important role in the understanding and management of the nutrient contamination issues and the pollution of rivers.

Seasonal pattern

A percentage annual load of the water pollutants relative to rainfall and flow was used to compare the seasonal pattern of load exports into both Morland and Dacre Becks (figure 5.16). From the chart, it can be seen that the lowest flow and the lowest nutrients and sediment exports occurred in spring in both catchments. The highest nitrate data was recorded in winter. Again, this underscores the importance of flow as one of the key factors governing the dynamics of water pollution in the Eden catchment.

Another important highlight in this chart is the difference in the TP and TRP percentage loads between the data generated from the relationship of flow and the one calculated from the near continuous monitoring (CM) equipment. In the former TP and TRP loads were highest in the season with the highest flow whereas autumn and winter loads were about equal in data generated by the latter. This shows once more the draw back with prediction of the data using regression analysis (being flow ‘weighted’). Notwithstanding this limitation the rating relationship still offers a reasonable insight into a study into study of this nature considering the cost implication that the bankside (CM) instrumentation incurs (Wade *et al.*, 2012).

5.4.3. Load exceedance and comparison of nutrient and sediment transfer

The load exceedance approach enabled the investigation of pollutants transferred under different flow types: high flow, mid flow and low flow. The procedure followed the pattern used to construct a FDC in which the percent exceedance is calculated after ranking the flow and pollutant loads from the largest to the smallest. Data are then extracted from the percent exceedance class that is related to each of the flow types. High flow falls within the upper 10 %, mid flow is classified as the flow from10 to 90% while the lower 10% contains the region designated as low flow. This is in phase with apportioning 90th flow percentile to condition when diffuse nutrient source dominate and 10th flow percentile to low flow condition associated with point source when it is accompany by graph showing dilution effect (Halliday *et al.*, 2013)

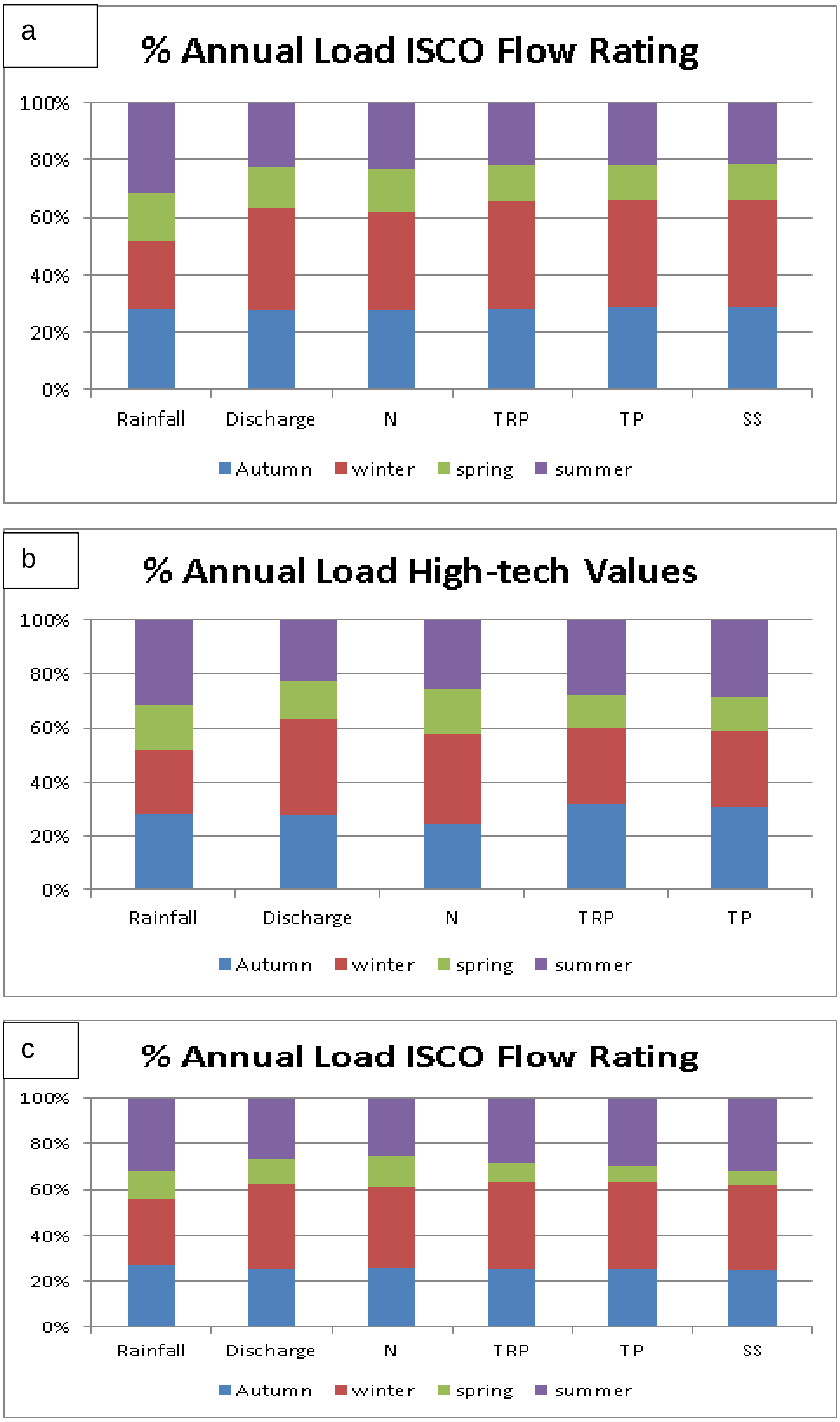


Figure 5.16 Seasonal comparison of rainfall, flow and water quality parameter transferred in Morland Beck outlet- using (a) Autosampler data and (b) CM data and – (c) the Dacre Beck outlet from October 2011 – September 2012

Table 5.9 compares the percentage annual loads of TP, TRP, SS and N in Morland based on the data collected from both the autosampler and the CM equipment. Most of the TP, TRP and SS loads were exported in the Morland Beck during high flows whereas N was mostly exported at mid flows. For all the nutrients and sediment the smallest loads were exported at low flows. The pattern was similar for Dacre except that less percent TP, TRP and SS are transferred at high flow but have higher percentage load for these parameters at mid flow (table 5.10). The lower percent P and SS load in Dacre at high flow relative to Morland may have be due to exhaustion due to less agricultural activities and presence of rocky outcrops (Allen *et al.*, 2010).

Total Value				**% Annual Load (Autosampler)**			
	Time	**Rainfall**	**Flow**	**Nitrate**	**Reactive P**	**Total P**	**Sediment**
Highflow	10	35.1	46	39.6	78.6	86.2	90.3
Midflow	80	59.7	52.1	57.9	21.1	13.7	9.7
Lowflow	10	5.2	1.9	2.5	0.3	0.1	0.07

Total Value				**% Annual Load (CM)**			
	Time	**Rainfall**	**Flow**	**Nitrate**	**Reactive P**	**Total P**	**Sediment**
Highflow	10	35.1	46	47.6	70.3	81.4	N/A
Midflow	80	59.7	52.1	50.7	29.2	18.3	N/A
Lowflow	10	5.2	1.9	1.7	0.5	0.3	N/A

Table 5.9 Comparison of rainfall, flow and nutrient, and sediment export in Morland using Autosampler data and CM data for the period covering October 2011 – September 2012

Total				**% Annual Load**			
Value	**Time**	**Rainfall**	**Flow**	**Nitrate**	**Reactive P**	**Total P**	**Sediment**
Highflow	10	37.8	46	38.1	60.7	67.3	75.1
Midflow	80	58.1	52.7	59.9	38.7	32.4	24.7
Lowflow	10	4.1	1.3	2	0.6	0.3	0.2

Table 5.10 Comparison of rainfall, flow and nutrient, and sediment export in Dacre using Autosampler data for the period covering October 2011 – September 2012

5.5. Summary

This chapter has highlighted the catchment characteristics in the Eden DTC catchments and particularly reveals how the unique hydrological characteristics within the study period relate to the nutrients and sediment dynamics in the River Eden. The advantage that the near continuous monitoring equipment presents in the understanding of processes driving the nutrient transport was explored and comparisons were made with data generated through rating relationship where necessary. Except with nitrate concentration where the rating relationship (concentration vs. flow) was weak, data generated with autosampler have good agreement with the data from the bank side monitoring; therefore, data generated were found to be useful in describing water pollutant dynamics in the River Eden. In many instances they are comparable in pattern to the CM data. The results considered show that hydrology and land use are principal factors controlling nutrients dynamics in these catchments among others thus supporting the observation in the CHASM sub-catchments. Land use has also been demonstrated to be linked to soil type and associated land management. All other nutrients and suspended sediment show more consistent positive gradient when related with flow unlike nitrate that appears to show dual relationship and can sometimes appear constant depending on prevailing flow band. This is in line with the dual nitrate-flow relationship spotted under the CHASM study platform that was reported in chapter four. While other nutrients are largely exported at high flow, nitrate is largely exported at mid flow. The concentration, load and yield increase with intensity of land use and there is clear upland-lowland variation.

Therefore, by analysing the near continuous data from the DTC project, it appears that storms event results in high losses for SS and TP whereas, except for the peculiar summer period, the loss was less in the case of N and it is dominated by leaching and groundwater. Apart from the general pattern of nutrient transfer into the river, assessment of the storm events presents an opportunity to see the individual nature of losses. Similar to the general pattern, turbidity (the proxy for SS) and TP reveal pattern that is consistent with the general pattern earlier noted. By matching the flow peak, turbidity/SS might have been considerably sourced from channel or near channel sources whereas TP that narrowly lagged the flow peak might be coming from a source that arrive a little later suggesting field/tile drain. TRP initially rises with flow but dipped at flow peak before rising and then follow flow pattern eventually suggesting a complexity which involve variations in prevalence of near, point and distant sources respectively within a short period of time. In addition to showing dilution effect suggesting a constant source (e.g. groundwater), there is an instance of acute N loss in response to heavy storm. This findings supports previous work that have shown how changes in weather pattern can drives variations in surface water quality and mask the contribution of primary drivers of water quality in a catchment. Nitrate concentration can also be almost constant in dry periods. This result enables the processes underlying the pollution problem to be identified and understanding these patterns will help inform stakeholders involved in catchment/sub-catchment management on possible management options. The next chapter focuses on providing more explanation to support the results reported in Chapter 4 and this chapter.

Chapter 6: Discussion of Findings from the CHASM and DTC Studies

6.1. Introduction

The results of two out of the three key studies addressing questions raised in this research have been reported in the previous two chapters. The two studies which involve CHASM and the DTC projects present a unique combination of study platforms to appraise the spatial dependency in nutrients transferred into the River Eden, and the use of near-continuous data to investigate the key drivers of nutrient exports into the River Eden respectively. In the Eden catchment, hydrology and land use are the two key catchment characteristics identified as drivers amongst others. This chapter sets out to offer explanation and considers the implication of these findings. It is divided into separate sections that consider the influence of hydrological processes and land use on nutrient losses under the CHASM and DTC study platforms and thereafter discusses other secondary catchment characteristics and processes that are relevant to nutrient dynamics in the River Eden.

6.2. Hydrology and water contaminants transport using the spatial scale CHASM study

6.2.1. Rainfall and flow pattern in 2012

The unusual long dry spell that started in January 2012 and lasted until May 2012 and the wet summer that followed seem to have a significant implication on the nutrient input from the Eden catchment. Although lower emission into water bodies is expected during the dry period because of limitations in wetness or flow, which is a critical factor in nutrient loss from catchments, the wetness may have been sufficient enough in addition to warmth to encourage nitrate mineralisation during this period. This agrees with Halliday *et al*. (2013) who reported that a drier soil in the forested lower Hafren can lead to increased soil N mineralisation compared to Moorland. Mineralisation is a biological process when nitrogen in reduced and organic form is oxidised to nitrate by some microbes (e.g. *Nitrosomonas* sp). The process is enhanced by a well aerated soil and warmth. The mineralised nutrient (N) along with residual nutrients (N and P), arising from excess supply from fertilizer and manure application above crop requirements, are delivered into the water course during the next wetter season or period.

An additional feature of this period (dry spell) that is important is the favourable climatic conditions for eutrophication that it ensures; the same reason that cropping is intensified during a typical spring and summer. Thus, the period of low flow during spring and summer has been designated by some authors (Jarvie *et al.*, 2006; Wall *et al.,* 2011) as the ecologically sensitive period for rivers. Given that the peculiar attribute of these seasons is low flow and the warmth and stimulation of biological processes, it can be assumed that the winter period of the low flow from January – part of March will experience limited nutrient transport. The part that fall within the spring, characterised by low flow, would have most likely exhibited some degree of ecological risk leading to in-stream nutrient exhaustion. The record wet summer might have shared similarity in nutrient flux with typical late autumn to winter seasons (Withers and Lord, 2002), when all the nutrients that are transport-limited in the terrestrial catchment are flushed into the fluvial system.

However, nitrate and phosphorus often respond to flow in different ways due to many factors ranging from variations in their physical properties (adsorption to soil matrix) and chemical reactions (solubility) with water on one hand and the influences of some catchments characteristics, particularly land use and soil types/properties, on the other hand. A rating curve, where nutrients are related to the corresponding flow at the time of sampling provides a means of assessing the nutrient-flow relationship which can provide hints on sources, and some catchment characteristics and processes. A nutrient-flow relationship can also be used in evaluating yield (e.g. Julien, 1998).

6.2.2. Nutrient and sediment rating curves

A typical nutrient rating curve has nutrient concentration plotted against flow. Unlike nitrate (N), phosphorus (P) and suspended sediment (SS) almost always have a positive relationship with flow in the River Eden catchment. Phosphorus is attached to soil particles and sediment and these are transported by overland flow via the erosion process if conditions are favourable. Erosion is triggered by rainfall impact having enough energy to detach soil particles and this occurs more frequently in soils whose particles are loosely bound together (i.e. having a weak soil structure) particularly when such soils are exposed. Other conditions that favour erosion are slope, bare and sealed surfaces or poorly drained surfaces (e.g. bare clay soil), and poor land management such as cultivation or ploughing in the direction of slope etc. Thus runoff with adequate erosive force picks up the detached particles which in turn peel off other particles through scouring. Catchments characterised by some or all of these conditions are expected to show a positive relationship between P, SS and flow. Other possible sources of P and SS are the in-channel or near-channel sources while other pathways that can result in positive P gradient with flow is the tile or field drain, road cutting through the field and watercourse etc. Such road exists in Ravenstonedale and Smardale. In contrast to P and SS, N tends to have a negative relationship with flow in the Eden catchment.

Generally, there was a negative slope in the nitrate rating curve or the nitrate-flow relationship (table 4.3) in almost all the CHASM catchments when all the data collected were put together. This is probably due to a different source (see section 6.4.3) and the different soil-nitrate chemical processes compared with P and SS. Nitrate is a soluble chemical component of soil and the process of N loss is described as leaching. Nitrate leaching is the loss of nitrate from the soil due to interaction of soil with rain and other sources of water input. Factors that influence leaching include soil properties such as texture, porosity, presence of fissures and processes such as by-pass flow which may arise due to the installation of under drains. Organic nitrogen mineralisation is another critical factor that enhances leaching by making more nitrate available, and it is a biological process that is critical to the mobilisation of N. The process is favoured by warmth, a factor that probably contributes to seasonality in soil N content and delivery in catchment outlets. Exposed aquifers (or permeable rock outcrops) also connect nitrate to a subsurface pathway. This ensures that nitrate is not only lost through the surface or near surface flow but comparatively substantial amounts are also lost via a subsurface flow pathway (groundwater). A previous study indicated that groundwater having elevated N can maintain a constant value of N particularly during the base flow period (Jarvie *et al.*, 2008) and this is further discussed in section 6.4.2. There is the possibility of this occurring during the ecological risk period mentioned earlier. Taken together the relationship of N with flow can thus be more complicated than that of P.

One unanticipated finding was that the nitrate-flow relationship at Gais Gill (1.1 km^2), a CHASM headwater catchment, shows a positive slope albeit a weak relationship

(R^2 = 0.24). The catchment is an upland catchment (470 m elevation), consisting of substantial areas of land covered by rough grassland and semi-natural vegetation, and has a comparatively low stocking density of sheep. The land area surrounding the gauging station, where water and soil samples were collected, was often saturated with visible overland flow for appreciable periods during this study implying a catchment with remarkable hydrological connectivity. A possible implication of this is that the overland flow and near surface flow readily transport nitrate from sheep droppings to the catchment outlet with probably none or limited groundwater influence. This suggested flow path is supported by the fact that Gais Gill is covered by shallow soil and that the observed soil depth throughout the period the soil was sampled during this study was usually no deeper than 50 cm (see section 6.8 for more details on Gais Gill).

The nitrate rating curve for Temple Sowerby is also somewhat surprising. The scatter plot for the four seasonal campaigns (from autumn 2011 to summer 2012), when put together, started with a negative slope before changing to a positive one (figure 4.9). With the exception of the data collected on 21/11/2011, the points coinciding with the positive slope predominantly came from autumn 2011 and data collected on 16/12/2011 (early winter 2011) (table 6.1).

A possible explanation for the points making the positive slope of the graph is that they may have resulted from 'incidental losses' when fertilizer and manure spread on the surface gets washed off before it can be equilibrated into the soil (Haygarth and Jarvis, 1999; Withers and Lord, 2002). The record kept for the last visit during the autumn campaign (24/11/2011) indicated that the river level was high and the river was turbid unlike the previous visit (21/11/2011) when it was clear (table 6.1). The accumulated nutrients from the previous cropping season, particularly in the lowland, and tillage for winter wheat implies that the high flow in late autumn to early winter is capable of delivering nutrients into the watercourses, corroborating the findings of previous work in this field (Jarvie *et al.*, 2008). Great Corby (1373 km^2), a catchment further downstream with an arable farm (with associated fertilizers applications) adjacent to the river, also showed some degree of increase in nitrate emission with flow when the flow increased to 39.6 m^3/s and above.

Date	Flow (m3/s)	N mg/l
01/11/2011	21.9	4.55
03/11/2011	25.5	5.26
21/11/2011	5.4	7.76
24/11/2011	42.0	5.70
16/12/2011	27.8	7.90
06/03/2012	8.8	5.38
14/03/2012	5.6	6.65
19/03/2012	5.3	6.53
21/03/2012	4.6	7.37
02/05/2012	7.2	5.01
09/05/2012	5.6	5.80
16/05/2012	10.3	4.25
21/05/2012	6.6	5.00.
25/06/2012	19.6	3.52
23/07/2012	7.2	6.15
26/07/2012	7.3	5.89
31/07/2012	6.8	5.15
06/08/2012	9.5	4.26
19/09/2012	8.3	3.71

Table 6.1 Nitrate concentration and corresponding flow from autumn 2011 to summer 2012 at Temple Sowerby

A catchment in the upland zone where cattle were sometimes seen grazing a pasture adjacent to the stream, Smardale (37 km^2), despite being home to Smardale Gill National Nature Reserve, also showed a similar tendency at high flows. Apart from hydrology it seems possible that the increased availability of nitrate at Great Corby and Smardale was made possible by the arable farming and cattle stocking respectively (i.e. near nutrient sources), and may have enhanced the nitrate delivery leading to the positive slope. Both the arable land at Great Corby and the grassland where the cattle are grazing in Smardale are adjacent to watercourse and can accurately be described as Critical Source Areas (CSAs). Neal *et al*. (2004) also attributed mixed signals in nitrate concentration in Lambourn and Pang catchments to channel removal processes, crop uptake and dilution from fissure flow for the negative gradient, whereas the positive gradient is associated with leaching/flushing from excess fertilizers sources from the land.

6*.2.3. Point sources in the Eden catchment*

Although recent study in the Upper Eden catchment (Barber, 2013) extending up to Appleby excluded point sources from their export coefficient modelling stating that they are notoriously difficult to estimate and that population density in the Eden is low, an attempt was made to do an approximate estimation in this section. This is to enable a fairly reasonable conclusion to be drawn, based on quantitative data, on the contribution of point source to nutrient load in some catchments. It is based on the assumption that septic tank systems (STSs) in the Eden are point sources even though STS has been classified as both diffuse (Wither *et al.*, 2012; Bowes *et al*., 2015) and point sources (Jarvie *et al*., 2010; Palmer-Felgate *et al.*, 2010; Wither *et al.*, 2011). The assumption also allows the use of comparatively higher value of nutrient export from STS (0.54 kg P person^{-1} yr^{-1} and 2.5 kg N person^{-1} yr^{-1} for P and N respectively (Halliday *et al.*, 2014) instead of the lower values of sewage water works (STWs) reported in literatures (0.053 kg P person^{-1} yr^{-1} for sewage system without stripping (Johnes *et al.*, 2003) and 0.0053 kg P person^{-1} yr^{-1} for those with P removal, Anglian Water, pers. Commun.). If soil P retention were known and used in the calculation, then the value of the contribution from the STSs or point source(s) will be yet lower than what is reported in the table 6.2. Another assumption made is to use these values along with the data on population for each catchment based on Parish (except otherwise stated) from www.neighbourhood.statistics.gov.uk. All these asumptions become necessary considering the challenges facing the rough estimation of septic tank and indeed point source contribution to nutrient concentrations in rivers. Brownlie *et al.* (2014) well recognised lack of information on number, age, condition, efficiency, frequency of desludging, downstream processing of P in soils, hydrological variations, proximity of water courses at a site level and human domestic behaviour on P loading, as challenges facing estimation of P linked to STSs.

For this study, the estimate of export from point source is obtained by multiplying the value of nutrient export from STS by the population in each catchment and this is presented in table 6.2. Generally, STSs account for only a limited amount of P input into the river in most of the catchments. Except for Ravenstonedale (72.4%) and Dacre (255.9%), the contribution of STSs to stream P concentration range from 0 - 28% in all the other catchments in the River Eden. The high value in Ravenstonedale

	STS P kg/yr	River P kg/yr	%P	STS N kg/yr	River N kg/yr	%N
Gais Gill	0	27.4	0	0	1943.0	0
Ravenstonedale	983.0	1358.1	72.4	6576.0	119418.6	5.5
Smardale	0	2280.7	0	0	238339.8	0
Gt. Musgrave	273.0	8428.0	3.2	1826.8	4726261.0	0.04
Appleby	5044.0	18546.3	27.2	33745.7	9257501.0	0.4
Temple Sowerby	873.8	39256.1	2.2	5845.7	25523546.0	0.02
Gt. Corby	3569.5	42554.0	8.4	23881.1	19223692.0	0.1
Dacre	2379.7	930.0	255.9	15920.7	4670.0	340.9
Morland	619.0	2210.0	28.0	4140.7	13650.0	30.3
Blind Beck	0	226.4	0	0	39495.6	0

Table 6.2 Estimate of point source in the Eden

and in particular Dacre could be due to high P retention in-stream. Wither *et al.*, (2012) reported vale as high as 127% in Modre catchment in Norway and suggested that P retention occur within the stream system between the point of discharge and the catchment outlets. Other P contributions from STS (0 – 28%) in the Eden also agree with the range reported by these authors. It agrees with less contribution of both STWs and STSs anticipated in the earlier study making them to ignore point source estimation for the export coefficient model for the Upper Eden due to low population density amongst other (Barber, 2013). Thus, agricultural source dominate the contributor to P in the River Eden.

The contribution of STSs to N in the Eden is even lower than that of P. With the exception of the DTC sites (to be discussed in more details in section 6.4.1) the STSs contribution to N ranges from 0 – 5.5% and it may be due to the low population density. It also suggests that the general tendency for the negative gradient (concentration vs. flow) must be coming from another constant source which is diluted as flow increases. This can only be groundwater source and this supports the EA reports stating that groundwater has a marked contribution to N load in the Eden (EA, 2013).

6.2.4. Influence of the synergy between hydrology and land use on the spatio-temporal variation in the strength of the rating curves

The results shown in table 4.3 summarises the R^2-values across the sub catchments and seasons investigated under the CHASM study. Notwithstanding a few surprises where there are deviations from the norm in terms of the slope of the contaminant rating curve for the Eden catchment, there is also a downstream increase in the R^2-values which are comparatively-speaking best in autumn. These spatial and seasonal influences on the R^2-values seem to be due to two key factors: land use and hydrology. The agricultural land use is most intense in the lowland areas than the upland areas in the River Eden basin and the land use is in turn related to soil type and elevation. The larger catchments are at lower elevation (lowland Eden) and therefore have higher agricultural activities when compared with the relatively smaller upland catchments. This is corroborated by the findings from the near-continuous data acquired under the DTC study (table 5.5 a-c), where there was a higher contaminant concentration observed in Morland sub-catchment (lower elevation) compared with the Dacre sub-catchment that is at a higher elevation, and the R^2-values were also higher in Morland sub-catchment (table 5.3). Higher agricultural activities/land use may translate to higher nutrient availability for mobilisation and delivery into the water bodies draining the basin. A report from previous studies (Jarvie *et al.*, 2008) indicated that the autumn season is always rich in nutrient supply due to nutrients inherited from previous seasons. Therefore, larger sub catchments during autumn should be richer in nutrients.

The hydrology is critical to mobilisation and delivery. Flow was generally highest in autumn and least in the winter (late British winter) (table 6.3) during the period the CHASM study was conducted and appears to support the pattern shown in figure 4.10. Suspended sediment and TP was highest in the wettest autumn whereas N was highest in the ‘driest’ winter (winter samples were taken in March 2012). Table 6.4 takes the entire season into consideration (except otherwise stated) and the seasonal flow pattern differs. Flow during the winter was highest whereas spring was the least and quite explains figure 5.8 where N was highest in the spring. Nitrate was driven by groundwater seeing that it dominate flow in the dry season. Obviously, the SS and TP are storm/runoff driven and they were from diffuse source that include agricultural (including tile drain), near channel and in-channel sources (see Section 5.3.5).

Station/area (km^2)	Mean corresponding flow (m^3/s)						
	Autumn	Winter	Spring	Summer	SSQ	NQ	PQ
Gais Gill (1.1)	0.0755	0.0515	0.0513	0.0608	0.0686	0.0686	0.0598
Ravenstonedale (26)	0.9254	0.828	0.8005	1.018	1.361	1.089	0.8930
Smardale (37)	1.641	1.458	1.437	1.786	3.056	1.899	1.591
Great Musgrave (223.1)	11.26	2.53	3.073	3.06	22.77	7.293	4.979
Appleby (334)	13.64	4.848	5.608	5.948	10.16	10.16	7.509
Temple Sowerby (616)	23.69	6.045	7.408	7.698	34.84	19.15	11.21
Great Corby (1373)	36.9	20.58	24.43	26.88	63.0	42.47	27.19
Blind Beck (9.2)	0.1413	0.1333	0.1153	0.1043	0.2241	0.2241	0.1235
Kirkby Stephen (69.4)	3.936	0.8026	1.50	1.291	6.799	2.204	1.869
Morland (10.5 km^2)	-	0.245	-	1.282	0.832	0.832	0.832

Table 6.3 Mean of flow data for the periods spot samples were collected in CHASM and when the autosampler was in operation in the DTC (Morland) sub-catchment

Note: Winter investigation was conducted in March 2012 under the CHASM study. Flow data designated as SSQ, NQ and PQ represent averages of the flow data corresponding to the time that samples were taken, from the beginning of the field work in November 2011 to the end of it in April 2013. This period applies to nitrate and SS only. For P the period ended at the fourth seasonal campaign in August 2012. With the exception of Gais Gill, Blind Beck and Appleby, SS data were merged with those reported by Mills (2010). Data for the Morland sub-catchment represent the mean flow that matches the period the ISCO autosampler was in operation.

Station/area (km2)	Mean of flow data over the sampling period (m^3/s)					
	Autumn	Winter		Spring	Summer	Annual
		Dec-Feb	March			
Gais Gill (1.1)	0.067	0.085	0.054	0.057	0.073	0.0682
Ravenstonedale (26)	0.595	1.468	0.845	0.963	1.220	1.062
Great Musgrave (223.1)	8.949	12.94	2.912	5.397	8.169	8.853
Temple Sowerby (616)	18.44	26.38	6.393	10.66	17.28	18.17
Morland (10.5 km^2)	0.315	0.397	0.228	0.161	0.253/0.60	0.281
Morland (max value)	4.96	7.12	-	5.62	8.00	-

Table 6.4 Mean of near-continuous flow data for selected sub-catchments covering September 2011 – August 2012

Note: Here the table shows a mean flow over the entire season. Winter was split into two columns to give an idea of flow during the month of March when the CHASM winter campaign was conducted. Two readings were recorded at Morland outlet for the summer; the second captured the times that the autosampler was put to use.

Since both flow and land use increase downstream, it is almost certain that there is a strong synergy between land use intensity and hydrology, and the strength of the nutrient-flow relationship. This finding supports previous research which links a relationship between catchment area and P patterns in the Oona Water to changing hydrology and the cumulative effects of nutrient supply from point sources (Jordan *et al.*, 2005). Put in another way, provided there are neither supply nor transport limitations, the R^2-value for the contaminants increases downstream if the agricultural land use increases and is well connected to the catchment outlets or have a marked contribution from near channel and in-channel sources or both. This underscores the importance of agricultural land use intensity and hydrological connectivity of nutrient sources in this catchment. However, the R^2-values of reactive P (RP) are lower compared with the other water quality determinands. Its tendency to be sorbed by soils and some degree of solubility guarantee that both erosion and leaching processes took place, and there are surface and subsurface transport pathways respectively. It is also possible that the relationship may have been affected by biological uptake being the bioavailable P fraction. These are likely to weaken the strength of its positive relationship with flow.

6.3. Spatial pattern, elevation and land use effects in nutrient and sediment concentrations and yields, using a spatial-scale CHASM programme

Before the discussions of the spatial patterns, this section begins with the description of the contaminant concentrations and the yields in the River Eden in relation to both the other catchments and also the environmental standards in the UK.

6.3.1. Comparison between nutrient and sediment concentrations and yields in the Eden, and other catchments

Phosphorus

Gais Gill sub-catchment (GG, 1.1 km^2) provided the lowest mean concentrations for all the water quality variables. The mean TP sampled across the catchment ranged from 0.14 mg l^{-1} P at GG to the highest value of 0.069 mg l^{-1} P at Temple Sowerby (TS, 616 km^2). It is important to note that these values do not represent the entire range of flows. Sampling at peak flow was difficult due to logistical constraints and therefore mean nutrient concentrations could be an underestimation of the true value for each of the CHASM sub-catchments. For instance, Morland (~10 km^2), one of the DTC sub-catchments that have entire year near-continuous data, has a mean TP concentration of 0.142 mg l^{-1} P that was higher than both TS and Blind Beck (BB, 9.2 km^2). Blind Beck, a sub-catchment known for high agricultural intensity had a TP concentration of 0.056 mg l^{-1} P. The RP followed a similar trend and reasoning. Gais Gill sub-catchment had a mean concentration of 0.007 mg l^{-1} P, while TS had the highest mean concentration (0.032 mg l^{-1} P) amongst the CHASM sub-catchments; the mean TRP in Morland sub-catchment was 0.039 mg l^{-1} P. Although the maximum concentration of TRP in Morland sub-catchment (0.248 mg l^{-1} P) falls within the long term range (0.234 – 1.069 mg l^{-1} P), the mean TRP is relatively low compared to the long term UK average (1980 – 2011) for the northwest England, which is put at 0.656 mg l^{-1} P (Defra, 2012).

The specific yield of TP followed the same trend as its concentration. For TP the mean of the specific yield was highest (64 kg km^{-2} yr^{-1}) at TS while the GG yield was the lowest (25 kg km^{-2} yr^{-1}) among the CHASM sub-catchments. In the DTC sub-catchments, the Morland TP yield was 172 kg km^{-2} yr^{-1}. These results agree with those reported in the literatures (table 6.5). For TRP, contrary to expectation, BB together with GG, and Great Musgrave (GM) generated some of the lowest yields (12, 13 and 13 kg km^{-2} yr^{-1} respectively) while the highest from the CHASM sub-catchments was recorded from Smardale (SD) (29 kg km^{-2} yr^{-1}). Again higher yields (172 kg km^{-2} yr^{-1}) were calculated from the data obtained from the CM monitoring equipment at Morland (a DTC sub-catchment) when compared with the CHASM sub-catchments. It was also somewhat surprising that TP and RP concentrations (0.048 and 0.028 mg l^{-1} respectively) at Great Corby (GC, 1373 km^2), were below TS and its yields (19 kg km^{-2} yr^{-1}) were also below some other smaller catchments. Although the results show some unanticipated findings they still however fall within the range presented in the literature for UK watercourses (table 6.5).

Sediment

Except for Appleby (AP, 9.735 mg l^{-1}) and GC (12.37 mg l^{-1}), mean sediment concentrations increased from the headwater sub-catchment GG (0.827 mg l^{-1}) in the upland area downstream to TS (44.60 mg l^{-1}) in the lowland area in the Eden catchment.

Catchment	Nutrient	Yields (kg km^{-2} yr^{-1})		Author
		Min	**Max**	
Wye	TP	15	93	(Jarvie *et al.*, 2003)
	TRP	4	67	
	Nitrate	225	3030	
Taw	TP	62	425	(Wood *et al.*, 2005)
Upper Bann & Colebooke	TP	-	80	(McGuckin *et al.*, 1999)
	RP	26 (improved grassland)	62 (non-improved grassland)	
Severn, Avon, Exe, Dart	TP	162	210	(Russell *et al.*, 1998a)
	TN	1871	3503	

Table 6.5 Range of nutrient export into the UK rivers

Catchments	Max concentration (mgl^{-1})			
	TP	**RP**	**SS**	**N**
GG (1.1 km^2)	0.027	0.019	1.8	0.22
KS (69 km^2)	0.090	0.070	211.1	4.09
GM (223 km^2)	0.077	0.038	232.0	5.33
AP (334 km^2)	0.165	0.059	91.7	6.80
TS (616 km^2)	0.248	0.096	611.1	8.93
GC (1373 km^2)	0.086	0.059	123.0	10.90
BB (9.2 km^2)	0.153	0.066	16.3	20.09
Morland (~10 km^2) Autosampler	0.951	0.248	386.0	2.95
Dacre (~10 km^2) Autosampler	0.406	0.065	122.0	0.56
Morland (hi-tech)	0.991	0.342	*	30.00

Table 6.6 Maximum concentration of sediment and nutrients in selected sub-catchments under both the CHASM and also the DTC Schemes

Note: * indicates that the high-tech monitoring station cannot measure SS directly but measures turbidity as a surrogate for SS.

The CM equipment that measures near-continuous data in the DTC catchments cannot measure SS directly; however the value derived from the regression relationship between the SS data from ISCO samples (i.e. data measured from samples taken by an autosampler) and the CM turbidity data indicates a mean concentration of 8.1 mg l^{-1} at Morland outlet. The maximum concentrations of suspended sediment in selected CHASM sub-catchments further confirmed this trend. Two DTC sub-catchments (Morland and Dacre) were also reported (table 6.6).

Apart from the lower yield at GC (14.0 t km^{-2} yr^{-1}), it is interesting to note that the SS yields increase from the headwater (1.766 t km^{-2} yr^{-1}) down to Appleby (27.72 t km^{-2} yr^{-1}) to TS (41.43 t km^{-2} yr^{-1}). All these yields agree with the range reported by Walling and Webb (1987).

Nitrate

Unlike P and SS the mean nitrate concentration increased with catchment size within the CHASM nested subcatchments from 0.046 mg l^{-1} NO_3-N at GG to 7.07 mg l^{-1} NO_3-N at GC. The highest mean concentration 11.42 mg l^{-1} NO_3-N among the CHASM subcatchments was observed in BB, a subcatchment that has been reported to be subject to intense agricultural land use. It was 8.23 mg l^{-1} NO_3-N in the Morland subcatchment. Compared with the long term (1980 – 2011) averages for the UK which ranged from 11.24 mg l^{-1} NO_3-N to 24.23 mg l^{-1} NO_3-N (http://www.defra.gov.uk/statistics/environment/inland-water/), the nitrate concentration in the Eden was relatively low.

The average nitrate yields from the Eden sub catchments follow the same pattern as the mean concentrations with a smooth increase form 106 kg km^{-2} yr^{-1} at GG to 5850 kg km^{-2} yr^{-1} at GC. Blind Beck has a yield of 7697 kg km^{-2} yr^{-1} and Morland's was 8053 kg km^{-2} yr^{-1}. These values relate to the range reported by Jarvie *et al.* (2003) in table 6.5. This clear downstream increase in nitrate appears to be consistent with the idea that nitrate should be viewed as if all the catchment area potentially contributes to the river because of its peculiar chemistry in the soil environment (Withers and Lord, 2002). It undergoes leaching, which implies that apart from linking the river with the surface and the near surface it could percolate deep into the groundwater and then re-emerge into the surface water.

6.3.2. Sediment and nutrient exceedance and water quality limits

The exceedance curves were constructed for selected catchments so as to relate the concentration in the watercourse to the environmental standards. Great Musgrave was chosen for the CHASM catchment instead of Kirkby Stephen because Kirkby Stephen did not have continuous (15 minute time step) flow data for the year 2012 and this is necessary to generate a continuous nutrient and sediment concentration time series using a nutrient rating coefficient. Reactive phosphorus was not included for GM because the R^2-value (0.003) was too weak. The data acquired in Morland with the CM equipment provide the continuous data for all the nutrients except SS data, which were generated from a relationship with turbidity. Table 6.7 shows that the recommended TP and SS concentration limits were exceeded in GM for 0.03% and 3% of time respectively; the nitrate admissible concentrations allowed in drinking water by the EC of 50 mg l^{-1} NO_3-N were not exceeded. However, Jarvie *et al.* (2003) suggested that inorganic N concentrations as low as 1.5 to 6.5 mg l^{-1} N, which translate to nitrate concentrations much lower than the permissible limit, can trigger eutrophication. Figure 6.1 indicated that GM and GG (figure 4.11), despite the low nitrate concentrations, have undergone eutrophication during the 2005 summer period and at the end of spring 2012 respectively (22/07/2005 and 31/05/2012 respectively).

The watercourse at Morland outlet (Morland Beck) exceeded the recommended limit for SS, TP and RP for 4%, 12% (~44 days in a year) and 57% (more than half a year) of time respectively; the NO_3 permissible limit was not exceeded. There is a possibility that P fractions are having a negative impact on the quality of this watercourse, and this finding justifies the earlier studies that have canvassed for the inclusion of the tributaries in future management plan (Jarvie *et al.*, 2006; Howden *et al.*, 2010).

Uncertainty

The rating curve used to derive the data for constructing the exceedance curve for GM may have underestimated the concentration of the river constituents since it was difficult to sample the full range of contaminant concentrations due to the constraint of not being able to collect grab samples at peak flow.

WQV	**Recommended concentration Upper limit mg l^{-1}**	**% age time exceeded**	
		GM	**Morland**
SS	25	3	4
TP	0.1	0.03	12
SRP	0.03	-	57
NO_3	50	0	0

Table 6.7 Percent exceedance of selected Eden sub-catchments

Figure 6.1 Algal growth at Great Musgrave (source: Mannix, 2005)

Besides, there is weak relationship (R^2-value = 0.11) for the TP; however, N (R^2-value = 51) and SS (R^2-value = 0.71) appear more reliable. These results therefore needed to be interpreted with caution.

6.3.3. Influence of land use distribution on the contaminant content of the River Eden: Gais Gill vs Blind Beck

Gais Gill (1.1 km^2) and Blind Beck (9.2 km^2) are tributaries to the River Eden of contrasting land use. Gais Gill, a headwater sub-catchment in the Eden, has a higher elevation (470 m), covered by peat (100%, HOST classification) and less agricultural activities (managed grassland, tilled land and urban are 0%, and unmanaged grassland, 70%) compared with Blind Beck, a sub-catchment that flows into the Eden downstream of Great Musgrave (233 km^2), is at a lower mean elevation (220 m), covered by free drain and poorly drain soils (100%, HOST classification) and is known to be intensively used for farming (managed grassland, 42%, unmanaged grassland, 31% tilled land, 6%, urban, 2%). Although Blind Beck has equal phosphorus yield as Gais Gill, the SS and N were higher showing the impact of the more intensive agricultural activities in Blind Beck (table 6.8). The predominant soil association in Gais Gill is Brickfield 1 (cambic stagnogley soil), characterised by waterlogged conditions for a long period which restrict rooting. Despite drainage, the soil remains susceptible to poaching and compaction thus, it is agriculturally limited. Blind Beck, on the other hand, is covered with soils belonging to Clifton association (fine loamy stagnogleyic argillic brown earths) that are reported to have a moderate cation exchange capacity and are inherently fertile. The land is mainly under grassland and it is reported to be capable of supporting cereals and root crops for feeding livestock. The surprising low P may have been caused by soil decalcification down to 80 cm depth in a soil formed on a calcareous parent material. The mobile calcium sorbs P when the soil P level is less than 0.8 mg l^{-1}, and it is likely to have reduced the soluble P in the river (Jarvis *et al.*, 1984; Holford *et al.*, 1990). Another factor that may have reduced the P in BB, relative to GG, was plant uptake being intensively cultivated.

	Yield (T km^{-2} yr^{-1})			
	TP	**RP**	**SS**	**N**
GG	0.02	0.01	1.76	0.11
BB	0.02	0.01	4.29	7.70

Table 6.8 Comparisons between contaminant yields at Gais Gill and Blind Beck

The variation in both land use and contaminant yield in the upstream headwater (GG) and downstream River Eden tributaries (BB) is typical of the upland-lowland contrast in the contaminant composition in the Eden catchment. It is almost certain to have an influence on the downstream increase in nutrient and sediment transport along the River Eden. Some workers have identified variations in dominance process(es) accounting for differences in nutrient concentrations between the upstream and downstream reaches of River Hafren (Halliday *et al*., 2013) and River Enborne (Halliday *et al*., 2014). The upstream was controlled by biological uptake effect which peaks during the warm season whereas downstream was a combination of processes including advection, soil processes (e.g. mineralisation as a result of drier soil) and nitrate uptake in response to forest management in River Hafren. Mills and Bathurst (2015) found that suspended sediment was higher in lowland sub-catchment in the Eden and it was due to combination of higher land use intensity and greater extent of superficial sediment deposits which resulted in higher erosion susceptibility.

6.3.4. The spatial variability of nutrient and sediment concentrations in the nested Eden catchment

There is a clear and significant increase downstream ($P<0.001$) in nitrate concentrations within the nested catchment system (i.e. without BB and KS) from the headwater sub-catchment Gais Gill to Great Corby in the lowland Eden across all seasons. Although the spatial variability is not as distinct with P and suspended sediment, there is a significant increase ($P<0.05$) in the nested sub-catchments when the sub-catchments downstream are compared to the headwaters (figure 4.12a). However, the variability appears clearer in some seasons than others and for certain P or SS than the other. Except for the unanticipated drop in concentration at GC, SS exhibited a clearest scale effect in autumn while TP exhibits a scale effect that is clearest in summer; RP almost smoothly increased downstream to GC in summer. There are two likely causes for the increase in SS concentration moving downstream. Firstly, autumn is known for considerable harvesting and drilling activity for winter cropping; these two agricultural practices that both expose the soil surface and also aid detachment and transport by agents of erosion. The other reason is the wetness in the autumn as earlier discussed (see section 6.7). The wetness and runoff from storm events serve as agent of erosion with more flow, high velocity and greater capacity to cause erosion downstream. Improved spatial pattern of phosphorus concentration in the summer, a season typically associated with the application of fertilizer to crops, may have been helped by the application in addition to the manure contributed by livestock. This is expected to increase downstream considering the fact that agricultural land use intensity increased downstream (section 6.3.3). There is a clearer spatial increase in RP up to the GC sub-catchment that could easily be linked to inorganic fertilizer in the summer and this appears to strengthen this theory.

Another possible way of viewing the spatial dependency in nutrient transport in the Eden catchment is the idea presented as the upland-lowland domain concept used to explain the spatial pattern in sediment delivery into the River Eden (e.g. Mills, 2009a). It is thought that Great Musgrave is the transition between the two domains: the upland area having less human impact and less sediment transferred compared with the lowland area. In addition to human impact due to farming, there is also greater susceptibility to erosion due to presence of superficial deposits in the lowland sub-catchment as earlier noted (Mills and Bathurst, 2015). There are similarities in the inputs of SS and nutrients into the River Eden in the earlier (Mills, 2009a) and current studies respectively (figure 4.12a). Furthermore this study has demonstrated that Gais Gill (GG, 1.1 km^2), a headwater and tributary to Scandal Beck at Ravenstonedale (RD, 26 km^2) and Smardale (SD, 37 km^2) sub-catchments, in the cold period of the year was feeding ‘zero’ nitrate into higher order river (RD & SD) in the upland Eden catchment. The annual mean nitrate concentration recorded for GG was 0.046 mg l^{-1} NO_3 when compared with Blind Beck (BB, 9.6 km^2), a tributary near the River Eden at Great Musgrave which contributed an annual mean nitrate concentration of 11.42 mg l^{-1} $NO_{3.}$ Therefore, it can be argued that the upland reaches of the River Eden is receiving ‘cleaner’ or nutrient-poor water from its tributaries leading to dilution and consequently lower concentrations compared to the lowland river reaches. This is expected to be common in the wetter season but as the tributaries flow reduces in the drier period the contribution from the ‘clean’ upland headwater reduces and this might be the reason that nitrate concentration tends to increase in the dry period compared with the wet. This finding accords with an earlier idea that the increase or decrease in a nutrient (e.g. P concentration) as the catchment area increases can be traced to the input from diluted sources of flow feeding the rivers which in turn constitutes a dilution effect on the nutrient content of the receiving rivers (Sharpley and Tunney, 2000; Jordan *et al.*, 2005; Jarvie *et al.*, 2008) or concentration increases as a result of dominance of supply from nutrient-rich groundwater source at low or moderate flows (Tesoriero *et al.*, 2013). It may also be viewed as dominance of groundwater nutrient over more diluted nutrient from soil water (provided there is no condition leading to nutrient accumulation) at low or moderate flow.

6.3.5 Spatial distribution of sediment and nutrient load and specific yields

Figures 4.15 and 4.16 show that there were steady increases in SS and nutrient loads, along the river continuum, from the headwater to the sub-catchments downstream. Apart from upland to lowland increase in agricultural land use mentioned in the preceding section another reason for the trend is the increase in flow downstream, an important variable that is well known to drive contaminant export into water bodies. The specific yield describes the sediment and nutrient load per unit catchment area. Although there is an increase with increasing catchment size in the specific yield of nutrients and sediment when the headwater sub-catchments are compared with the downstream sub-catchments, the increase was somewhat complex especially with P. There was a steady rise in P from the headwater sub-catchments to Scandal Beck and Smardale in the upland domain before a fall at Great Musgrave, where another increasing trend resumed in the lowland domain before another drop at Great Corby. With the exception of GC, SS yield shows a steady rise down to Temple Sowerby. Despite a higher yield at Smardale, there has been a clearer increasing trend as catchment size increases compared with P. Nitrate yield was highest at GC.

The nutrient and SS yields have been categorised into two domains in Section 4.3.3: the tributary and main Eden domains. The tributary domain comprises of the first trend of increase in the contaminants concentrations comprising three of the seven nested sub-catchments studied and they are tributaries that joined the main Eden at Great Musgrave (GM). The sub-catchments are Gais Gill (GG), Ravenstonedale (RD) and Smardale (SD). For the other domain, the main Eden domain, P and SS concentration increases up to Temple Sowerby (TS) but drop at GC. For nitrate, there was downstream increase to GC. This two-domain spatial pattern in yield (figure 4.16) matches the spatial pattern in cultivable soil and managed grassland (See section 4.3.3, figure 4.12b). This suggests that the land capability and the associated soil-based land management (fertility and field drainage management) determine the intensity of land use (managed grassland) which in turn controls the stream nutrients and SS yields.

There are two possible explanations for the drop in P and SS yields at GC. One, River Eamont, a tributary of GC, flow from Lake Ullswater which must have trapped SS and its sorbed P. Thus River Eamont constitutes a source of ‘clean water’ to GC. Besides, GC consists of a comparatively higher free drain soils (45% and only next to Smardale, 56%) compare with all the other sub-catchments within the nested system. Temple Sowerby which is next biggest catchment has the highest per cent poorly drain soil (42%). With more free drain there will be more infiltration and more nitrate leaching but less SS and associated P yields. This is reversed for a soil or catchment that has higher poorly drain waterlogged soil (see figure 4.13b).

The tilled land (figure 4.12b) appears to explain the downstream increase in nitrate yield from GM all the way to GC in the main Eden domain. Thus, the downstream increase observed in N up to GC partly suggests that nitrate is more sensitive to agricultural land use such as cereals production etc. for human and/or livestock consumption. Increase in livestock production, particularly dairy, in the lowland area and losses from farmyard and slurry storage are potential point sources of nitrate.

Another possible explanation is the catchment-wide or wider connectivity in groundwater flow and its nitrate content which it is receiving through nitrate leaching etc. across the entire catchment. Some authors, as discussed earlier, have speculated that because of the solubility and leaching attribute of nitrate, it should be conceptualised that the entire catchment is contributing nitrate into surface water (Withers and Lord, 2002) and load should increase with catchment area if all other factors are kept constant (e.g. local variation in land use as observed in high N concentration in Blind Beck, see figure 4.10).

There are two likely causes for the higher yield at Smardale. Firstly, catchment characteristics such as lower mean elevation and higher percentage of managed grassland in Smardale compared with Great Musgrave as reported by Mills (2010) seems to enhance the supply of contaminants. These characteristics are only slightly lower than the values measured at Appleby. The second factor is that the sampling location is surrounded by managed grassland, one field adjacent to the stream which was seen to be stocked with cattle on some of the field visits in the current study. This is an obvious critical source area (CSA) and it is probably responsible for this higher yields. There is also a vehicular road (ford) cutting through the stream.

It is therefore almost certain that beyond the two key factors (hydrology and land use) that appear to drive contaminant transfer in the Eden catchment that there are other factors that play a considerable role. These are considered further in section 6.8.

6.4. Hydrology and contaminant transfer using the high resolution DTC study platform

6.4.1. Rating curve

Both nutrient and sediment rating curves plotted from the concentration data from discrete samples collected by the autosampler and measured by the CM equipment, confirm the relationship obtained from the grab samples in the spatial scale-related study (CHASM). SS and P have a positive slope when charted against flow whereas nitrate has a negative slope showing dilution effect when the data from the discrete samples were used. The relationship of nitrate with flow was not clear when the near-continuous data from the CM were used. This is partly due to the complex nature of the nitrate rating curve where it sometimes show dilution and some other times tends to increase when flow reaches a high value (figures 5.4 and 5.5) which confirms the observation discussed under the CHASM study platform in Section 6.2.2. It is probably a case of catchment-wide diffuse N source (Bowes *et al*., 2015) during the June 2012 event when nitrate emission was highest (figure 5.9b). Tripkovic (2013) observed that enhanced rainfall increased N concentration 2.5 times in a hillslope study in Blind Beck (BB).

6.4.2. Point sources in the Dacre and Morland

An estimate of point source for the Eden, which includes the Dacre and Morland, has been shown in table 6.2. It was based on the per capita N and P emission values for septic tank systems and the population reported by www.neighbourhood.statistics.gov.uk (see Section 6.2.2 for the discussion). The point source contribution to Dacre (255.9% P, 340.9% N) appears high for possible two reasons. One, the population record (1438 persons) for such a small catchment (10.2 km^2), in the Eden catchment known to be low in population density (Barber, 2013), seems suspicious. Two, there is also a possibility of high in-stream retention for P as reported by Wither *et al.* (2012) when they observed a contribution of 127% P for one of their catchments. The contributions from Morland are 28% and 30.3% for P and N respectively. These values are little above a quarter of the nutrient yield coming from point sources, implying that bulk of P source are diffuse sources (catchment-wide agricultural source, tile drain, bed suspension etc.; see Section 5.3.5). The N source that was fairly constant for large part of the water year was likely a combination of another constant source (e.g. groundwater; Jarvie *et al*., 2008) while the nitrate flush in the summer of 2012 following long dry period was probably from catchment-wide agricultural source (Reynolds and Edwards, 1995; Halliday *et al*., 2013).

6.4.3. Event storms

Analysis of nutrient and SS concentrations response to daily and sub-daily event in Morland sub-catchment enables more insight to be gained in nutrient dynamics in the Eden (see figure 5.10 to figure 5.14). In all the events TP, turbidity (the CM equipment do not measure SS but measures turbidity as a surrogate for SS) and TRP concentrations (for almost all the events) rise with a rise in flow as earlier discussed. In many of the events however TRP concentration dropped within the peak period, then rises prior to falling again during the falling limb of the hydrograph.

The reason for this is not fully clear but it may have something to do with initial mobilisation of the reactive fraction followed by exhaustion before the arrival of source such as tile drain. In three out of the five events considered including the contiguous rainfall and flow, nitrate decreases with an increase in discharge. However, the pattern changed during the high intensity rainfall on the 28/06/2012 leading to the highest flow recorded during this study for this location (rainfall circa. 26 mm in 2 hours; flow circa. 7.4 m^3s^{-1}). Nitrate concentration increased with the increase in flow and this is consistent with the observation of Jarvie *et al.*, (2008) in the Avon and Wye streams. Similarly, in the graphs for the whole of the (dry) March 2012 (flow 0.05 – 0.2 m^3s^{-1}), nitrate concentration was almost constant for most of the period (6 - 10 mg NO_3 l^{-1} as against 8 – 22 mg NO_3 l^{-1} in June 2012). This supports the former discussion showing that, although nitrate has a tendency to be negatively related to flow the relationship can sometimes be influenced by the range of flow and the antecedent catchment condition leading to a marked rainfall and flow event. The ‘constant’ values in March were likely to be influenced by nitrate from the groundwater source, a flow pathway that is known to support baseflow during such a dry period (Jarvie *et al.*, 2008). During low flow and in the lower Eden catchment, a previous report has suggested that groundwater contributes half the nitrogen load (EA, 2003).

6.4.4. Sediment and nutrient source

Sources of sediment and nutrient can be inferred from the slopes of the sediment and nutrient rating curves. Prior studies have noted that a RP concentration that is positively correlated with flow is derived from a diffuse source whereas a negative correlation translates to a point source (Jarvie *et al.*, 2006; Wall *et al.*, 2011). A constant nitrate concentration has also been linked to the contribution from groundwater. Thus it can be suggested that SS, TP and SRP/TRP, with positive slope relative to discharge, are from diffuse sources. The diffuse sources depend on droppings and poaching from grazing animals, bed suspension and near channel sources, manure and fertilizer applications (see Sections 4.3.1 and 5.3). With this complexity in the relationship of nitrate with flow as shown in this study, it can be argued that multiple sources are expected to combine. At high flows nitrate reaching the river is likely to be primarily accounted for by a diffuse source while at lower flows, when there is negative slope, nitrate is almost certain to be derived from point sources such as groundwater, septic tank systems and sewage treatment waterworks (see Sections 6.2.2 and 6.4.2) (Withers and Lord, 2002; Neal and Jarvie, 2005). These authors used boron as a conservative tracer to establish a source of RP from sewage treatment plants. Another possible support and criteria for the point source explanation is that, under CHASM studies, nitrate was comparatively high during the dry month of March 2012 when compared with the other seasonal campaign.

6.4.5. Relationship with turbidity

This section relates to sediment and nutrient rating curves. A strong relationship between turbidity and SS has been reported in the literature (Sharpley and Tunney, 2000; Ziegler, 2002a; Terry *et al.*, 2014). It makes economic sense if the same turbidity probe has good relationship with other contaminants that it can then be used to generate near continuous data for those contaminants. The current study found that there were strong relationships between the turbidity and SS, TP and TRP but the relationship with nitrate was weak (table 5.3). It seems possible that this result is due to the sorption property of P with solids that render water bodies turbid. Unlike N, TP and TRP/SRP are known to have sorption properties (Sharpley and Tunney, 2000) through an association with charged surfaces present in water such as soil or SS that are measured as turbidity. The relationship is generally stronger when the contaminants measured (from discrete event samples) collected by the autosampler are related to the corresponding turbidity value at the time of sampling compared with when the near-continuous TP and TRP, are related to near-continuous data from the turbidity probe. A possible reason for this is the presence of outliers in the CM data as reported in the previous chapter (figure 5.7).

Similar to what was observed in the nutrient- flow rating curve the R^2-values for the contaminants are stronger in Morland subcatchment (having higher agricultural intensity) than Dacre subcatchment also showing that the nutrient-turbidity relationship was sensitive to the influence of land use. The turbidity rating curve also has a positive slope and thus has the potential to respond to the influence of hydrology in a catchment in a way similar to a conventional nutrient rating curve, involving a plot of flow against either SS or P.

6.5. Elevation, Soil and land use effect using the high resolution data from the DTC study

6.5.1. Dacre vs Morland

These DTC sub-catchments having different elevation and land use were chosen to represent the upland-lowland contrast that characterised the spatial scale-related study. Dacre sub-catchment has an outlet at Nabend between Great Mell Fell (537 m) and Little Mell Fell (505 m) that is at a higher elevation, but contains a smaller percentage of agricultural land use compared with Morland sub-catchment (234 m mean elevation). Sheep grazing often dominates the grassland areas at higher elevation whereas there are arable farms, cattle and other livestock in addition to sheep in the lowland. In Dacre sub-catchment for instance, improved grazing comprising cattle and sheep covers 41 % of the land area while rough grassland grazed by sheep alone covers about 46 % of the catchment, whereas in Morland sub-catchment the percentages are 76 % improved grazing 10 % rough grazing and 6% arable land (Eden Demonstration Test Catchment, 2014a). Although, Morland have more potentially cultivable soil (100%) than Dacre (71%), they are largely poorly drain seasonal waterlogged soil (84%) against 53% in Dacre (HOST classification). It means that higher land use intensity reported in Morland must have been made possible through installation of field/tile drain. This will increase nutrient and sediment concentrations and yields in Morland especially nitrate if the density is high (Gall *et al.*, 2015). In comparison with Dacre, Morland sub-catchment thus provided the higher nutrient concentrations in the current study (table 5.5). Thus land use, soil and elevation are interwoven catchment characteristics that may have influenced this.

6.6. Linking the DTC study to the CHASM study

The DTC high resolution data have made it possible to confirm a consistent pattern of influence of elevation and soil, on land use intensity in the River Eden basin. This agrees with the upland-lowland increase in land use that was observed in the spatial scale related CHASM study. The more the intensity of land use, the more the soil disturbance, the more the input of nutrients and sediment that can be mobilised and delivered into the river system. The two studies also showed the role of hydrological processes on how and when the nutrients and sediment are lost. Thus the two processes exhibit a dominant control on nutrient transport into the River Eden, and thus appear to provide insights into mechanisms of nutrient loss in a spatial scale context.

There are other secondary catchment characteristics and processes that have considerable influences on the nutrient dynamics in the Eden sub-catchments.

6.7. Seasonality in the concentrations of the water quality parameter

One of the issues that emerged in the previous chapters is the seasonal pattern in the input of suspended sediment and nutrients into the River Eden and its tributaries (figure 4.10, figure 5.8 and figure 5.9a,b). SS, TP and RP concentrations were highest in the wetter period, particularly in autumn, and lowest in the dry period. As mentioned earlier, this finding mirrors the idea reported by other authors (e.g. Wither and Lord (2002)) stating that nutrients accumulated over the previous seasons are flushed into the watercourses during the wetter autumn. The high RP and TP concentrations recorded in the summer 2012 can be attributed to high flow rates in June that flushed out nutrients following the accumulation of nutrients in spring. The accumulation of nutrients in spring may have been partly due to fertilizer applications during cropping and partly due to the peculiar long dry spell reported in Chapter 5 (figure 5.1) leading to a nutrient transport limitation. This idea is in accord with the findings of Wither and Lord (2002) who reported that the risk of N loss is hardly a risk when applied in spring and even in a winter experiencing a dry spell.

Nitrate input is somewhat different from P and SS. The highest nitrate concentration measured from CHASM grab samples was observed during the driest campaign (late in the (British) winter). Unlike P and SS, it is interesting to note that the lowest nitrate concentration was recorded in one of the wettest seasons (late autumn and early winter) in the DTC sub-catchments. This demonstrated a dilution effect on constant/point source as flow increases as discussed in previous sections. Two conditions for a nutrient to be designated as coming from point source, as earlier noted (Jarvie *et al.*, 2008), are a negative regression relationship and a high concentration during the season characterised as having low flow and described as a period of high ecological risk. These two conditions appeared to have been met by nitrate during this study and therefore suggest that the nitrate is from point source(s). The complex nature of stream nitrate signals was previously demonstrated when high stream nitrate concentration was recorded in June 2012, a summer that has been described to have a peculiar wetness following a dry spell. Both the June wetness and pre-June dry conditions combined to influence this signal. Tripkovic (2013) has recognised the role of enhanced rainfall in increasing nitrate loss on hillslope soil study in an Eden catchment. The process of accumulation of nitrate during drought has been attributed to increase in nitrate in soil water due to evapotranspiration. There is also a reduction in nutrient uptake and microbial mineralisation due to moisture stress imposed by the dry condition. However, large amount of nitrate is made available for leaching in the immediate post-drought period as a result of microbial stimulation upon re-wetting (Reynold and Edwards, 1995).

The theory of increased stream nitrate concentration during cold weather is somewhat similar but not exactly the same as the one described in the preceding paragraph. The high nitrate concentration occurred due to low or arrested biological activity both on land and in-stream. A reduction in biological in-stream processes such as algal growth for instance, can make nitrate that will otherwise have been used for cellular activities, available in the stream.

6.7.1. Headwater system and seasonal variability

In the current study of one of the headwater sub-catchments in the Eden catchment (Gais Gill) a distinct variation in nitrate concentration between cold and warm weather was showed, and this was related to algal growth (table 4.4 and figure 4.11). There was a detectable nitrate concentration only from late autumn and through the winter (21/11/2011 – 14/03/2012) and this was repeated in another cold period that ranged from 14/01/2013 to 10/04/2013. It was noteworthy that the weather in 2013 was still wintry in early April and GG for instance was inaccessible for sampling on 26/03/2013 because of snow cover. The barren growth during the cold period makes it appear that there was less demand by the plant for the nitrate in the river resulting in the increased nitrate concentrations measured during this period. Outside these periods a non-zero nitrate concentration was not detectable, that is, the laboratory equipment returned zero readings implying that it has been taken up by plants whose growth have been enhanced as a result of the return of the warm weather. The clear seasonal nitrate dynamics characterised by temperature-dependent biological uptake as the dominant process controlling the nutrient dynamics categorises Gais Gill as a natural system. It does not exhibit anthropogenic impact

(Halliday *et al.*, 2014). Otherwise, other processes such as microbial mineralisation or fertility management (e.g. fertilizer application) may conceal the effect of the temperature-driven biological uptake (Halliday *et al.*, 2015). Land use-induced changes influence the dominant process in catchment which in turn drives the spatial differences in surface water quality.

The variation in GG between the warm and cold periods could therefore, be explained by the impact of the weather on both land and in-stream biological processes. The climatic impact on the in-stream biological processes is evident in the pictures taken on 31/05/2012 during the summer showing lush algal growth, but algal growth was sparse in the subsequent winter considering the picture taken on 27/02/2013 (figure 4.11). Higher plants also exhibited meagre growth around this period by turning brown. The implication is that more nitrate was extracted from the water body by the algae during the warm period leaving nitrate at an undetectable level (i.e. effectively zero nitrate concentration). Wall *et al*., (2011) listed nutrients and hydromorphological attributes of rivers as possible causes of excessive algal growth. Other factors that promote vigorous algal growth during the growing seasons (from spring to early autumn) are higher water residence times, sufficient photoperiod and high water temperatures (Jarvie *et al.*, 2006) and less flushing.

The occurrence of eutrophication in the GG, despite the pristine status and low nitrate concentration that ranged from 0.08 – 0.26 mg NO_3-N l^{-1} shows how a much lower concentration, compared to permissible limit stipulated by the Nitrate Drinking Water Directive (50 mg NO_3-N l^{-1}), is capable of triggering eutrophication in the headwater system. This corroborates with the earlier studies which reported that inorganic N concentrations within the range of 1.5 - 6.5 mg N l^{-1} are capable of causing eutrophication, which is, comparatively, by far a lower nitrate concentration than is allowed in the Nitrate Directive (Burt *et al*., 1993).

Besides nitrate that showed clear spatial variation across all seasons, spatial variations of P and SS were more discernible in certain seasons than in others (figure 4.10 and figure 4.12a).

6.8. Relationships between the concentrations of the water quality contaminants and the riparian soils in selected catchments

Soil is another catchment characteristic that both mirrors land use and responds to climatic and seasonal variations (see Section 4.3.3). The higher nutrient concentrations in Blind Beck (BB) compared with Gais Gill (GG) were due to fertilizer applications and comparatively higher manure inputs. Gais Gill has considerable areas of land covered by rough grassland and other semi-natural plant species unlike BB that is reported to be intensely cultivated (Barber, 2008). The result indicates a positive correlation of P in the thin riparian soil in BB, with water P which confirms P loss through erosion. This results match those observed in earlier studies (Olarewaju *et al.*, 2009) which links the correlation of stream nutrients and soil nutrients in the top soil to erosion loss.

Interestingly, the seasonal variability in soil properties shown in figure 4.14c appears to corroborates Halliday *et al.* (2015) view on changes in dominant process driving spatial surface water quality. In this case the soil organic matter in BB dipped in the warm period, unlike GG, which may be due to favourable temperature for microbial activities, luxuriant crop growth and associated nutrient demand. Therefore, the drop in organic matter may be due to microbial activities whereby the favourable weather enhanced mineralisation of the added manure. The nitrate released may be washed off and increase stream nitrate concentration. It is also possible to have been partly taken up by plant and/or temporarily rendered unavailable by microbial uptake for cellular activity, a process known as immobilisation. The expected death of the microbes together with decomposed plant residue may have returned nutrients to the soil as shown by the higher P and N in previous autumn and summer 2012 (a summer soil sample was taken on 31/07/2012). This seems to support the earlier argument on the residual nutrient availability that became washed off during the storm events that follow in wetter seasons, such as the summer (peculiar to 2012) and autumn.

6.9. Implications for water quality management

One of the main goals of any research is to appraise a problem and proffer a solution or recommend further studies that might lead to its solution in the final analysis. This study has been able to relate the spatial dependency in nitrate and phosphorus, and associated suspended sediment to land use and hydrology among other factors.

More specifically the downstream increase cultivable soil linked to increase in agricultural activity (managed grassland, tilled land and livestock farming) and flow from the upland to the lowland area play important role in the nutrient transfer into the River Eden and its tributaries. The seasonal variability appears to be both climatically and cropping dependent.

Taken together, a policy that encourages cover cropping, crop rotation etc. or supports on-going research efforts in mitigation measures that slow down contaminants from diffuse sources during any of the typical flushing season such as autumn should be sustained until a solution is accomplished and the findings implemented. A back-up plan that can promptly respond to an occasional pseudo-flushing season as occurred in summer 2012 could be considered. This gives an idea of possible climate change impact. The use of managed algal in a mitigation pond to extract nitrate, which can be harvested and ploughed in as manure, or processed into bio-fuels, could also be considered.

The practice of establishing grassland adjacent to watercourses also has implication in their ecological health based on the observations at Smardale and Blind Beck. Incentives that will encourage a farmer to give up a portion of this land as a sanctuary for aquatic life and to also secure the health of future generation through safe drinking water are worth encouraging. The extent of such zones should be studied and may need to be considered in the current national catchments project. In any mitigation plan this study support recommendations that attention be paid to tributaries (Jarvie *et al.*, 2006; Howden *et al.*, 2010). Precision farming may be encouraged, through incentive, along with other measures that can reduce nutrient input into the system and reduce impact on groundwater and ecological status of water bodies.

6.10. Summary

The chapter provides explanation to the synergy between land use and hydrological processes as the driving force for the downstream increase in contaminant transport in the River Eden. The study shows that both the land use and flow increase downstream and appear to influence the downstream improvement in the strength of the R^2 value of the nutrient rating curves. One of the key reasons for an upland-lowland spatial variation is the less intensive agricultural activities in the headwaters in the upland area compared with the lowland area, where there are sheep, cattle and arable farming. It implies that comparatively ‘nutrient-clean’ waters are fed into to larger water bodies in the upland area and thus resulting in a dilution effect. Thus the upland-lowland variation reported by some authors was supported. Variations in the response of nitrate, for instance, relative to flow when compared with phosphorus and suspended sediment were often linked to point sources and are seasonally dependent. Phosphorus and suspended sediment were linked to diffuse agricultural sources. The relationships between soil, land use and the seasons and nutrients were discussed. For instance, the study demonstrates that soil, land use (e.g. managed grassland) and nutrient and suspended sediment yields shows similar pattern. Nitrate concentration in the main River Eden appears to match the per cent tilled land. The identification of seasons when each of the nutrients were more likely to be transferred were identified and the complexity of the nitrate transferred mechanism was discussed leading to suggestion on possible management approach that can be encouraged or explored. Nitrate in the peculiar wet summer offers a glimpse into possible climate change impact. Nitrate dynamics in a headwater system such as Gais Gill raise an argument for policy in favour of a lower nitrate concentration as an ecological standard. This will not only ensure the safety of drinking water but also the ecological status of the watercourses, and with a call that adequate attention be paid to tributaries. Thus both the scale related CHASM study and the high resolution DTC data study has been able to show how, where and when nutrient losses occurred.

The need to generalise the findings beyond River Eden demands the use of a modelling tool which is explored in the next chapter.

Chapter 7: Modelling Nutrient Concentrations in a River Eden Subcatchment

7.1. Introduction

The deployment of a Minimum Information Requirement model (MIR model) is a good way to test the hypothesis on how catchment characteristics and processes drive the nutrient concentrations in the River Eden. MIR models i.e. metamodels of physically based models are the simplest model structure whereby parameters take on a physical significance. In addition to having physical significance it requires less data and takes less time to set up compared to the physically-based distributed models. Thus it is capable of representing hydrological processes and land use management processes more easily (Quinn *et al.*, 2007). This chapter reports the use of TOPCAT-NP, an MIR, to generalise the processes that controls nitrate and P concentration in the Eden catchment. This chapter include the description and calibration of TOPCAT-NP and the model results from various scenarios representing hydrological and land management techniques. The results are used to evaluate the extent to which TOPCAT-NP can be used as a decision-making tool in nutrient transport in river basins. More information on model classification can be found in chapter 2 of this thesis.

7.2. Nutrient concentrations simulation using a minimum information requirement model

TOPCAT-NP, an MIR model combines three MIRS sharing the same flow paths and soil types and is used to simulate both hourly and daily fluxes of nitrate and P (figure 7.1). The model is built into an Excel interface making it easy to operate (figure 7.2). The first is the TOPCAT model, an MIR version of TOPMODEL (Quinn and Beven, 1993). The other two: N-MIR and P-MIR evolved from the EPIC model (Williams *et al.*, 1990). EPIC and TOPMODEL are physically-based and quasi-physical models respectively. The EPIC model evaluates nitrate and phosphorus fluxes at the plot scale for a range of soil and land uses while TOPMODEL estimates subsurface and hillslope flows for any catchment size. In this section only the description of the physical processes and a summary of the mathematical theory/physics of each of the three MIRs will be presented along with some critical model parameters. Details can be found in (Quinn *et al.*, 2007).

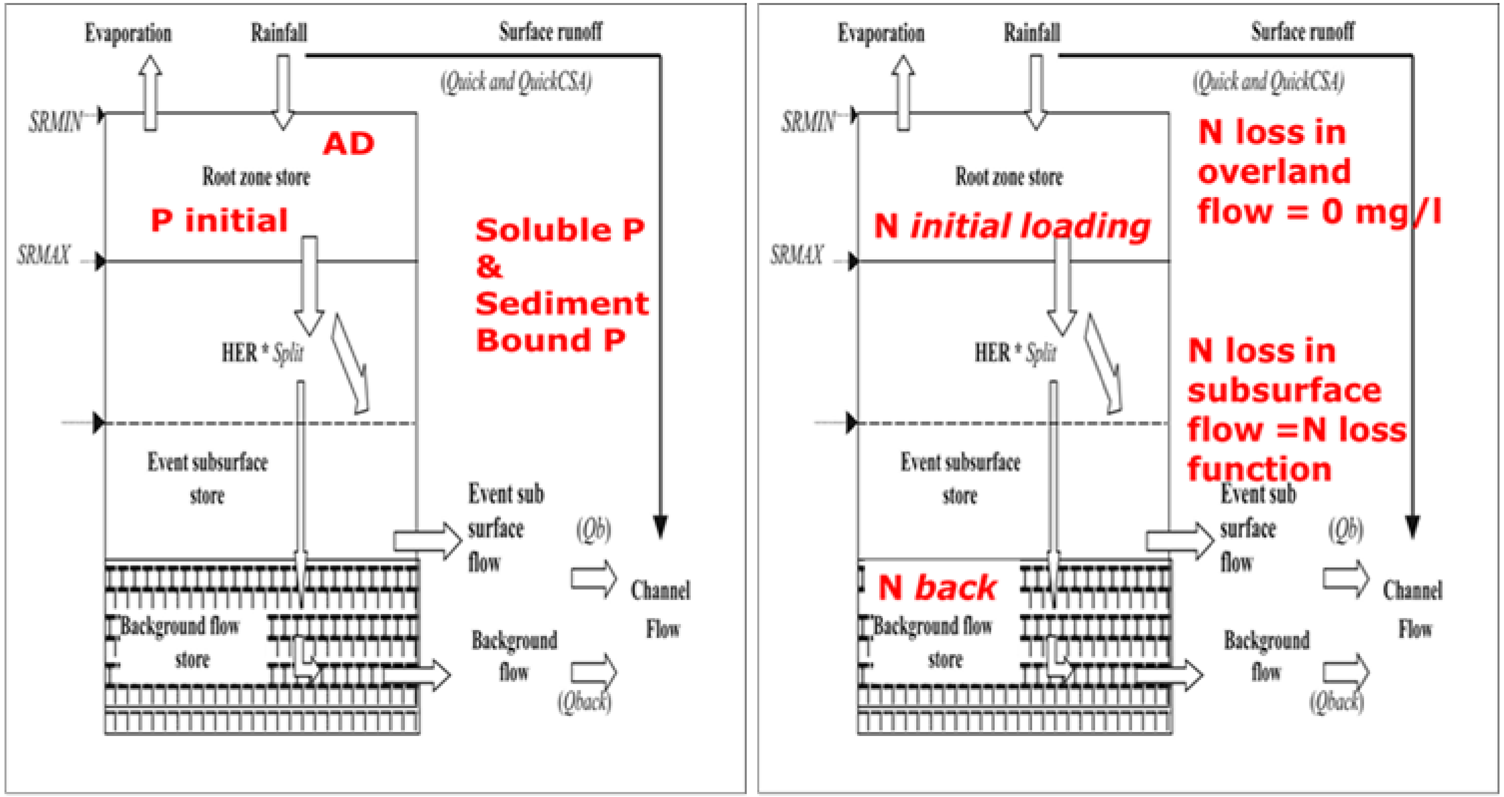
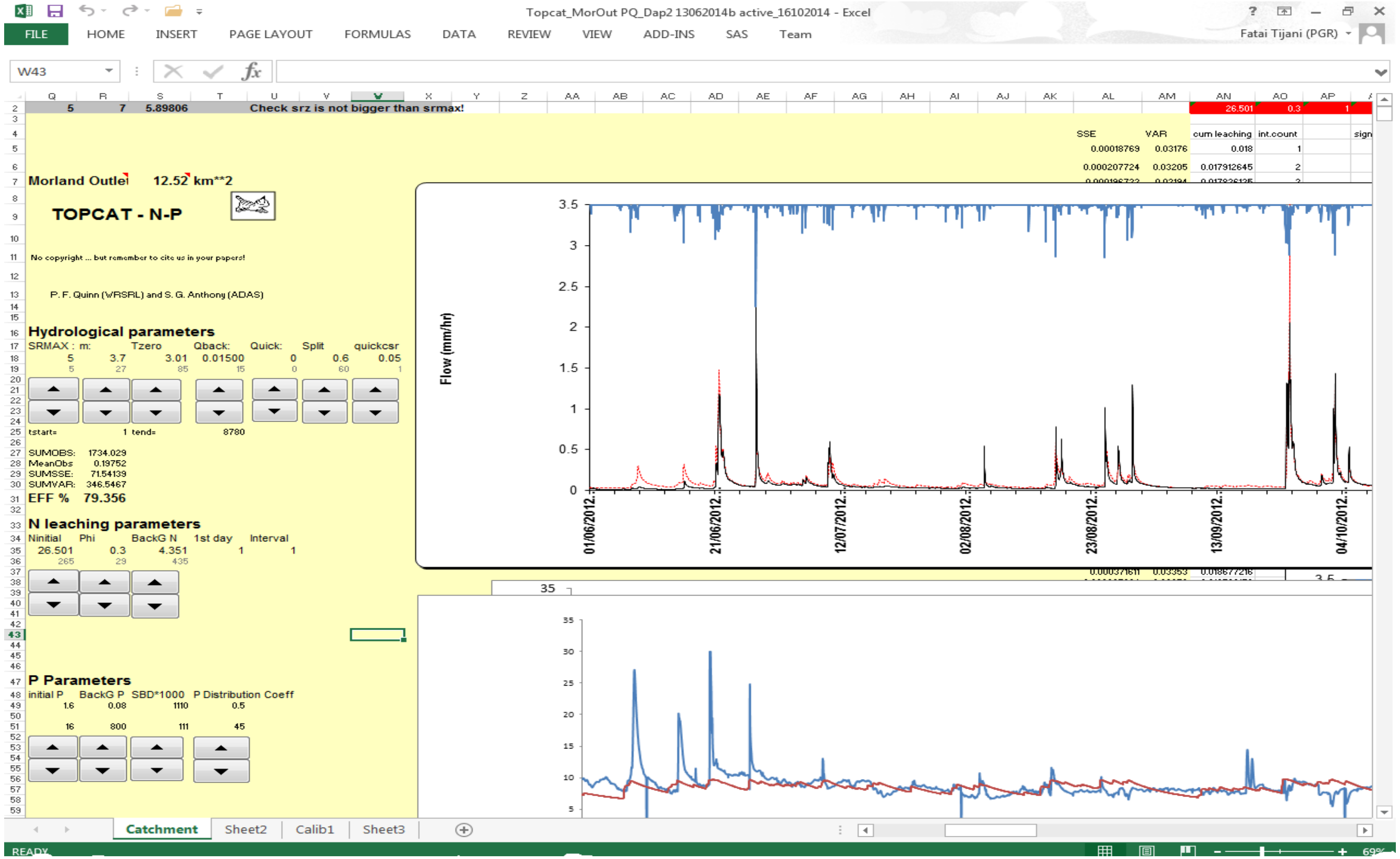


Figure 7.1 Schematic diagrams showing the flow and nutrient components and parameters used in the TOPCAT-NP model (Quinn unpub. Lecture notes)



5 7 5.89806 Check srz is not bigger than srmax!

Morland Outlet **12.52 km**2**

TOPCAT - N-P

No copyright ... but remember to cite us in your papers!

P. F. Quinn (WRSRL) and S. G. Anthony (ADAS)

Hydrological parameters

SRMAX :	m:	Tzero	Qback:	Quick:	Split	quickcsr
5	3.7	3.01	0.01500	0	0.6	0.05
5	27	85	15	0	60	1

tstart= 1 tend= 8780

SUMOBS: 1734.029
MeanObs 0.19752
SUMSSE: 71.54139
SUMVAR: 346.5467
EFF % 79.356

N leaching parameters

Ninitial	Phi	BackG N	1st day	Interval
26.501	0.3	4.351	1	1
265	29	435		

P Parameters

initial P	BackG P	SBD*1000	P Distribution Coeff
1.6	0.08	1110	0.5
16	800	111	45

		26.501	0.3	1
SSE	VAR	cum leaching	int.count	sign
0.00018769	0.03176	0.018	1	
0.000207724	0.03205	0.017912645	2	

Figure 7.2 Screenshot of the user-friendly MS Excel interface of the TOPCAT-NP model

7.2.1. The hydrological model - TOPCAT

There are three moisture stores built into TOPCAT representing the hydrological model. These are the unsaturated root-zone store, the saturated ‘event’ subsurface store and the ‘old’ subsurface or background flow store. The moisture content at the root-zone varies between the SRMIN and SRMAX parameters. SRMIN is the moisture content that relates to the permanent wilting point of the soil while SRMAX relates to the field capacity of the soil and the actual rooting zone of the vegetation cover. At SRMIN, evaporation is zero. When the soil content reaches SRMAX, at the soil surface there is quickflow (to be discussed later) and at the subsurface soil there is percolation of what is termed “hydrological effective rainfall” (HER). Any HER is assumed to move vertically into the subsurface in one time step. HER is partitioned into two pathways; one fraction enters the event subsurface store generating the event subsurface flow (Q_b) (see below) whilst the other fraction percolates into the background flow store generating background flow (or baseflow) (Qback) (figure 7.1). The component of HER that translates into the subsurface store is controlled by the parameter termed SPLIT. Although the background flow store is conceptualised as having an infinite storage capacity, generating a constant baseflow (Qback), a catchment dominated by the event subsurface flow will have the SPLIT set at 1 or 100% which means the Qback should be adjusted to zero. Qback can be measured during dry spell when there is extended low flow following recession or obtained via model calibration.

An exponential function expresses the rate at which Q_b leaves the subsurface store. This is taken from TOPMODEL (Quinn and Beven, 1993; Quinn *et al.*, 2007) and is expressed as

$$Q_b(t) = Q_0 \, exp^{SBAR(t)/m} \qquad (7.1)$$

where $Q_b(t)$ is the event subsurface flow. SBAR is a moisture deficit taken as a positive term representing the current moisture status in the event subsurface store. The recession parameter m (one of the key model parameter) can either be estimated by studying the recession rate or obtained from model calibration. Q_0 expresses the flow from the catchment when the soil moisture deficit is lowest. The topographic index is one of the terms in the TOPMODEL theory describing Q_0 (Beven *et al.*, 1995) and it is set at a constant value of 7 in TOPCAT.

It is only use to calculate the water table but does not affect runoff rates in TOPCAT as it does in TOPMODEL.

As SRMAX controls the HER rate and the associated hydrological parameters such as Q_b and Q_{back}, it also triggers the quickflow. Quickflow is assumed to reach the channel within one time step. Of the two hydrological parameters embedded in quickflow, overland flow (Quick) is assumed to be predominant in TOPCAT. It is the overland flow associated with farmland usually occurring as winter washoff. Thus it is linked to land use and has effect on the erosion rate and nutrient losses. This parameter is a fraction that lies between 0.05 and 0.3. The second component of quickflow is nutrient-related runoff that reflects the interaction of an area rich in nutrients with flowing water leading to a direct connection to the channels (e.g. areas close to the channels, impermeable roads, and their associated ditches, farm buildings or fields that are crossed by tyre tracks etc.). The parameter is therefore designated as a critical source-area (CSA) quickflow (QuickCSA) and its value usually lies between 0 and 0.05. It can operate in any storms generating a smaller chronic pollution while the former, from the wider catchment, generates the acute pollution. These two parameters are each multiplied by rainfall during time step t to give parameters described as: surface runoff (generated from quickflow); ROQuick(t), and surface runoff (generated from CSAs); ROCSA(t), in each time step t. Adding these two flows together gives an expression for the total quickflow in time step t, ROTotal(t):

$$\mathrm{ROTotal}(t) = \mathrm{ROQuick}(t) + \mathrm{ROCSA}(t) \qquad (7.2)$$

The total flow (Q(t)) combines all the flows from the various stores in TOPCAT, representing the total stream flow at time step t.

$$Q(t) = Q_b(t) + \mathrm{ROTotal}(t) + \mathrm{Qback} \qquad (7.3)$$

7.2.2. The N-MIR

The primary mechanism of nitrate loss is leaching (figure 7.3). With the assumption of no losses of nitrate through overland flow, the driving force in this model is the HER component of the hydrological model. It is essential to recall at this point that the three MIR models in the TOPCAT-NP share the same flow paths and soil types. Therefore the HER is linked to TOPCAT-N (N-MIR). In a more general sense, the

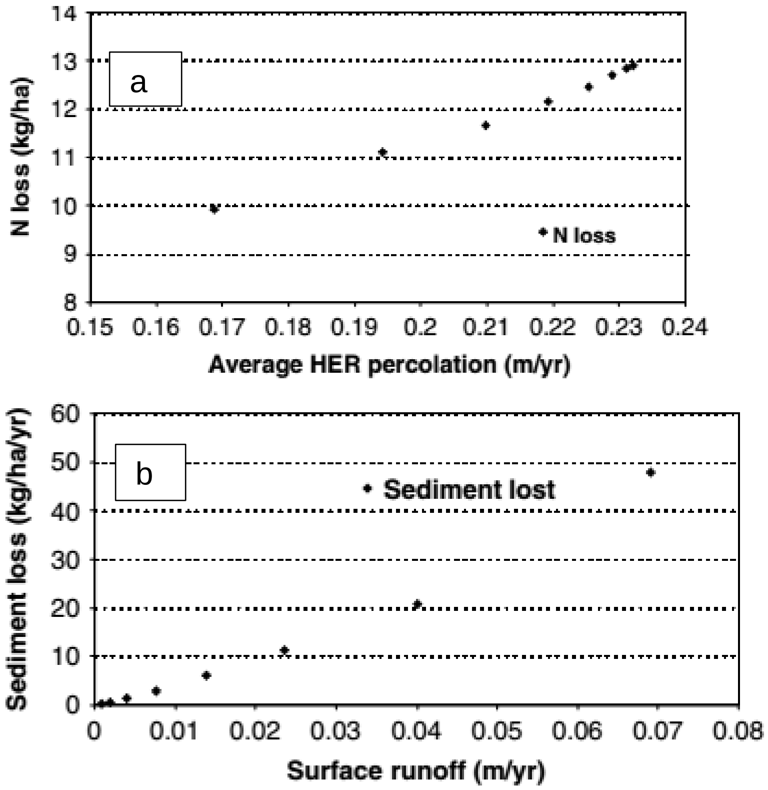


Figure 7.3 EPIC simulations showing (a) a relationship between annual nitrate loss and annual HER (b) the relationship between surface runoff and sediment losses from (Quinn et al., 2007)

nitrate loss (N_{active}) depends on the nitrate available at the root zone ($N_{initial}$), leaching efficiency of the soil and HER. Ninitial is the mass of nitrate in the root zone prior to the date set as the beginning of leaching in a region. It is the mass of N at the beginning of the cropping season, usually September in Europe, a period when this nutrient is considered to be most available following the completion of the previous season. The amount represents the balance after the crop uptake is subtracted from nitrate sources in the soil (e.g. fertilizer application etc.). Ninitial is determined from either the field sampling, an estimate of 'average' nitrate status of a representative farm, or an existing soil crop nitrate cycle models or can be calibrated (Anthony *et al.*, 1996). It is set at its maximum value at the beginning of a model run or every 365 days for multi-year simulations.

EPIC was used to create the N-MIR model (figure 7.3) and produced a six-year simulation for a range of soil type showing a direct relationship between the nitrate loss and HER up until a point where the total nitrate in the root zone becomes depleted (Quinn *et al.*, 1999). The amount of nitrate loss in time step t is given by

$$N_{active} = [f(t-1) - f(t)] * N_{initial} \tag{7.4}$$

where f is the cumulative proportion that depends on the soil nitrate leaching function that in itself depends on the ratio of HER to the soil water holding capacity (φ).

The other component of nitrate built into the model is the background nitrate concentration (i.e. the nitrate in the background flow) (Nback or BackN). Grab samples taken during extended low flow analysed for nitrate concentration give an estimate of Nback. A mixed load Lm is obtained through a simple mass balance given by

$$Lm(t) = Nactive(t) * Qb(t) + 0 * ROTotal + Nback * Qback \tag{7.5}$$

and the final stream concentration C_N is calculated by

$$C_N = Lm(t)/Q(t) \tag{7.6}$$

7.2.3. The P-MIR

The P-MIR or TOPCAT-P like TOPCAT-N, derives from EPIC. P is known to be associated with sediment and the EPIC simulations of sediment are depicted in figure 7.3. Several simulations from EPIC and reports from literature (Sharpley and Menzel, 1987; Brazier *et al.*, 2001) highlighted the mechanisms of P loss into stream leading to the simplified version of EPIC in TOPCAT-P. Phosphorus (either soluble or particulate) in surface water is primarily associated with overland flow and the concentration depends on the soil P status (the fraction that is actively available for loss that is termed $P_{initial}$) particularly in the top 1cm of the soil. The soil P content in the top 1 cm, the root zone and the soil type determines the soluble P loss into the stream. The soluble P fraction is also mixed with the fraction transported by Q_b and Q_{back}. The EPIC simulations also showed that the total overland flow responds to soil type, the local slope and the soil tillage regime.

There are two P fractions that are represented in the model output (as concentrations): total and soluble P. Total P consists of soluble reactive P (SRP) and sediment P. There are also components of TP, namely insoluble reactive P (RP) and soluble unreactive P that are not included in the model, and henceforth the SRP component will be referred to as “soluble P”. Sediment P loss is a component of the erosion model and depends on soil type/texture, arable crop value and the land management practices. Sediment P loss relates to the amount of sediment in the runoff and the amount of P that is attached to the sediment, a term described by an enrichment ratio (ER). The enrichment ratio varies with soil type. The ER together with erosion (a process that affects the upper soil layer) links into the overland flow component of the hydrological model in TOPCAT.

The mechanics of P loss incorporated into TOPCAT-P are summarised below, full details can be found in Quinn *et al.*, (2007). It starts with the calculation of P that is available in the top 1cm of the soil, PTOP(0)

$$PTOP(0) = P_{initial} * PDC \qquad (7.7)$$

Where $P_{initial}$ is the TP in the root zone of the soil, PDC is the P distribution coefficient. PDC is used to partition P between either the top 1 cm or the remaining root zone.

The value of PTOP(t), i.e. available P in each time step, is used to calculate the soluble P (PSOL(t)) that is mixed with overland flow. PTOP(t) is then updated by subtracting PSOL(t). This depletion and updating process is applied in every time step. Another important term in the calculation of soluble P is the extraction coefficient K which is set to 1/175 as used in EPIC. It is an expression for the tendency of chemical species to sorb to sediment, also termed partitioning (Logan, 1995). Thus, PSOL(t) is expressed as

$$PSOL(t) = PTOP\ (t) * K * ROTotal\ (t) \qquad (7.8)$$

Where PSOL(t) (kg m^{-2}) is the soluble P in runoff in time step t and K is the extraction coefficient. The concentration of soluble P transported in overland flow, one of the components of the stream soluble P is given by

$$C_{PHOS}(t) = PSOL(t)/ROTotal(t) \qquad (7.9)$$

The two other components of soluble P are the concentration of P in background flow (Pback or BackP) and the concentration of P in the event subsurface flow in time step t (PSUB(t)). Pback is estimated from the field measurements of P in low flow periods. PSUB(t) is based on the leaching function, f, used in TOPCAT-N for the nitrate leaching calculations. The only modification is the introduction of the adsorption/desorption coefficient, AD, of the soil. Although it is recognised that its value could be higher in an older soil with a long history of P loading, AD is set to 0.1 in TOPCAT-P with an assumption that 90% of the leached P is re-adsorbed by the soil when it passes through the profile.

There is also the stream particulate P which is the sediment P described earlier. TOPCAT-P incorporated the work of two authors. Firstly, (Brazier *et al.*, 2001) developed a MIRSED model from WEPP model and produced a matrix of sediment transport rates (expressed as kilograms per 1 mm of quickflow per metre width of hillslope) for various land use and soil conditions in the UK. The axes of the matrix are soil type (expressed as the clay fraction in the soil), the crop under cultivation and the local slope (generating overland flow in the TOPCAT model). The work is summarised as

$$SED_{(d)}(t) = SED_{(l)}(t) * ROTotal\ (t) \qquad (7.10)$$

Where $SED_{(d)}(t)$ is the sediment flow and $SED_{(l)}(t)$ is the sediment loss per unit depth of quickflow per unit width of hillslope. The work of the other authors (Menzel, 1980; Sharpley and Menzel, 1987) obtained a relationship between the ER and P and the ER and sediment respectively. They arrived at,

$$\ln(ER(t)) = 2 - 0.2\ln(SED_{(d)}(t)) \qquad (7.11)$$

The application of Menzel's equation in the TOPCAT-P model calculates the sediment P load as:

$$PSED(t) = (PTOP\ (T) * SED_{(l)}\ (t) * ER(t))/SBD \qquad (7.12)$$

Where PSED(t) is the load of sediment-attached P and SBD is the effective soil bulk density. The sediment P concentration in the runoff, C_{PSED} is calculated using

$$C_{PSED} = PSED\ (t)/ROTotal\ (t). \qquad (7.13)$$

When combined together the equations used in TOPCAT-P calculate a mixed load in the form (7.14 and 7.16):

$$PSOLLOAD\ (t) = PSUB\ (t) * Qb(t) + PSOL(t) * ROTotal(t) + PBACK(t) * Qback(t) \qquad (7.14)$$

Where PSOLLOAD(t) is the mixed soluble P load, PSUB(t) is the P concentration in the event baseflow runoff, Pback(t) is the soluble P concentration in the background flow and PSOL(t) is the soluble P concentration in the overland flow. The in-stream soluble P concentration C_{PSOL} (mg l^{-1}) can be expressed as

$$C_{PSOL} = PSOLLOAD(t)/Q(t) \qquad (7.15)$$

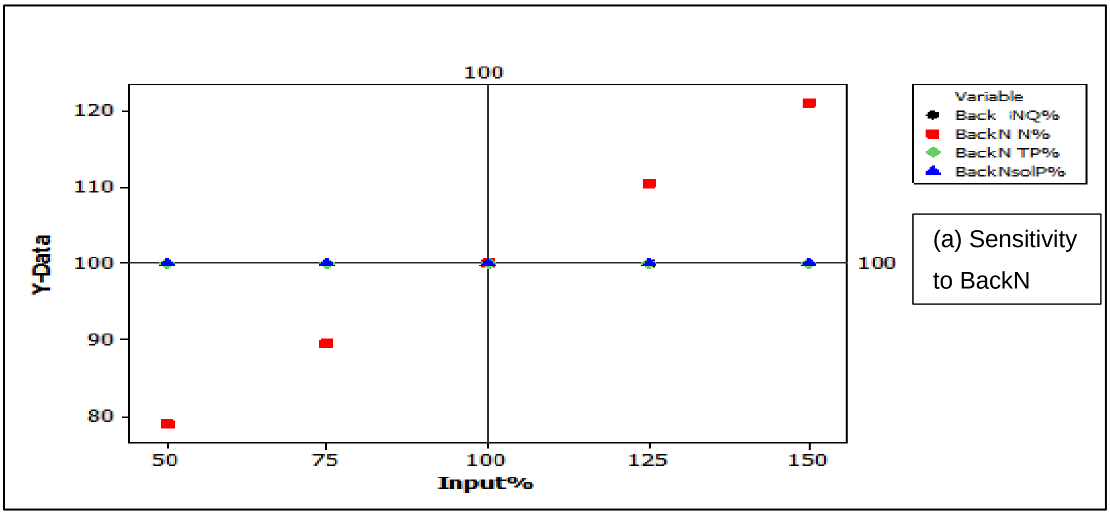
$$PLOAD(t) = PSOLLOAD(t) + PSED(t) * ROTotal(t) \qquad (7.16)$$

The in-stream TP concentration, C_{PTotal} is calculated by

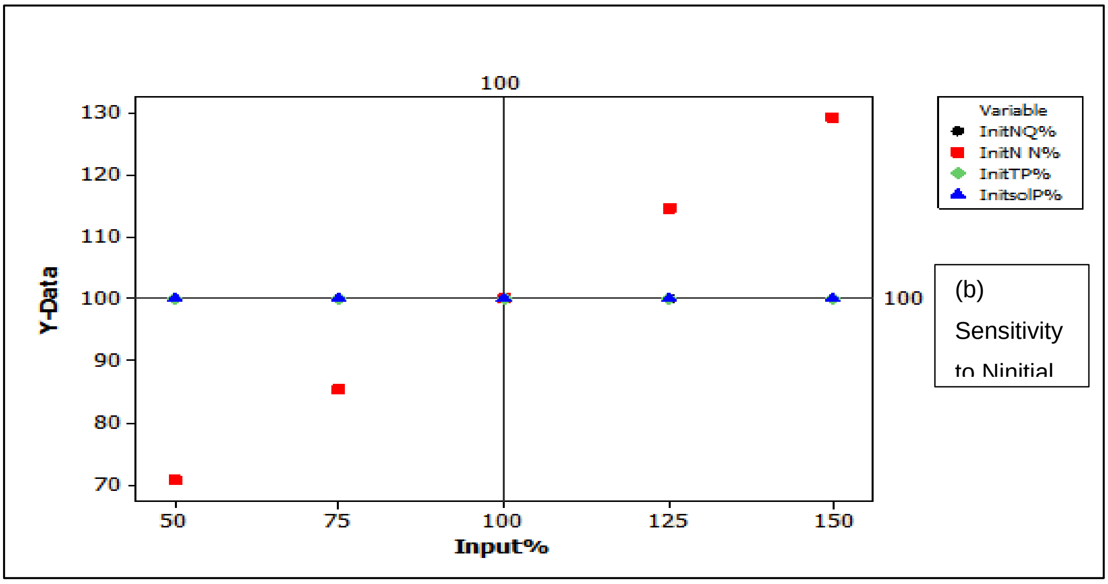
$$C_{PTotal} = PLOAD(t)/Q(t) \qquad (7.17)$$

7.3. Sensitivity test

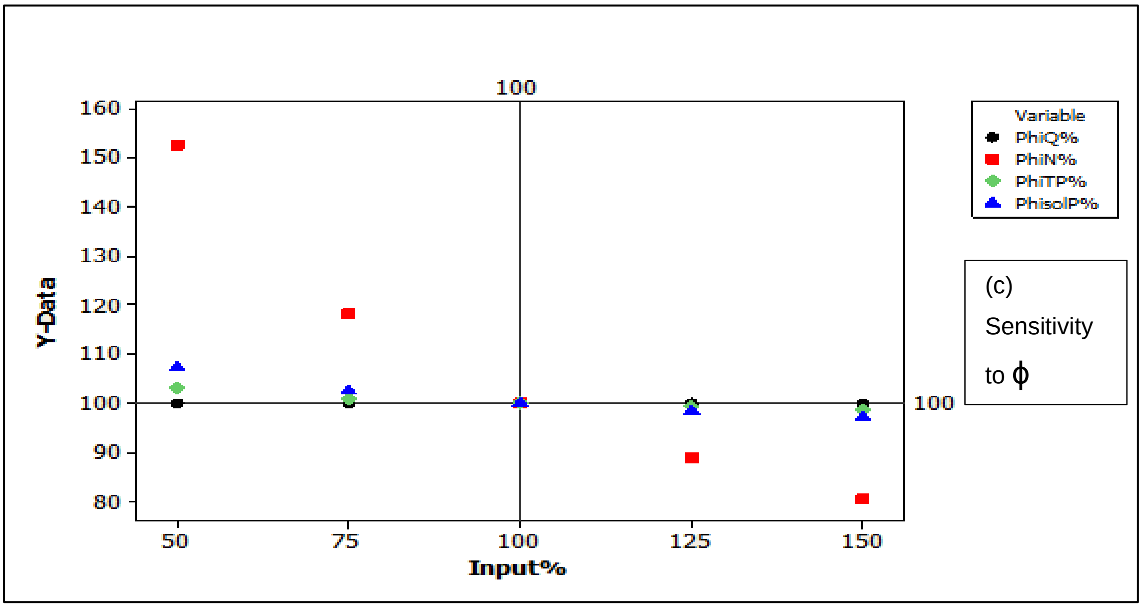
To analyse the effects that the model parameters have on simulations in order to gain the experience needed to perform calibration and scenario simulations, a sensitivity assessment was performed on a test-run version of Morland model on a set of data covering four months (November 2011 – March 2012) by a member of the Eden DTC team. For the sensitivity analysis, a single parameter was considered at any time by altering the calibrated value, by a fixed percentage fraction, while the values of the other parameters were kept constant. The percentage response of flow, concentrations of NO_3, TP or soluble P respectively (the labelled Y-data on the graphs represents percentage sensitivity) is plotted against the percentage change from the calibrated value of the input parameter (i.e. the parameter under consideration). Results showing significant response to these changes are presented in figure 7.4a-k. The graphs show that NO_3 is quite sensitive to BackN, Ninitial and ϕ.



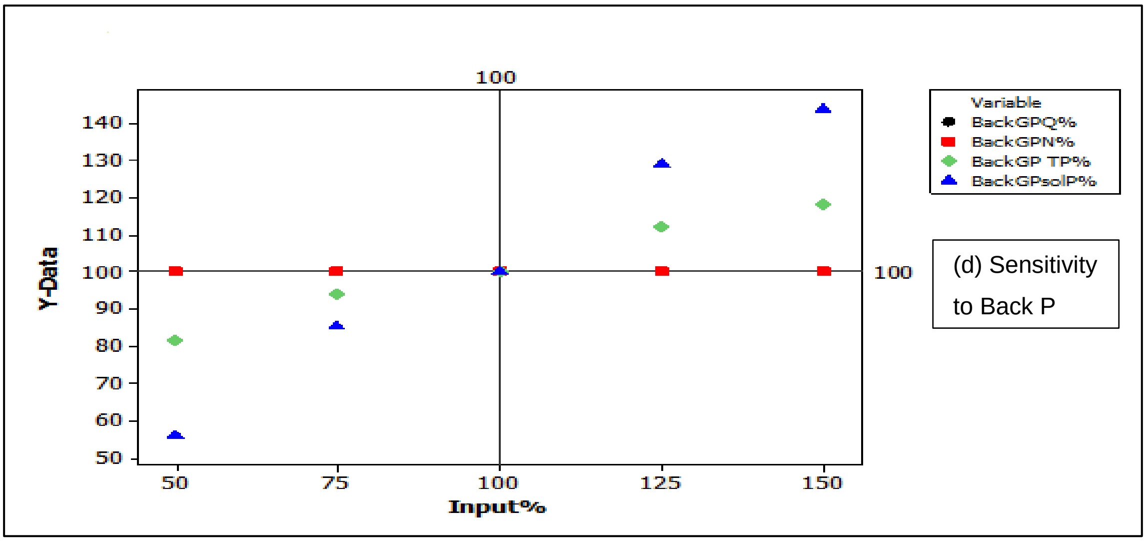
(a) Sensitivity to BackN



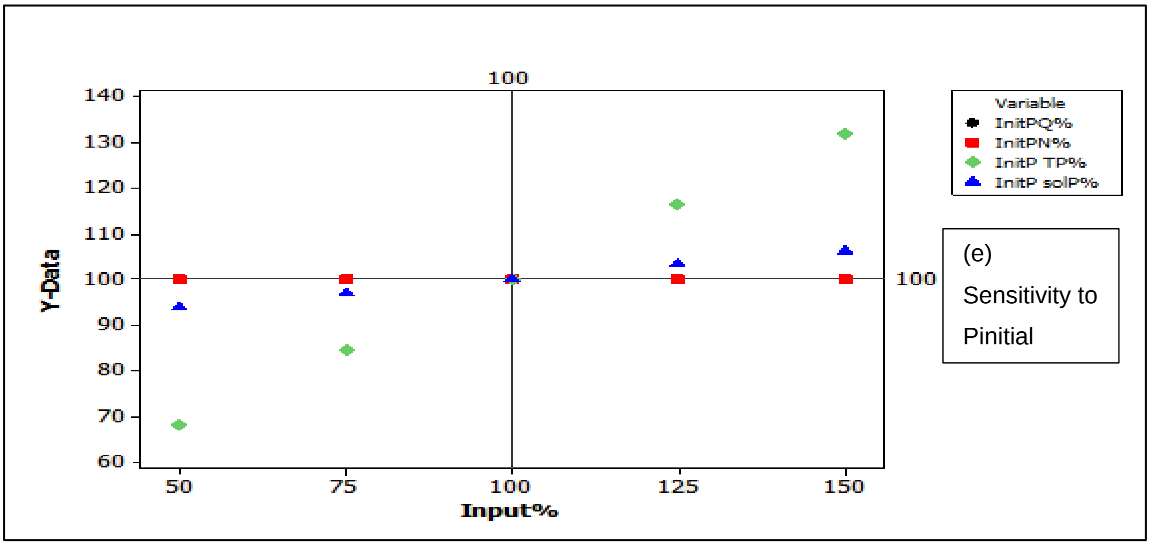
(b) Sensitivity to Ninitial



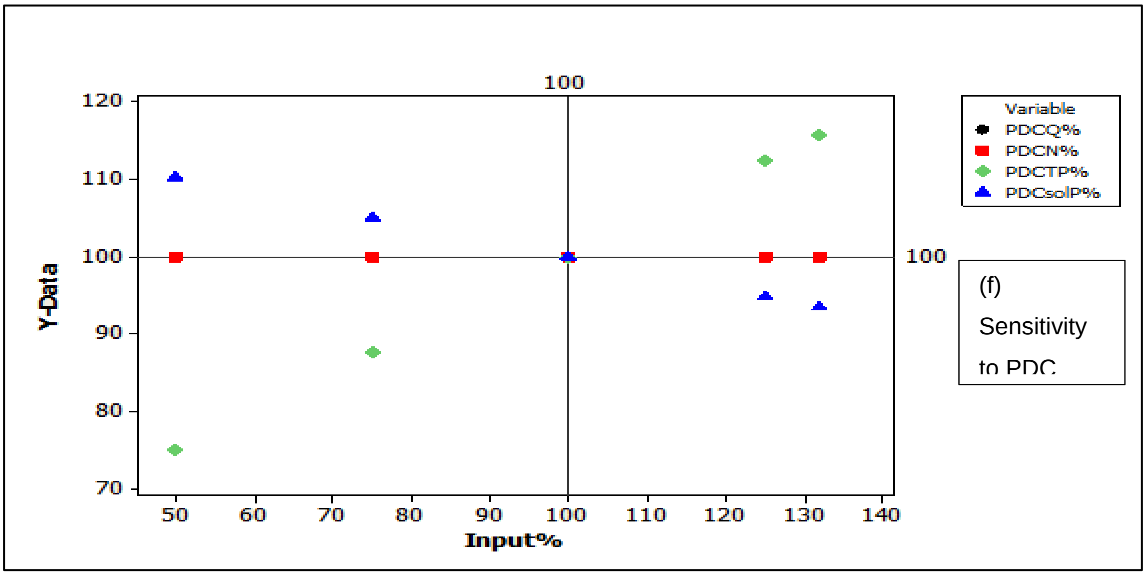
(c) Sensitivity to ϕ



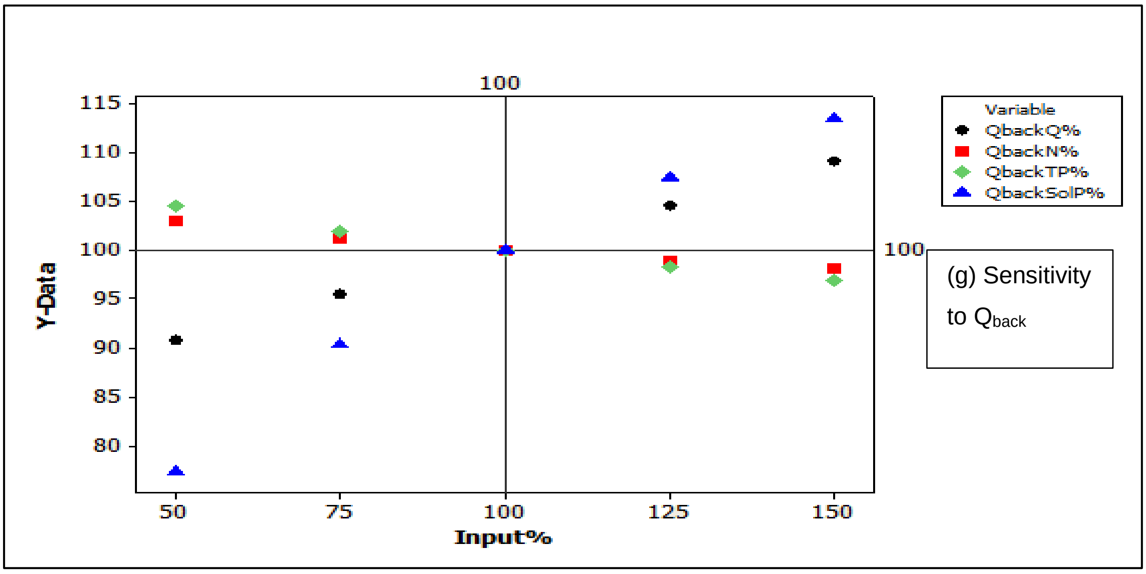
(d) Sensitivity to Back P



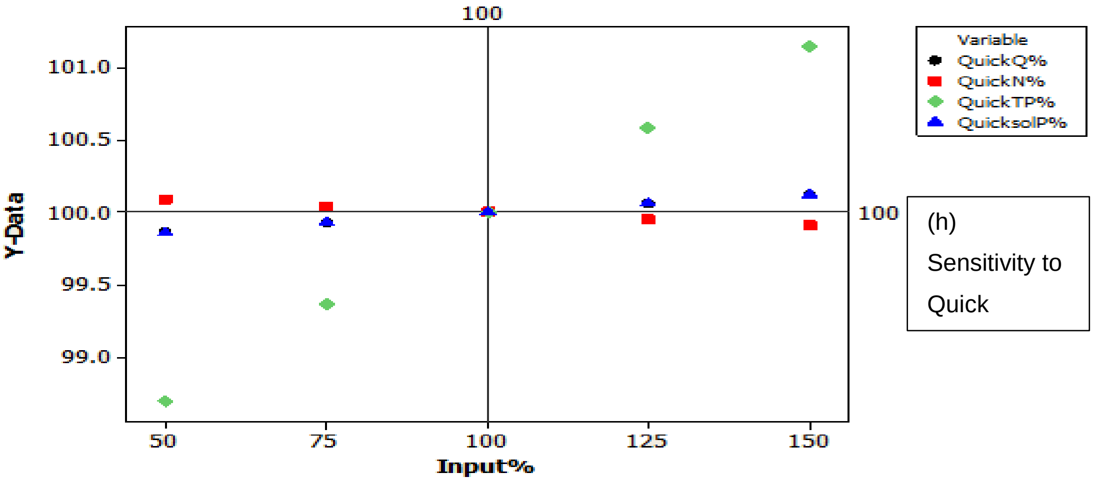
(e) Sensitivity to Pinitial



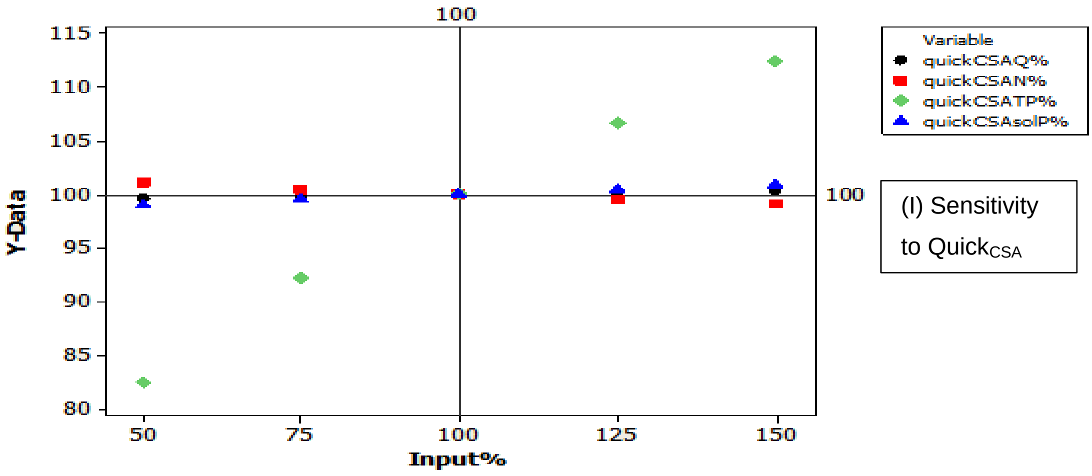
(f) Sensitivity to PDC



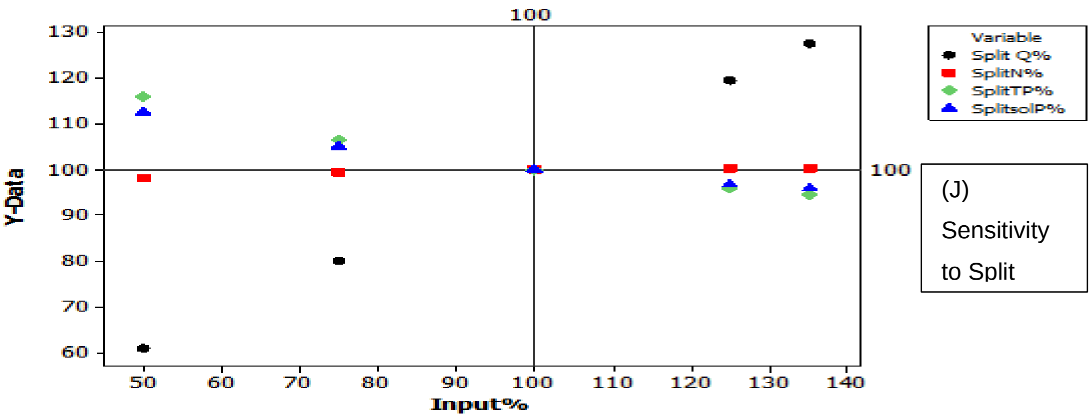
(g) Sensitivity to Q_{back}



(h) Sensitivity to Quick



(I) Sensitivity to Quick$_{CSA}$



(J) Sensitivity to Split

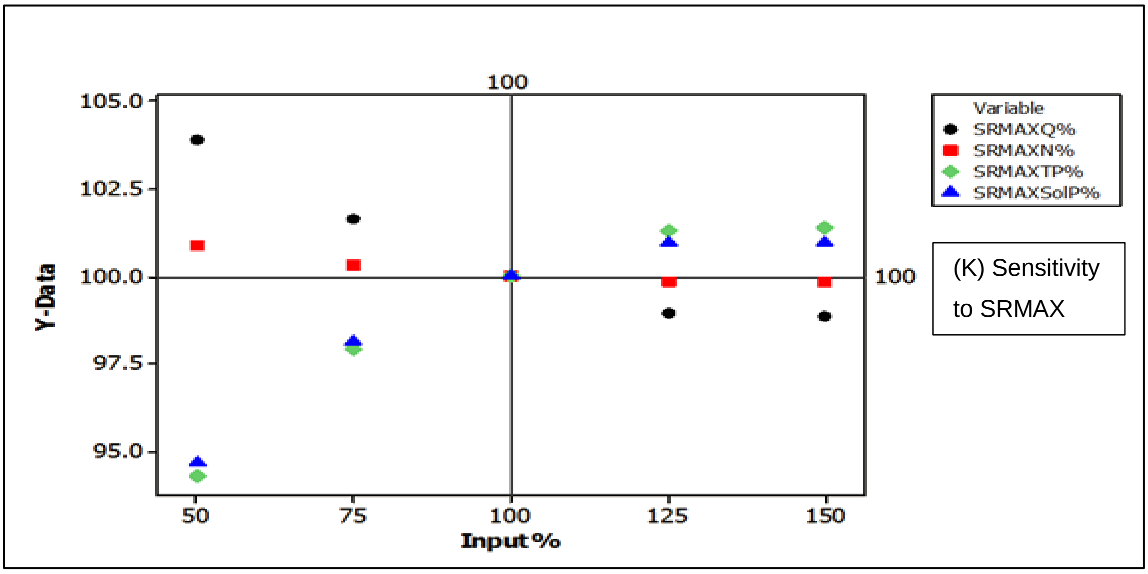


Figure 7.4a-k Sensitivity test for the Morland catchment for parameters (a) BackN, (b) Ninitial, (c) ϕ, (d) BackP, (e) Pinitial, (f) PDC, (g) Qback, (h) Quick, (i) QuickCSA, (j) split and (k) SRMAX respectively

TP is also sensitive to Pinitial, Qback, PDC, BackP and QuickCSA. Experience (and the above equation number) also show that only soluble P is simulated when Quick and QuickCSA are set to zero (See Section 7.5). Soluble P and flow are particularly sensitive to BackP and Split respectively. These findings constitute a guide to future applications and improvement of the model (e.g. scenario analysis, calibration for other catchments etc.).

7.4. TOPCAT-NP set-up and calibration

The model of the Morland data is presented here. The details of the catchment characteristics and the nutrient regime etc. can be found in Chapters 3 and 5. The DTC catchments were instrumented with the continuously monitoring (CM) bankside equipment such that both the hydrological data and the water quality data were measured at a 15 minute timestep all year round. There were also autosamplers that sampled water for laboratory analysis against which the data from the CM equipment was compared. The data used for this model were collected by the ‘CM equipment. Again, details can be found in Chapter 5. It was produced by the DTC team based in the Water Resources Engineering group in the School of Civil Engineering and Geosciences in the Newcastle University. The model was then set-up using these data.

7.4.1. Model setup

The observed data used in the model cover a period ranging from June 2012 to May 2013; carefully chosen so as to minimize gaps in the water quality (nitrate and P) data. The stream nitrate TP and TRP concentrations were measured in milligrams per litre from the Morland Beck, from an in-situ analysis using the CM equipment, and later transformed to hourly data by the DTC team. Hydrological data such as precipitation and evaporation were also measured at a 15 minutes timestep and then converted to millimetres per hours since the modelling is running at an hourly timestep.

The nutrient parameters in the model, Nintial and Pinitial, were obtained by deriving a nitrate index from the land cover maps using a GIS database of agricultural statistics. The Ninitial and Pinitial values were the aggregate of their respective individual values derived for each of the land uses, based on the values reported in Anthony *et al.* (1996). This was then optimized by fitting them to the model (Quinn, 2004).

Other nutrient parameters and hydrological parameters such as Nback, ϕ, Pback, PDC, Qback, m, SRMAX, SPLIT, Quick and QuickCSA were all fitted by the modeller to the data and were thus obtained by calibration.

7.4.2. Calibration of TOPCAT-NP Model

The theory of the model has been able to show how various flow components are mixed together to produce stream flow and also influence nitrate and phosphorus concentrations and loads in the river. Therefore, the accurate simulation of nitrate and P concentrations relies largely on the correct calibration of the hydrological parameters governing overland flow, event subsurface flow and background (or baseflow). The procedure followed in calibrating the model is an interactive process that was based on curve fitting by eye. The parameters were manipulated based on the experience gained from the sensitivity test amongst others, and the model quickly updated in response to a change in the parameter values. This was then checked against the time series of observed data in the Excel interface (figure 7.2). For instance, Qback was first fitted to the observed low flow in summer and m was then fitted to the continuous recession limb of large storms in the winter season. SPLIT (very important when there is significant percolation to groundwater), SRMAX and parameters representing overland flow were then adjusted as appropriate. Pintial and Ninitial triggered major fluxes from the nutrient model while the Pback and Nback concentration parameters were fitted to the background concentrations of TRP and NO_3 respectively in the observed nutrient time series.

The observed NO_3 data seemed to vary across the season from wash off events to dilution events and only one of these period could be calibrated to because it was not possible in this version of TOPCAT-NP to fit the model to both events. Therefore, the simulation of only the mean NO_3 value could be achieved. For the P component, the model generated spikes for the total P (TP) but overestimated these. It predicted the background value of the soluble P but missed the spikes observed in the soluble P. TOPCAT is usually run as fine as daily time step but seems to be missing some diurnal dynamics.

The Pearson's correlation (*r*) and Nash Sutcliffe Efficiency (EFF% or *E* or NS value) (Nash and Sutcliffe, 1970) are the quantitative techniques used alongside with the visual fitting in estimating the performance of the model. *E* is given by,

$$E= 1- \frac{\sum\left(q_{obs-}q_{sim}\right)^2}{\sum(q_{obs-}\overline{q_{obs}})2} \qquad (7.18)$$

Where q_{obs} is observed flow and q_{sim} is the simulated flow at each time step, $\overline{q_{obs}}$ is the mean observed flow, the summations are over all time steps and *E* has a range from –infinity to 1. The calibrated parameters and their values are shown in table 7.1.

Hydrological parameter	N leaching parameter	P parameter
SRMAX = 5	$N_{initial}$ = 27.001	Pinitial = 2.8
M = 3.7	Φ = 0.23	Back P =0.02
Q_{back} = 0.015	Back N = 3.151	PDC = 0.68
Quick = 2	EFF%: <0	TP EFF%: <0
Split = 0.6	r(x,y): 0.12	r(x,y): 0.06
QuickCSA = 0.05		
EFF%: 79.208		Sol. P EFF%: 0.8
r(x,y):0.85		r(x,y): 0.46

Table 7.1 Model parameters for Morland (12.5 km^2)

Further calibration efforts showed that it is only possible to improve the Nash-Sutcliffe Efficiency for flow, albeit insignificantly i.e. without any meaningful beneficial impact on the model fit for the nutrients and therefore this was ignored. The final set of parameter values adopted (table 7.1) also considered the expert judgment (i.e. the DTC team). The graphs comparing the simulated and the observed data for flow and nutrients are shown in figure 7.5. Generally, the simulated flow fitted to the observed peak and baseflow values. The hydrograph demonstrated that the catchment is a fast responding system with high connectivity. Thus, it reflects a catchment with a flashy response and low baseflow. The peaks, the recession and the low flow period were well represented by TOPCAT, with an E value of 79% and the Pearson correlation r(x, y) value of 0.85 indicating a good fit. The calculated E for the observed nitrate data was <0% showing a poor fit and r(x, y) value is 0.12 showing little correlation. Although it is not precise, the model captured the overall pattern of nitrate losses that was reflected in the r(x, y) value except for the nitrate spikes that were observed in early summer 2012 and spring 2013 (April and May). It missed some dilution events. For the total phosphorus (TP), the E value was <0% while the r(x, y) value is 0.06, showing a poor fit and correlation respectively. There was a marked over-prediction of the observed value of the TP by the model (figure 7.5). The soluble P had an E value of 0.8%, a weak fit, and r(x, y) value of 0.46 which reflected the ability of the model to capture the background concentration of

Figure 7.5 Observed and simulated flow, N, TP and soluble P simulations for the Morland catchment in the River Eden, UK

TRP measured across all seasons. Judging the model solely on the poorer fits shown by the E values for the nutrients underscores a possible limitation in relying on these statistics alone in assessing how a model reproduces the observed values (Quinn *et al.*, 2007).

Although the latter part of the winter season experienced low flows in 2013 (figure 7.5), there was a clear seasonality in the catchment hydrograph and include a record wet summer recorded in 2012 (Met Office, 2012). With the exception of some of the spikes and dilution events, there was less seasonality in nitrate concentration for most of the period covered by the data. There was some evidence of minor peaks followed by recession that related not only to quickflow but also quickCSA across the seasons. One of the CSA events appeared to generate one of the highest losses of nitrate to the stream in June 2012 (on 09/06/2012). The graph appears to show that the model poorly predicted TP in 2012 compared with 2013.

Seasonal evaluation of the calibration

Data for the months of July 2012 and December 2012, representing summer and winter seasons respectively, were extracted and plotted so as to compare predictions for the two seasons. The E values for the hydrology and WQP are shown in the table 7.2. The statistics, for the fit (table 7.2) particularly the Pearson correlation, and the graphs (figure 7.6 and figure 7.7) show that the simulations fit the observed flow data for the two seasons. There is high E value of 81.7 % and r(x, y) value of 0.94 reflecting a very strong prediction of the flow over the winter period. The recession and base flow were well captured and nearly all the events.

	Winter (December 2012)		**Summer (July 2012)**	
	E value (%)	**r(x, y)**	**E value (%)**	**r(x, y)**
Flow (Q)	81.7	0.94	57.6	0.85
N	<0	<0	<0	0.3
TP	<0	0.18	<0	0.05
Sol P	<0	0.19	<0	0.44

Table 7.2 Nash-Sutcliffe efficiency E and Pearson correlation showing the fit of the model across seasons

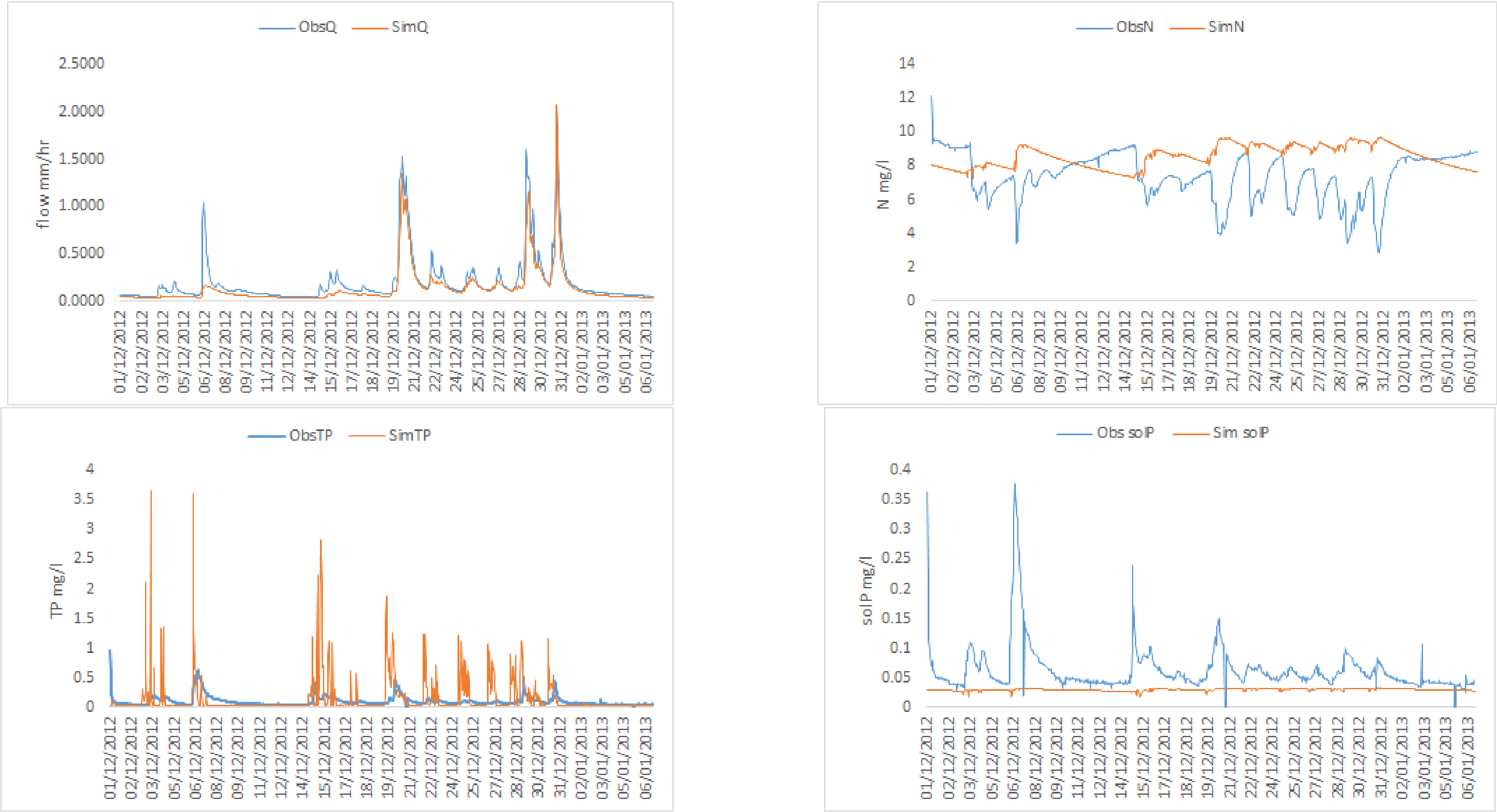


Figure 7.6 Observed and simulated flow (Q), nitrate, TP and Sol P for the Morland catchment during winter)

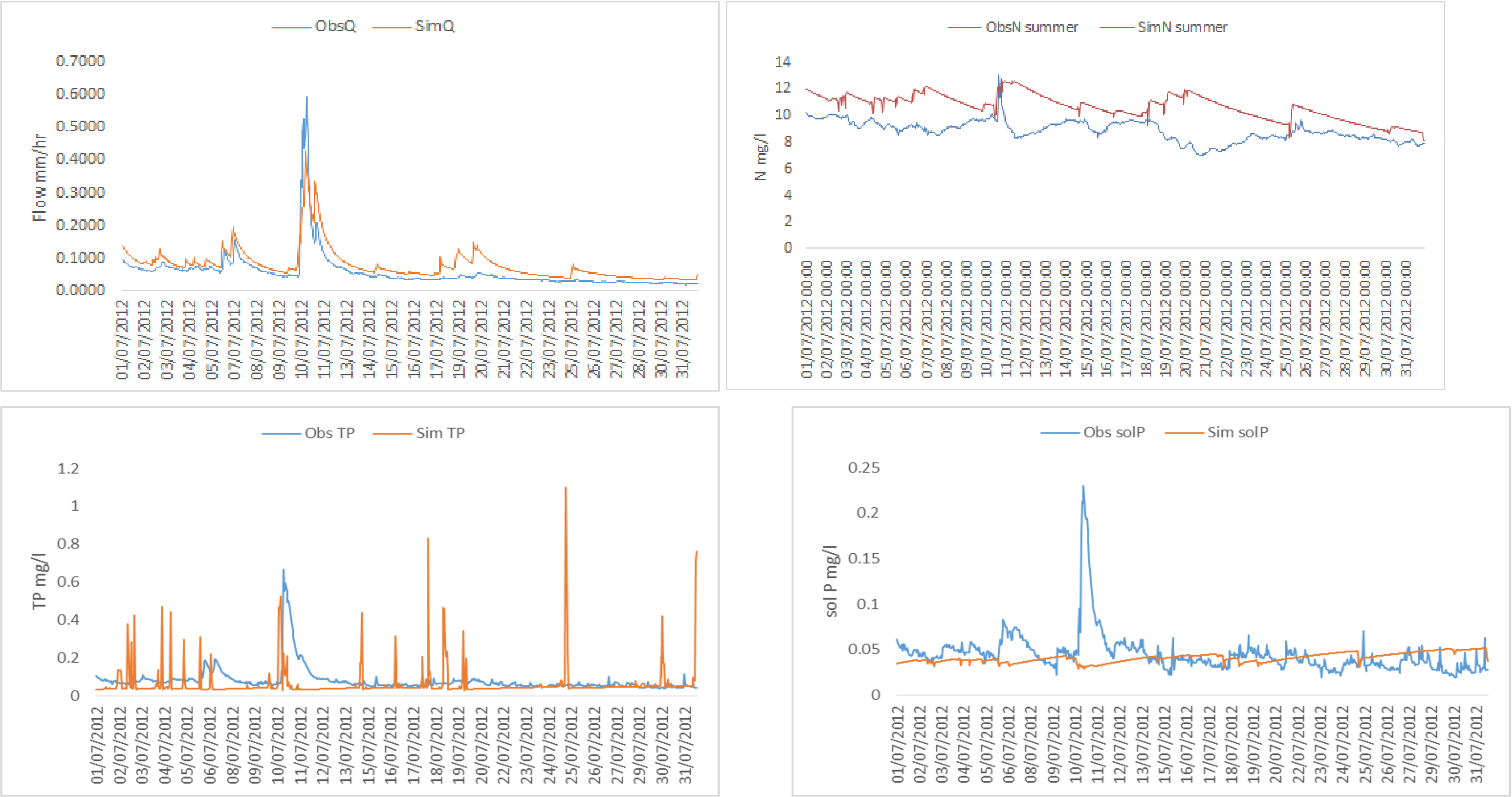


Figure 7.7 observed and simulated flow (Q), nitrate, TP and Sol P for the Morland catchment during summer

However, the E values for the nutrients show poor fit for the two seasons. With the exception of TP, the r(x, y) indicates a better nutrient simulation in the periods selected for the summer than for the winter. TP is better predicted in the winter. Unlike the observed data that show higher concentration during the winter, the predicted soluble P is constant throughout the two seasons. The dilution effects shown in the nitrate concentration during winter was not quiet captured by the model.

7.4.3. Re-calibration of the TOPCAT-NP model

Based on the unsatisfactory prediction of the dilution effect on N signal in the observed data in the winter, the model was recalibrated to fit the winter by lowering the Nintial and increasing the BackN parameters. Figure 7.8a-b and table 7.3 show that reducing the nitrate input into the catchment in the model from 27. 001 to 13.101 and increasing the contribution from groundwater (Back N) from 1.151 to 10.001 improves the prediction of nitrate loss from the catchment particularly during the period between October to November 2012 (E=0.39) but misses the loss between June to July 2012. The recalibration produced a model that could not mimic the wash off events following a prolonged dry spell as seen in the observed data in the summer. There was a shift from wash off to groundwater controlled nitrate concentration in the catchment in the observed data. It was not possible for TOPCAT to fit to both events (Figure 7.9a-b). Although high groundwater nitrate study have not been specifically conducted in Morland to verify the high BackN but report of study reported by the EA in 2003 indicated a remarkable groundwater nitrate contribution in the Eden. Ockenden *et al*. (2014) indicated 46% and 69% contribution of groundwater to stream flow in Blind Beck and Low Hall catchments for September – December 2008 respectively.

Looking at the limitation of the model in hydrological driver or nutrient flow pathways in Morland, there is therefore the need to review, the processes incorporated into the model theory, assessment of model performance and then make recommendations on how the model can improve prediction at a sub-daily time scale (see Section 7.6).

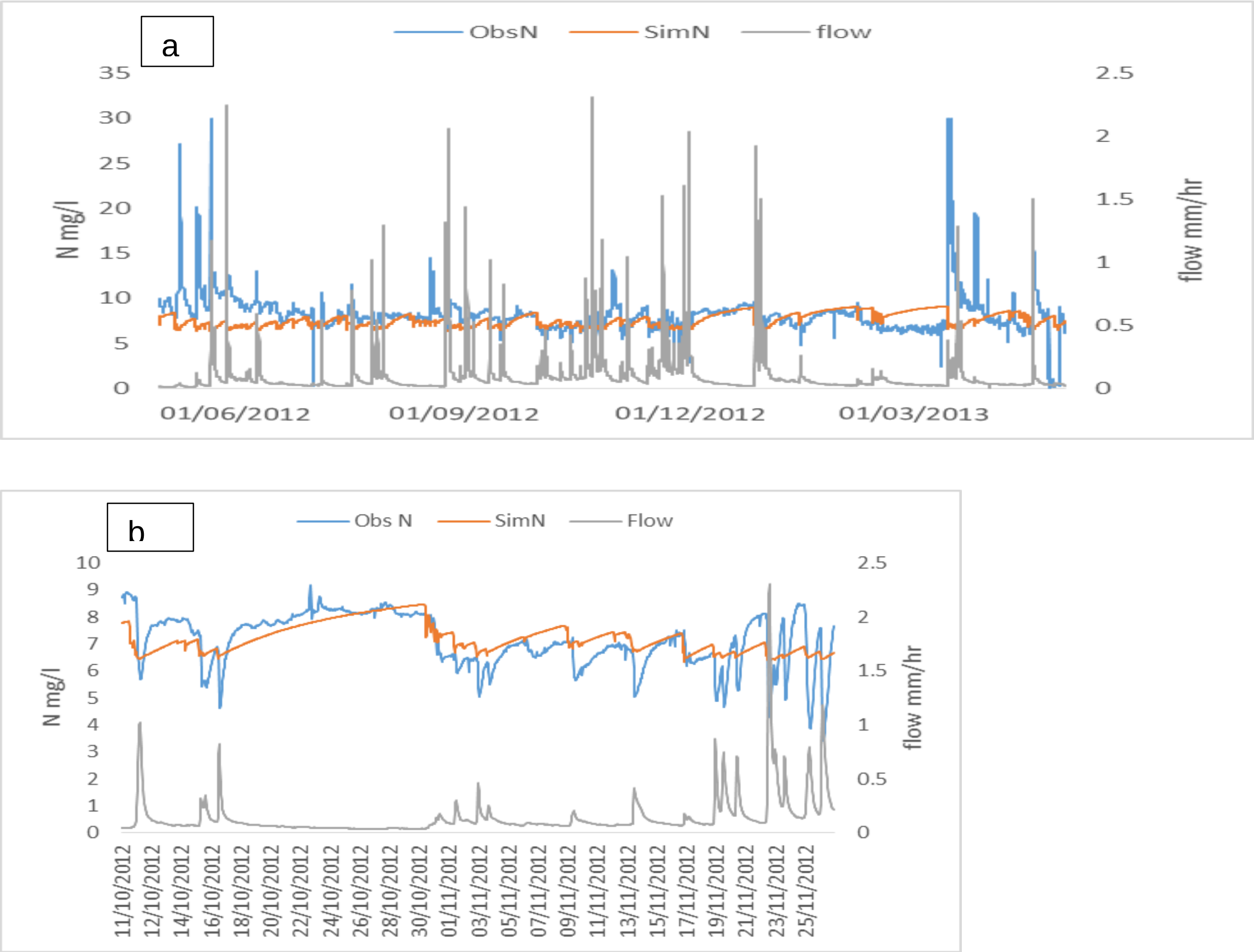


Figure 7.8 (a) Observed and simulated nitrate concentration for Morland after re-calibration (note the June period) (b) simulated nitrate during the wet period following recalibration

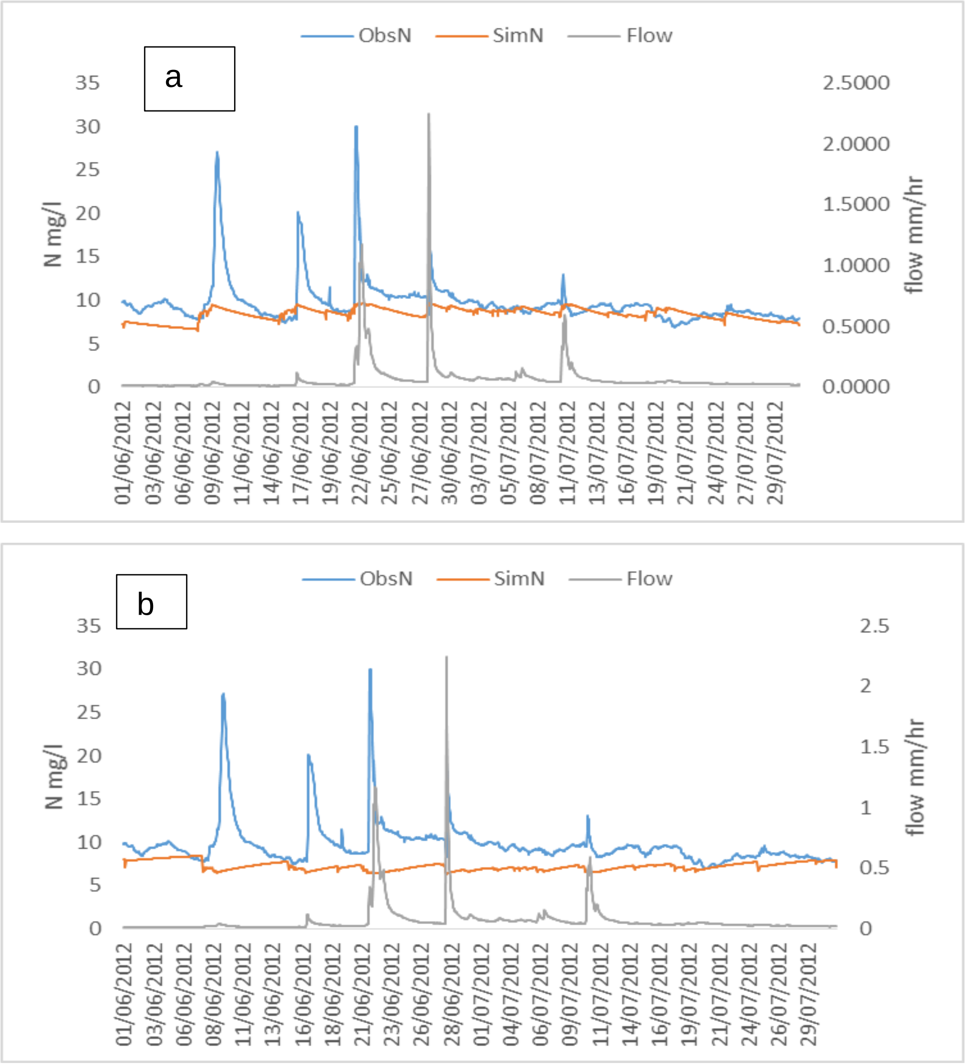


Figure 7.9 Observed and simulated nitrate concentration in the summer period in 2012 (a) before recalibration (i.e. after first calibration) and (b) after recalibration

Former N parameters	Recalibrated N parameters
$N_{initial}$ = 27.001	$N_{initial}$ = 13.101
Φ = 0.23	Φ = 0.23
Back N = =3.151	Back N = =10.001
EFF%: <0	EFF%: 0.39
r(x,y): 0.12	r(x,y): 0.64

Table 7.3 Comparison between the nitrate leaching parameters before and after recalibration

7.5. Discussion

7.5.1. Calibration

The simulation was run for a year between June 2012 and May 2013. The results of the calibration, in figure 7.5, show that the background TP and soluble P were well represented in the model simulation but the peaks were over-estimated for the former while the peaks for the latter were underestimated by the model. Nitrate had a better fit during June 2012 and during the spring in 2013. Table 7.2 indicated that both nitrate and soluble P were better predicted in the summer than the winter unlike TP. The poorer nitrate simulation in the winter may be as a result of supply limitation (in the observed nitrate) relative to the higher flows that this season is known for, and denitrification due to waterlogged conditions. Despite the high flows in June 2012, the higher nitrate application typical of spring and June together with the nitrate accumulated due to a drier 2012 spring may have resulted in a nitrate flux high enough to match the simulated data. Accumulation of nutrient and flushing into the fluvial system post-drought has been reported in literatures (Reynold and Edwards, 1995; Halliday *et al*., 2013). Taken together, the less overall accurate nutrient predictions may have been due to the fact that TOPCAT-NP has only been previously used as far as daily time scale (e.g. Quinn *et al*. 2007) and not at sub-daily time scale. The model needs further improvement for representation of such a finer temporal scale and this is discussed in Section 7.6. This has been recognised by Whitehead *et al*. (2007) who stated that modelling always require a considerable learning period as calibration and validation is applied at a range of scales.

7.5.2. Sensitivity test

As mentioned in the subsection describing the result of the sensitivity test, the simulations of N and P are sensitive to the parameters representing their input into the catchment system (i.e. Ninitial and Pinitial). In addition, the soluble nutrients are sensitive to their background component (BackN and BackP) which is influenced by leaching that in turn depends on the amount of N and P applied to the catchment. Like other models, TOPCAT-NP uses Ninitial and Pinitial values associated with fertilizer application or in a broader sense changes in land use management (NITS for SHETRAN, Birkinshaw and Ewen 2000; INCA N, Wade *et al*., 2002; INCA-chalk, Jackson *et al.*, 2007). Using historical data from River Thame, the rise in nitrate level was attributed to changes in land use (Howden *et al.*, 2010). Quinn (2004) pointed to ϕ and Nintial as two parameters to which TOPCAT-N is very sensitive and explained that any change in land use is communicated to the model through Ninitial. However, for the model to be reliable in testing land use scenarios at a sub-daily time scale, it may be necessary to review its catchment process representation amongst others, so as to improve its predictive capacity.

7.6. Comments on process representation and recommendations for improvement of TOPCAT-NP

The discourse in this section primarily focus on mode of assessment of the model performance, adequacy of available data on which the model was conceived and model structure.

Jackson-Blake *et al*. (2015) reported difficulty in modelling of P in agricultural catchments where the Nash-Sutcliffe (E or NS) value rarely exceeds 0.2. The value is worse for data at daily or finer resolution. Apart from the challenges in simulating some parameters, there is problem posed by means of testing the model performance. Questions are being asked about the appropriateness of using Nash-Sutcliffe (NS) and R^2 statistics to test model performance (Jain and Sudheer, 2008; Schaefli and Gupta, 2007). Jackson-Blake *et al*. (2015) wondered why NS will return higher value for a reach with fewer numbers of observations. They therefore canvassed for inclusion of more performance statistics as 'weight-of-evidence'. They also noted that there is dearth of NS and R^2 statistics at daily resolution where research at such fine resolution could be put in context as to what is class as good. Most authors prefer to first carry out temporal aggregation of the observed and simulated data. This data aggregation only serves a purpose of giving higher NS value so that the predictive capacity of such models is not questioned by reviewers. However, it was suggested that NS > 0.65 could be class as good for simulated flow. Going by this suggestion, TOPCAT-NP can be regarded as giving a good prediction of hydrology with a NS value approaching 0.80.

Another factor affecting the performance of TOPCAT-NP and on which improvement is necessary is the data on which the model is both built and also run. For the hydrological component of TOPCAT-NP and at a sub-daily scale, instrument for collecting sub-daily flow data have been around for a while (e.g. EA, CHASM (O'Connor et al., 2002) etc.). The performance statistics and visual assessment of the observed and simulated flow show that the hydrological response of Morland was well predicted (Section 7.4). However, acquisition of near continuous data for P and N is relatively recent and still limited because of cost amongst other challenges (Wade *et al*., 2012). Therefore, bank side monitoring that will have wider adoption will still be evolving for years to come. For the case of modelling Morland, as reported in this study, there is the challenge of error and missing data which if were available may likely fall within periods that matches the simulated data and improved the prediction. A way out of this is to consider a future modelling work when there would have been a privilege of long-term data bank on N and P. Questions need be asked as to what extent the model parameters used in TOPCAT-NP reflected current understanding on diurnal processes influencing nutrient concentration in rivers. Seeing that the nutrient component is built on multi-year simulation, using EPIC, from where a simple parameterisation of P and N loss process emerge (Section 7.2), it is doubtful if such data used include data at sub-daily scale. Besides, Jackson-Blake *et al*. (2015) mentioned data uncertainties in majority of agricultural catchments that relate to the magnitude, timing and location of fertilizer and manure inputs and septic tank inputs.

The hydrological component of the model, the TOPCAT, covers the entire flow pathway and succinctly reflects the role of HER in sub-surface storm flow and base flow (Section 7.2). Despite the good performance of the model in representing flow in Morland, an assumption of quick flow as a component of overland flow that is associated with winter wash off may be modified because it shares the same flow path with the nutrient component. The modification should accommodate the weather-induced variations that cause summer wash off following drought which have been reported in literatures and observed in the current studies. The MIR-N and MIR-P, the nutrient component of TOPCAT-NP, were based on EPIC (Section 7.2). The perceptual and conceptual model of EPIC may not actually reflect the new or recent process understanding emerging from the opportunity the new data from the near continuous monitoring provides. Vadas *et al*. (2013) acknowledges that many gaps remain in our qualitative understanding of agricultural P processes constituting challenges to good prediction. Inclusion of new insights into processes occurring at sub-daily time scale and associated diurnal dynamics in N and P signals in rivers, reported in some literatures (Wade *et al*., 2012; Bowes *et al*., 2015; Halliday *et al*., 2013; Halliday *et al*., 2014; Halliday *et al*., 2015), may be the missing link to providing solution to significant perceptual challenges to good high frequency simulations. Examples of such processes that exhibit diurnal signals are in-stream processes, temperature, biological uptake, turbidity cycle, etc. and their data are measured near-continuously by the bank side monitoring equipment and can be transmitted real-time to end-users. Some authors have also realised that the real-time warning of pollution events will likely alter our conceptual models (Scher *et al*., 2002; Feng *et al*., 2004; Kirchner *et al*., 2004).

Some assumptions in the model structure may need to be modified. For instance N concentration in overland flow was set at zero in TOPCAT-NP but this may not be through as some may actually be washed into water bodies through this flow pathway. An example is incidental loss in which fertilizer and/or manure are washed away by heavy storm events that coincides or occur shortly after application before equilibrating with the soil (Haygarth and Jarvis, 1999). Another is the insights from the past (Reynold and Edwards, 1995; Halliday *et al*., 2013; Bowes *et al*., 2015) and current studies where there were accumulation of nitrate during drought or nitrate were made available post-drought and are washed out into receiving river during wet period that follow. Experience in this study and other (Neal *et al*., 2004) show that nutrient can exhibit a complex relationship with flow and for a model built on an equation/assumption that only recognised dilution effect for N, for instance; this will constitute a simulation challenge. This is the case with TOPCAT-NP and has been demonstrated in the re-calibration of the model as earlier reported. In addition to other factors, the poor winter prediction of N may be due to challenge with the estimation of denitrification. Estimation of nutrient retention processes such as plant uptake, denitrification have been reported to be problematic (Silgram *et al*., 2008).

MIR-P assumes that overland flow drives the P and the adapted EPIC considers factors affecting these P fractions such as soil type, tillage regime and local slope. The sediment P is equally linked to factors such as soil type/texture, arable crop value and the land management practices. However, considering that the simulated P lagged the observed P, it is necessary that P loss through tile drain must also be factored in, particularly for catchment with appreciable per cent of poorly drain soil that is intensively cultivated such as Morland (Section 5.3). The turbidity response to event storm, for instance, matches the flow peak as discussed in previous chapter (Section 5.3.5) and this will surely have implication on sediment P. Another challenge with the simulated P is the over-prediction of the TP. This may be due to assignment of P majorly to the thin 1 cm depth of soil. Linking this with the overland flow path way means a very large proportion of P is loss through quick flow component. This may not be true considering that the top soil extending to 15 – 20 cm are actually laden with P and substantial amount of P has been reported down to 0.75 m depth in agricultural soils in Denmark (Rubaek *et al*., 2013). Ploughing and microbial activities (such as mycorrhizal association, a symbiotic association of a fungus with the vascular pant) are other factors that distribute P down the soil profile. A modification of the P distribution parameter, PDC, reflecting a distribution of P to a deeper depth may distribute the P over time leading to a better prediction. The distribution of P over time can be enhanced by the introducing a time delay function that gradually distribute total P with time and is already being considered as part of future work by the TOPCAT-NP modeller. The time delay function has the potential to both correct the over-prediction of total P and also effect the introduction of the fast flow component of soluble P.

Another challenge with the soluble P component may be the due to the fact that the bank side monitoring equipment measures the unfiltered total reactive P rather than the filtered soluble P recognised in the TOPCAT-NP. The issue with the retention process, P prediction, is also worth mentioning. Understandably, estimation of nutrient retention process such as plant uptake and adsorption is problematic and may be the reason it is set as 0.1 in the model, implying that 90% P are re-adsorbed by the soil. This may not be true considering the natural or artificial creation of large pore, and presence of low P adsorbing surface such as tile drain, etc. Compaction due to vehicular (e.g. farm machine) and animal traffic, tram lines, hard standings and open drainage channels around farm buildings may enhance transport of both particulate and soluble P fraction through overland flow pathway than envisaged and may justify the need to review the value of extraction coefficient, K.

Peculiar circumstances (e.g. weather-induced incidences and climate change) and local variation such as probable prolonged groundwater-induced constant (or almost constant) nitrate concentration in Morland are future conditional procedural codes that need to be injected to TOPCAT-NP in future development. This constant stream N concentration has also been reported in a tributary of Thames, River Enborne during the winter period (Bowes *et al.*, 2015). Heathwaite and Dils (2000) also put forward nutrient signals that have the potential to affect model prediction. They are sporadic nutrient losses during intense rainfall events from sources that are difficult to identify, quantify and control. Similarly, extreme rainfall coinciding with fertilizer or manure application especially on impermeable soil can also mobilised large amount of P than expected (Preedy *et al*., 2001).

7.7. Summary

The procedure for the simplified model structure and how it relates to catchment physical processes has been highlighted. The flow component of the TOPCAT-NP model was well simulated while the nutrient component was less accurate. The ability to study nutrient losses at such a high temporal resolution poses many problems to modelling. Event driven processes controlled by local land management makes the variability in the output difficult to simulate with simple assumptions. To improve the model performance, adjustments of some assumptions and parameters are necessary. For instance, setting nitrate in overland flow to zero and concentrating soil P to 1 cm soil depth need be reviewed and there should be a function to distribute P response over time. New insights gained from studies using bank side instrument to generate high resolution water quality data support the need for this review. There is also the need to revise the concept on which the model is built for it to have the capacity to predict signals occasioned by diurnal dynamics. The availability of high resolution nitrate and phosphorus data is relatively quite sparse and nutrient losses are very variable in space and time. With time, it is hoped that cost-effective technology for bank side instrumentation will be developed and adoption will become widespread and more data will be available to train and validate models with resultant improvement in predictive capacity. The metrics upon which model performance is assessed another factor that matters and a combination of different metrics is suggested.

Chapter 8: Conclusion

8.1. Introduction

This chapter concentrates on the findings relatives to the aims and objectives of the study and also states the significance and contribution of such findings to knowledge. There will also be considerations for policy implications and recommendations for future investigations.

This research provides unusual opportunities to combine two studies. The first of the two studies was undertaken to compare the spatial differences in contaminants transferred into and along the River Eden and the second set out to provide an explanation for the pattern by identifying the processes driving the contaminants transfer. This work also used a model to examine the application of the findings in a broader perspective. The following conclusions can be drawn based on the objectives of the study as stated in Chapter 1.

8.2. The CHASM study

8.2.1. Data sampling in a densely instrumented nested catchment

By using the study location, the River Eden catchment, with a dense network of hydrometeorological stations up to a mesoscale (~300 km^2) provided through the CHASM project, this study improves upon the previous literature on nutrient transport. The Environment Agency gauging stations made it possible to extend the study in the catchment further up to a basin scale (~1000 km^2). These stations logged data at 15 minute interval and are sited along the nested catchment. Discrete water samples were collected for nutrient and sediment analysis near the gauging stations across all the nine catchments simultaneously so as to ensure similar hydrological conditions. Soil was sampled seasonally on the same day across two selected catchments. Thus, concentration and flow data required for other assessments needed to achieve the overall aims of the study were provided.

By plotting the relationship between concentration and flow data, questions on where the nutrients and suspended sediment (SS) came from was addressed. The positive gradient shown in the relationship of P species (total P, total reactive P and soluble P) and SS is an indication of diffuse source: agricultural, channel and near-channel sources (Sections 4.3.1and 5.3.5). Possible pathways include overland flow, tile drain and those entrained by turbulent flow in-stream (Section 5.3.5 and table 6.2). Nitrate sources were complex. It shows both positive and negative gradient (Section 4.3.1 and figure 4.9) and can be constant with flow (Section 5.3.2 and figure 5.9b). With low population density in the Eden and low contribution from point source (Section 6.2.2 and table 6.2), the constant/point source reflected in the negative gradient (i.e. dilution effect) is probably groundwater. This is further supported with higher nitrate concentration during dry period (Section 4.3.2 and figure 4.10). It is therefore suggested to be primarily coming from groundwater source and secondarily diffuse source (provided certain conditions are met such as post-drought flushing following accumulation during the drought condition). The transport pathways suggested, therefore, are groundwater, overland, tile drain and direct contamination from livestock poaching.

8.2.2. Comparison of spatial relationship of catchment characteristics, stream concentrations of N, P and SS with the catchment area and quantification of contaminant load and yield

There was downstream increase in concentrations, loads and specific yields of the nutrients (nitrate and P) and suspended sediment relative to the headwater subcatchments. Nitrate showed the most obvious increasing spatial trend downstream among the nested catchments compared with P and sediment. The nitrate concentration and load increased all the way from a headwater subcatchment at Gais Gill (1.1 km^2) to Great Corby on the Eden (1373 km^2). Except for a higher nitrate yield at Smardale compared with Great Musgrave and Appleby there was also a clearer spatial pattern in nitrate yield compared with P yield. Question 2 that borders on the relationship of the determinands with catchment size has just been addressed but one is left with the question on the possibility of the size acting as proxy for some specific catchment characteristics which is what questions four and part of five focus on.

Within the nested catchment system, a negative power law relationship ($R^2 = 0.90$ but less for the negative linear relationship ($R^2=0.39$) was established between the elevation and land area but there are positive linear relationships between tilled land, managed grassland, soil type (cultivable soil comprising free drain and poor drain seasonal waterlogged soils) and area ($R^2 = 0.85$, 0.21, 0.20 respectively). It implies that upland area has less cultivable land and less intensive agricultural land use compared with lowland. The spatial pattern of soil and managed grassland that reveal two domains described in this study as tributary domain (upstream) and main Eden domain (downstream) may have accounted for the weaker linear relationships. The tributary domain is a continuum that starts from Gais Gill and end in Smardale while the other domain (main Eden) begins from Great Musgrave and forms another continuum down to Great Corby and overlaps the former (figure 4.12b). Interestingly, it matches the yield pattern described in previous paragraph (figure 4.16) (see Section 8.2.3 for explanation on the drop in SS and P in Great Corby). It suggests that soil type drives the agricultural land use and management which in turn control the spatial pattern in nutrient and SS yields in the Eden. This further supports the predominance of agricultural diffuse source for nutrients and SS in the Eden and provides a clue on area to target when planning mitigation.

The relationships between land use (managed grassland and tilled land) and the concentrations of the water quality determinands reveal that P species have stronger relationships with managed grassland (R^2 values for total P, TP, and soluble P, RP, are 0.79 and 0.88 respectively) compared with tilled land (R^2 values for TP and RP are 0.51 and 0.59 respectively). Nitrate (N) has strong relationships with both (R^2 for managed grassland and tilled land are 0.90 (exponential) and 0.80 respectively). For SS the relationships with managed grassland and tilled land are 0.51 and 0.31. This suggests that the nutrient concentrations are primarily driven by agricultural land use whereas the SS concentration has other sources that are also significant and this is probably the in-channel and near-channel sources. The in-channel and near channel sources such as bed erosion, bank side scar, livestock poaching, debris flow and vehicular crossing has been demonstrated in previous work in the Eden (Section 4.3.2)

When the cultivable soil was disaggregated into poorly drain and free drain soils classes and related to the concentrations of the water quality determinands, P and SS have stronger relationships with the poorly drain soil class (R^2 = 0.74, 0.66 and 0.31 for TP, RP and SS respectively) unlike free drain soil (R^2 = 0.3, 0.37, and 0.05 for TP, RP and SS respectively). SS was very weak with free drain soil and not very strong with poorly drain soil suggesting other sources and pathway beside agricultural field and overland flow or runoff pathway (associated erosion) respectively. This supports the in-channel and near-channel source mentioned in the previous paragraphs. It also suggests that poorly drain soil supports runoff and erosion. This is reversed for nitrate with stronger relationship with free drain soil (R^2 = 0.63) and linked nitrate to subsurface flow processes (e.g. groundwater). The scatter probably accounts for sporadic losses via runoff.

Another factor linked to land management is the relative differences in the contaminant concentration in the tributaries between upper reach and lower reach of River Eden. For instance the increase in these variables from Kirkby Stephen (69 km^2) to Great Musgrave (616 km^2) was in accord with the characteristics of their tributaries. Gais Gill, a feeder stream to Kirkby Stephen was nutrient-poor, recording undetectably low nitrate concentrations in a number of water samples while this investigation lasted, compared with Blind Beck, a feeder stream around Great Musgrave, which was relatively nutrient-rich due to higher fertilizer and manure input. The explanation given to the dip in SS and P input to GC, that is, the ‘clean’ River Eamont coming from Lake Ullswater, can be liking to the impact of any land management that slow down or trap water reaching a water bodies. Of the two land managements, the more common reflecting the upstream-downstream pattern is the fertility management.

8.2.3. Identification of key driver of the stream contaminant content and the variability relative to catchment size

This section draws from the findings in the Sections 8.2.1 and 8.2.2. and also provides answer to the question asked about the role of land use and land management in controlling the nutrient loss from the catchment. Land use represented by managed grassland and tilled land matches the spatial pattern in nutrient and sediment yield from Gais Gill to Great Corby (GC). The drop in P and SS yield in GC is probably due to trapping effect of Lake Ullswater. The concentrations of the nutrients also align with the land use. Tilled land particularly matches N concentration. Fertility management to enhance grass production for livestock consumption appears to play critical role in nutrient yield in River Eden. In addition manure and fertilizer application, soil water management in form field/tile drain, particularly on tilled land, may be influencing the stream N concentration. Since the managed grassland and tilled land increase downstream, it can be suggested that the land management will follow similar pattern. The surface flow pathway appears to transport the SS and P and the sub-surface flow pathway dominate the nitrate transport.

The switch in nitrate concentration-flow gradient in Temple Sowerby where it started with dilution effect (point or groundwater source) and then increase with flow (diffuse source), particularly at higher flows, partly reflect the importance of flow and partly highlights complexity in nitrate dynamics in this catchment. A similar flush of nitrate at higher discharges was also observed at Smardale in the upper reach and at Great Corby further downstream of Temple Sowerby. This switch from the conventional dilution effect supports the existing body of knowledge on nitrate-flow relationship.

There is downstream increase in discharge and land use, and land use and nutrient in turn show a good agreement. It may be the reason the nutrient-flow relationship improves downstream and point to the synergy between hydrology and land use in nutrient emission to the river. It adds to the growing body of literature indicating that changes in hydrological processes and land use intensities dominate the pollutant processes in large catchments.

Here are some secondary findings supported by this study:

8.2.4. Does soil and elevation play any role?

The headwater subcatchments in the upper reaches of the River Eden (at a higher elevation) are associated with a lower agricultural intensity compared with the lower reaches having a higher agricultural production. While elevation has negative gradient with catchment area, managed grassland and tilled land have positive gradient (Section 8.2.2). This is an indication of the indirect impact that elevation has on land use in this catchment.

Earlier in Section 8.2.2, it has been reported that there was similarity in soil and the contaminants yield spatial pattern in the Eden and that soil drainage class appears to control the transport pathways of the SS and nutrients. The pathway differs between nitrate and the other water quality contaminants.

Although only the riparian areas in the two sub-catchments (Gais Gill and Blind Beck) were sampled for soil analysis over the four typical seasons (once in every season) in England, from November 2011 to July 2012, both soil labile and bicarbonate P in the catchment (Blind Beck) with higher agricultural intensity positively correlated with stream P (Sections 4.3.4 and 4.3.6). The soil P can be said to mirror land use since it probably originated from P applications related to agricultural production. Therefore, its correlation with stream P further supports the role land use plays in the stronger nutrient-flow relationships downstream compared with the upper reaches of the River Eden. The soil organic matter (SOM) increased in the warm period in the soil at Gais Gill suggesting net decomposition of organic material and dominance of these temperature-dependent microbial processes. In Blind Beck there was decrease in SOM in spring and summer compare to the winter season. It shows that land use and more specifically, anthropogenic effect in form of crop uptake and land management (e.g. fertility and drainage management) masked the microbial decomposition effect. The nutrient demand by crop and drier soil in Blind Beck probably stimulate net mineralisation of SOM. The slight increase in the summer compared to the spring still points to fertility management. This suggests that the downstream variation in response of water quality contaminant is also linked to or influence by the downstream variation in the dominant physical, chemical and biological processes prevailing in the catchment.

8.2.5. Seasonality at the Eden headwater system at Gais Gill compared to the higher order watercourses downstream or elsewhere in the Eden

Unlike suspended sediment and P concentrations that were found to be inconsistent, nitrate was consistently lower in the warmer season and this was particularly obvious at Gais Gill, a subcatchment with low agricultural intensity, where a number of undetectably low concentrations were measured. The luxuriant in-stream algae growth in the warm season compared with the cold season at Gais Gill suggests that the reduction in nitrate was due to plant uptake (table 4.4; figure 4.11). Thus, this extends findings suggesting that in a catchment with low nitrate input, both the seasonal effect and the impact of biological uptake are easier to detect. This finding together with the finding on seasonal dynamics of soil organic matter reported in the preceding section combine to answer the questions asked on impact of weather-induced soil and in-stream processes on surface water quality.

Another important practical implication arising from the luxuriant algal growth mentioned above is the fact that it occurred at a low nitrate concentration implying that a concentration below that specified by the WFD standard is capable of threatening the health of watercourses. Besides, a tributary like Blind Beck exported more nutrients than many of the other subcatchments investigated. An implication of these findings is that tributaries have to be taken into account by catchment managers when planning measures to improve ecological status of water bodies in the UK.

Because the above findings arose from data obtained from discrete (grab) samples, the concentration measurements were then checked against samples obtained both from an autosampler and from field equipment that collected and analysed samples in-situ, which generated a near continuous time series of water quality variables. This is the essence of the DTC study.

8.3. Findings from the DTC study

8.3.1. Further investigation of catchment characteristics and processes, put forward by CHASM studies, using the DTC high resolution data

Introduction

In the CHASM study in the Eden catchment, we found that P and SS are primarily from diffuse source while nitrate is from both diffuse and point/constant sources with complex signals when related to flow due to rainfall event. Nutrients and SS concentrations, loads and yields increase downstream compared with headwater. The spatial pattern of nutrients and SS yields matches the spatial pattern of soil and land use. The study also reveals how stream signals of water quality determinands change with season/ weather and how this relate to dominance processes between upstream and downstream catchments having control on such signals. To address the uncertainty associated with the limited data that could be obtained from grab samples used in the spatial CHASM study, near continuous data from the EdenDTC project was studied. Two EdenDTC catchments (Dacre and Morland) having contrasting land use were investigated.

Using the fine resolution data from the Dacre and Morland subcatchments, located at different mean elevations and having contrasting land uses, the following are areas where findings from the DTC study agrees with CHASM’s:

1. Dacre, at a higher mean elevation has less agricultural activity and lower nutrient and suspended sediment concentrations and yields compared with

the Morland subcatchment that is at a lower mean elevation. This indirect association also extend to per cent cultivable soil (i.e. free drain and poorly drain seasonal waterlogged soil). Cultivable soil is higher in Morland (table 5.6).

2. Phosphorus and sediment concentrations increased with flow due to rainfall events, indicating a diffuse agricultural source (Section 5.3.2; figures 5.3 and 5.4).
3. Nitrate concentrations showed a complex response with increasing flow due to rainfall events (figure 5.9b; Section 5.3.5). It can either be negative trend (dilution effect), constant or show positive gradient with flow.

Thus, the DTC data and findings, having contrasting elevation and land use can indeed be used to explain the spatial scale variation down the Eden. It supports the downstream increase in nutrient and suspended sediment concentrations and yields relative to headwater subcatchments, as observed under the CHASM study.

8.3.2. Further insights gained through the DTC study

Source

The response of the contaminants to some events, in Morland, offers more details on possible sources of these contaminants (Section 5.3.5). Turbidity matches flow peaks indicating a source from an immediate environment. Bed suspension of sediment, bank erosion etc. are possible causals of these responses and therefore constitute part of the diffuse sources. Total P lagged the turbidity and sometimes the flow peak (figures 5.10 – 5.14) indicating a source that arrived shortly after. Tile/field drain from agricultural field and overland flow are possible flow pathways and agricultural source dominate the sediment P in this catchment. Artificial drainage must have been installed to support intensive agriculture (managed grassland, circa. 84%, tilled land, 3%) in a catchment dominated by poorly drain seasonal waterlogged soil (84%). Total reactive P initial rise was followed by drop at flow peak before rising again and then follow the flow pattern afterward. Nitrate exhibit both the dilution effect but also show positive gradient in one of the events (figure 5.11 and revisit figure 5.9b). The positive gradient lagged the flow peak suggesting distant source which is possible from agricultural field. This coincided with the period of nitrate flush in June 2012 as shown on the time series graph in figure 5.9b.

Seasonal effect

Further on point ‘3’ listed in the sub-section above and on the point raised about possible source of N in the immediate sub-section, the storm events in June 2012, generated a nitrate pattern where concentration increased with flow unlike the others. This followed a dry spell that extended from late winter to June, a period during which fertilizer is typically applied, implying that there was nutrient accumulation but transport limitation. In the ‘post-drought’ period, the nitrate flush in this summer, resembles the well-reported ‘autumn flush’. Thus, the weather-induced ‘spikes’ in nitrate concentration in June 2012, demonstrates that any condition that leads to the accumulation of nutrient in the soil (e.g. nitrate increase in summer (figures 5.9b and 5.11)) prior to an intense downpour can produce a nitrate chemograph that is similar in gradient to the ‘autumn flush’ (figure 4.9; Section 6.2.2; table 6.1).

Thus, using more detailed data from both the autosampler and the continuous monitoring bankside equipment, key findings from the spatial study platform that CHASM provided have been supported. The uncertainty associated with an inability to acquire enough samples at peak flow under the CHASM data collection project was also addressed.

There are also secondary findings arising from the DTC study.

Can a turbidity probe be used as a proxy for other contaminants along with the suspended sediment?

An additional finding suggests that turbidity data can serve as proxy data for total P and total reactive P, as has been reported for suspended sediment in the literature. When the turbidity relationships with nitrate, total P, soluble P and suspended sediment were compared, based on the periods that the autosamplers were in operation, the strength of the relationships of total P (R^2 value = 0.92), TRP (R^2 value =0.70) were comparable with what obtains with the suspended sediment (R^2 = 0.84). Nitrate had a weaker relationship with turbidity (R^2 value = 0.19).

To summarise, the spatial scale study and the investigation of the detailed DTC data, suggest that hydrology and land use control the upland/lowland contrast in nutrient exports into the River Eden. The land use is influenced by soil type and is linked to soil management. Considering the clear spatial pattern in nitrate concentration down the river and the clear seasonality effect shown at a low intensity headwater (Gais Gill), nitrate appears to be a better index of land use effects relative to the spatio-temporal dependency in nutrient transport in the Eden catchment, compared with P and its associated suspended sediment. The relationship of nitrate with discharge was complex. Nitrate concentration often decreased with an increase in discharge but was sometimes constant at low flow, and has been observed to increase at higher flow following environmental and anthropogenic conditions that enhanced the build-up of soil nutrient prior to a flush, irrespective of the season.

8.4. Modelling study

8.4.1. Assessing the potential of TOPCAT-NP applied to Morland in predicting impact of land use and management changes on nutrient content in rivers

TOPCAT-NP was deployed to simulate the nutrient concentration at hourly time step and to assess which land management scenario is best in sustaining the water quality of Morland, specifically, and other catchments in general. The model was able to simulate the flow successfully, and the predicted mean concentrations of the nutrients (N and P) were comparable to the observed mean of the nutrient concentrations. However, the model was less able to adequately represent the peak values of the observed data for the nutrients and cope with complex nitrate signals. Some modifications to the model were suggested to enhance the model performance.

This include a revision of some model assumption and parameters to reflect any important findings overlooked in the previous model structure and also to include recent insights gained using near continuous nutrient measuring devices. Over-prediction of P, for instance, could possibly be improved by adjusting the P distribution coefficient or distributing the loss of P from the catchment over time. This is based on the fact that high P concentration is not limited to only 1 cm depth, as assumed in TOPCAT-NP, but studies have shown that substantial amount of P can be found on top soil and even down to 0.75m (Section 7.6). The new findings emerging from the bank side nutrient measuring equipment requires that the concept on which TOPCAT-NP is built be revised to accommodate them. Model parameters must be informed by high resolution data from this measuring device if we must optimally simulate nutrient observed at daily and sub-daily time scales. The debate surrounding inadequacy of some means of testing model performance demands that a number of other statistical tests be brought on board.

8.5. Overall key findings

This study is probably the first to use a rare combination of the spatial study platform (up to ~1400 km^2) provided by the CHASM project and a high resolution data (daily and sub-daily) from the DTC project to give a more detail understanding of the process driving the spatial signals of nutrient and suspended sediment. This work is also one in a series of studies using the spatial CHASM study platform and is the first to study nutrient down to a relatively large scale (~1400 km^2) in the River Eden catchment. A number of insights are gained through this study.

The phosphorus (total P, total reactive P and soluble P) and suspended sediment are dominated by diffuse source. Phosphorus was primarily coming from agricultural fields and was probably transported through overland flow and field/tile drain. Suspended sediment sources appear to be a combination of field, near-channel and in-channel sources. The relationship with flow suggests that they were transported via overland and in-stream flow processes. Nitrate-flow relationship was complex, this together with its seasonal pattern suggest groundwater and agricultural fields as its sources. Groundwater source and flow pathway appear to dominate. The contribution of all the water quality determinands from point sources was minimal. Turbidity show strong relationships with phosphorus and suspended sediment and its relationship with flow provides additional evidence to the suspended sediment dynamics.

There was downstream increase in concentration, load and suspended sediment when compared to headwater at Gais Gill. Phosphorus and suspended sediment concentrations did not show a clear spatial pattern down to Great Corby unlike nitrate. Nutrient and suspended yields seem to largely follow the two-domain spatial pattern displayed by land use (managed grassland) and soil type. It suggests that soil type controls the land use which in turn determines the land management which drive the contaminants yield pattern. Elevation plays an indirect association with the land use variation in the Eden.

Spatial variation in land use/management, which is affected by some catchment characteristics, together with the weather/climatic pattern, control the dominant processes (in-stream processes, soil processes, crop uptake effect, drainage etc.) that determine stream contaminants signals.

The post-drought nitrate flush was supported by this study. There were ‘spikes’ in nitrate concentration in the peculiar wet summer of 2012 that follow a long dry spell earlier in the year.

Through the combinations of these studies, insights have been gained into how, where and when nutrient losses occurred. The key finding from this study is that targeted land management and better understanding of the hydrological processes that drive nutrient loss may be an effective way to reduce the problem.

8.6. Further Research

- Additional sampling at the nine CHASM catchments that could improve the contaminant concentration vs. flow curves that would lead to a reduction in error, improve the estimates of nitrates, P and suspended sediment (concentrations or yields), and consequently provide more reliable conclusions on the spatial variability of the contaminants. The use of the autosamplers and continuous turbidity probes in these catchments would generate data that better covers the full range of flows, improves the relationships between the contaminant and the catchment characteristics and improves the understanding of the processes leading to nutrient and sediment transfer to catchment outlet.
- Elaborate soil studies:
  These could involve sampling a transect cut along a topographical sequence at a smaller catchment scale to confirm or refute the relationship between soil nutrient status and the concentration in the river. This study may then be scaled up to a larger catchment using any complementary soil data bank.
  A future study could incorporate the investigation of sorption characteristics of soils and river-bed sediments relative to P. Such a study will also include an in-stream physio-chemical investigation to determine if there are both field and in-stream sources of P or if there is an in-stream self-cleansing mechanism. In more detail, the studies would include testing for calcite

saturation, iron and aluminium concentrations and possibly organic matter that could chelate some of these metallic cations. This is a step further to what was done by Tripkovic (2013).

Another work that can add to the understanding of nutrient transfer processes would be to check for the evidence for leaching by comparing simultaneously the concentration of basic cations in the topsoil and subsoil as done elsewhere. Leaching would be confirmed if there is evidence of loss of the basic cations in the topsoil and accumulation in the subsoil.

- Further studies at tributary scale to ascertain the influence of Lake Ullswater and River Eamont on P and SS response at Great Corby compared to nitrate.
- Future investigation of water quality could incorporate a boron test on water samples so as to check if there is any link to a sewage treatment plant.

The quantification of the potential of algal-embedded mitigation structures to contain nitrate export to rivers also appears an interesting future investigation.

Appendix

Appendix A – Stage-discharge rating co-efficient for some CHASM catchments

Site	h min	h max	A	B	Note
Appleby			21.98	2.103	
Blind Beck			2.135	2.296	
Gais Gill			6.244	2.321	
Ravenstonedale	0.00	0.60	4.297	1.717	Estimated from FDC*
	0.60	1.40	11.45	3.511	
Smardale			41.86	2.557	

Table A – Stage-discharge rating co-efficient for some CHASM catchments

*Established by Mills (2009)

Appendix B

Water quality data at Gais Gill

Suspended sediment

Date	Time	Flow (m^3/s)	SSC (mg/l)
1/11/2011	10:16	0.08	1.75
03/11/2011	11:01	0.07	0.00
21/11/2011	10:16	0.04	1.25
24/11/2011	10:16	0.12	1.50
16/12/2011	10:07	0.05	0.50
06/03/2012	10:31	0.06	0.83
14/03/2012	10:16	0.05	0.00
19/03/2012	10:03	0.05	0.50
21/03/2012	10:12	0.05	0.67
02/05/2012	09:07	0.05	0.42
09/05/2012	08:58	0.05	1.83
16/05/2012	09:14	0.06	0.33
21/05/2012	09:27	0.05	1.67
25/06/2012	09:38	0.07	0.33
23/07/2012	09:14	0.06	0.83
26/07/2012	09:04	0.06	0.50
31/07/2012	09:19	0.06	1.50
06/08/2012	09:08	0.07	0.67
19/09/2012	09:41	0.06	0.33
10/10/2012	09:26	0.05	0.00
07/11/2012	11:38	0.05	1.50
20/12/2012	10:00	0.11	0.83
14/01/2013	11:21	0.04	0.17
30/01/2013	09:47	0.14	1.50
27/02/2013	10:00	0.10	0.50
26/03/2013	Snow	Snow	Snow
10/04/2013	09:17	0.10	0.17
26/04/2013	09:43	0.13	1.08

Table B1.1 Sampled suspended sediment concentration and discharge values for Gais Gill

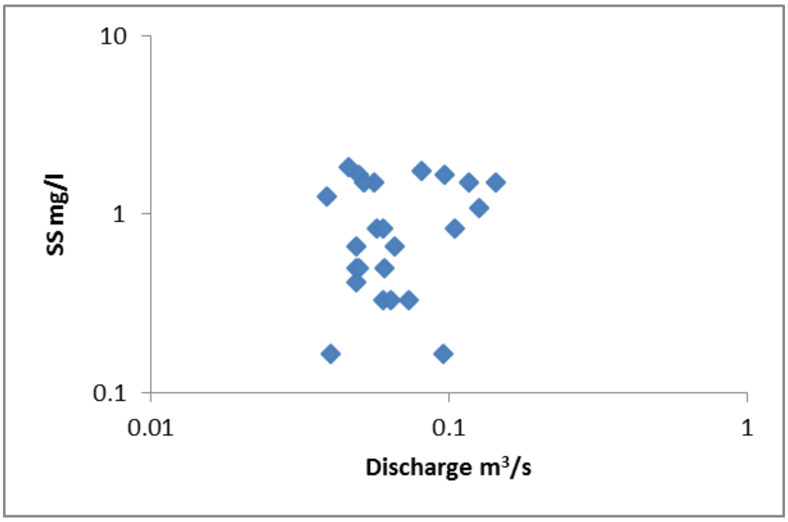


Figure B1.1 Scatter plot of suspended sediment concentration against discharge at Gais Gill

Date	Flow (m^3/s)	TP (mg/l)
01/11/2011	0.08	0.012
03/11/2011	0.07	0.010
21/11/2011	0.04	0.010
24/11/2011	0.12	0.016
06/03/2012	0.06	0.004
14/03/2012	0.05	0.027
19/03/2012	0.05	0.003
21/03/2012	0.05	0.010
02/05/2012	0.05	0.019
09/05/2012	0.05	0.004
16/05/2012	0.06	0.026
21/05/2012	0.05	0.023
23/07/2012	0.06	0.013
26/07/2012	0.06	0.019
31/07/2012	0.06	0.017
06/08/2012	0.07	0.015

Table B1.2 Sampled total phosphorus concentration and discharge values for Gais Gill

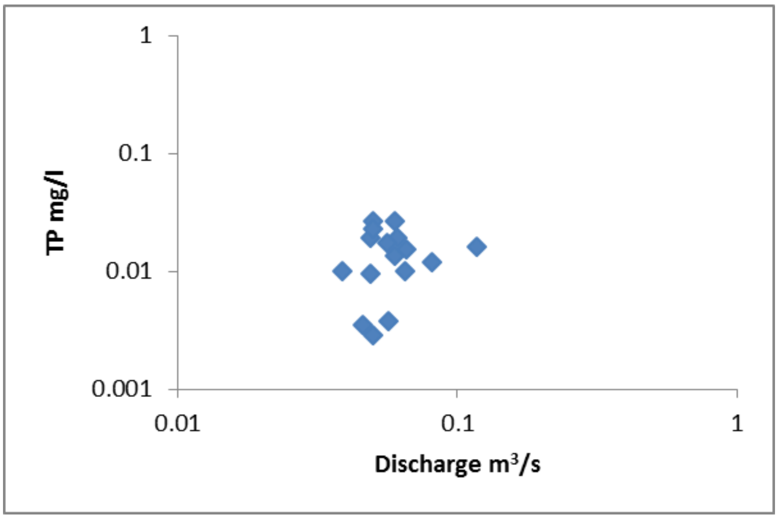


Figure B1.2 Scatter plot of total phosphorus concentration against discharge at Gais Gill

Date	Flow (m^3/s)	RP (mg/l)
01/11/2011	0.08	0.004
03/11/2011	0.07	0.000
21/11/2011	0.04	0.004
24/11/2011	0.12	0.007
06/03/2012	0.06	0.002
14/03/2012	0.05	0.011
19/03/2012	0.05	0.000
21/03/2012	0.05	0.006
02/05/2012	0.05	0.012
09/05/2012	0.05	0.001
16/05/2012	0.06	0.019
21/05/2012	0.05	0.012
23/07/2012	0.06	0.011
26/07/2012	0.06	0.009
31/07/2012	0.06	0.013
06/08/2012	0.07	0.006

Table B1.3 Sampled reactive phosphorus concentration and discharge values for Gais Gill

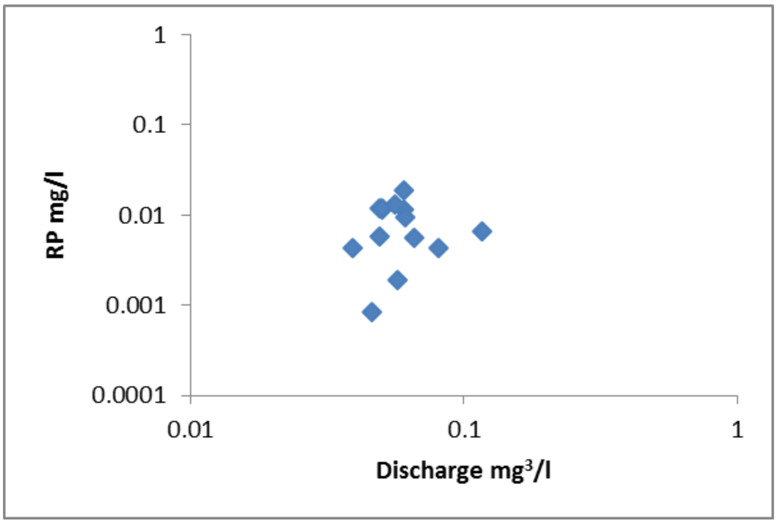


Figure B1.3 Scatter plot of reactive phosphorus concentration against discharge at Gais Gill

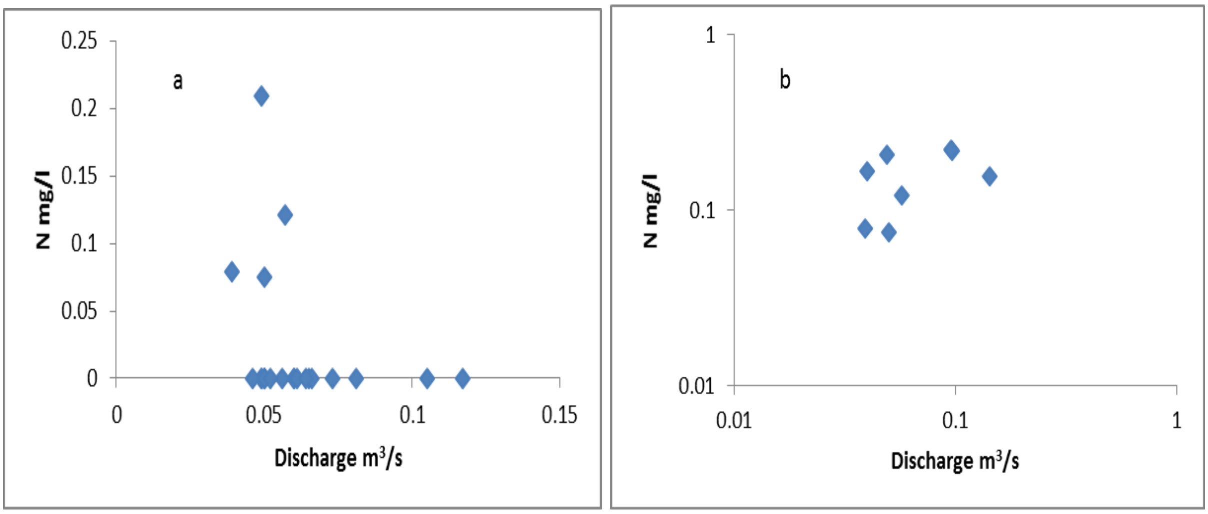


Figure B1.4 Scatter plot of nitrate concentration against discharge at Gais Gill for (a) all sampling visits (b) only visits that has non-zero nitrate concentrations

Date	Flow (m^3/s)	N (mg/l)
01/11/2011	0.08	0.000
03/11/2011	0.07	0.000
21/11/2011	0.04	0.080
24/11/2011	0.12	0.000
16/12/2011	0.05	0.210
06/03/2012	0.06	0.121
14/03/2012	0.05	0.075
19/03/2012	0.05	0.000
21/03/2012	0.05	0.000
02/05/2012	0.05	0.000
09/05/2012	0.05	0.000
16/05/2012	0.06	0.000
21/05/2012	0.05	0.000
25/06/2012	0.07	0.000
23/07/2012	0.06	0.000
26/07/2012	0.06	0.000
31/07/2012	0.06	0.000
06/08/2012	0.07	0.000
19/09/2012	0.06	0.000
10/10/2012	0.05	0.000
07/11/2012	0.05	0.000
20/12/2012	0.11	0.000
14/01/2013	0.04	0.167
30/01/2013	0.14	0.156
27/02/2013	0.10	0.218
26/03/2013	Snow	Snow
10/04/2013	0.10	0.223
26/04/2013	0.13	0.000

Table B1.4 Sampled nitrate concentration and discharge values for Gais Gill

Date	Flow (m^3/s)	SSC (mg/l)
01/11/2011	0.82	6.50
03/11/2011	0.67	4.00
21/11/2011	0.44	0.25
24/11/2011	1.78	11.5
16/12/2011	0.79	2.00
06/03/2012	0.94	1.83
14/03/2012	0.81	0.83
19/03/2012	0.81	1.83
21/03/2012	0.76	1.17
02/05/2012	0.78	2.08
09/05/2012	0.74	1.50
16/05/2012	0.92	2.00
21/05/2012	0.76	1.67
25/06/2012	1.34	3.00
23/07/2012	0.95	1.67
26/07/2012	1.03	2.83
31/07/2012	0.97	2.25
06/08/2012	1.13	3.67
19/09/2012	1.02	2.08
10/10/2012	0.95	1.50
07/11/2012	1.03	1.17
20/12/2012	2.17	5.83
16/12/2011	0.79	2.00
25/06/2012	1.34	3.00

Table B2.1 Sampled suspended sediment concentration and discharge values for Ravenstonedale

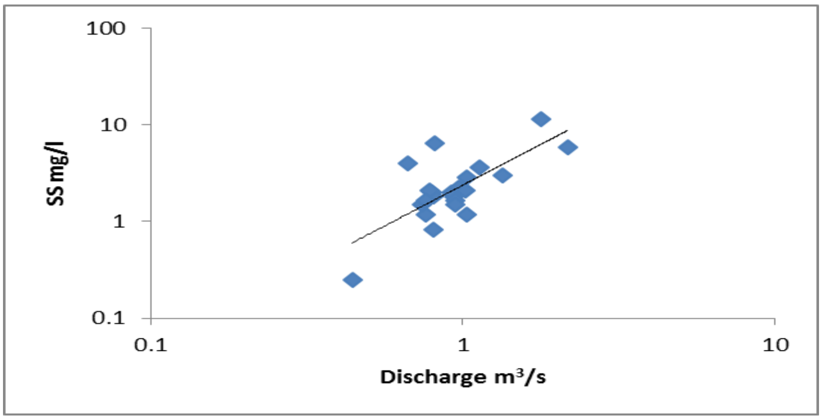


Figure B2.1 Scatter plot of suspended sediment concentration against discharge at Ravenstonedale

Date	Flow (m^3/s)	TP (mg/l)
11/01/2011	0.82	0.048
11/03/2011	0.67	0.054
21/11/2011	0.44	0.030
24/11/2011	1.78	0.077
03/06/2012	0.94	0.034
14/03/2012	0.81	0.048
19/03/2012	0.81	0.020
21/03/2012	0.76	0.019
05/02/2012	0.78	0.012
05/09/2012	0.74	0.032
16/05/2012	0.92	0.069
21/05/2012	0.76	0.044
23/07/2012	0.95	0.046
26/07/2012	1.03	0.044
31/07/2012	0.97	0.050
08/06/2012	1.13	0.083

Table B2.2 Sampled total phosphorus concentration and discharge values for Ravenstonedale

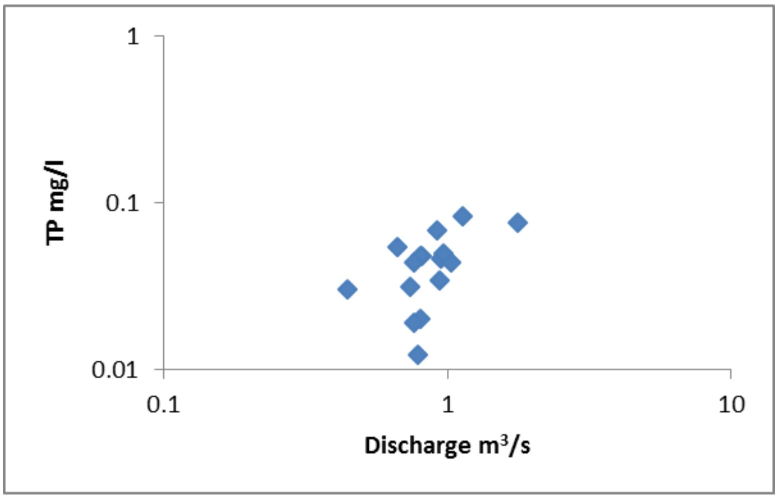


Figure B2.2 Scatter plot of total phosphorus concentration against discharge at Ravenstonedale

Date	Flow (m^3/s)	RP (mg/l)
01/11/2011	0.82	0.018
03/11/2011	0.67	0.013
21/11/2011	0.44	0.011
24/11/2011	1.78	0.031
06/03/2012	0.94	0.017
14/03/2012	0.81	0.015
19/03/2012	0.81	0.010
21/03/2012	0.76	0.013
02/05/2012	0.78	0.003
09/05/2012	0.74	0.015
16/05/2012	0.92	0.051
21/05/2012	0.76	0.021
23/07/2012	0.95	0.032
26/07/2012	1.03	0.025
31/07/2012	0.97	0.028
06/08/2012	1.13	0.044

Table B2.3 Sampled reactive phosphorus concentration and discharge values for Ravenstonedale

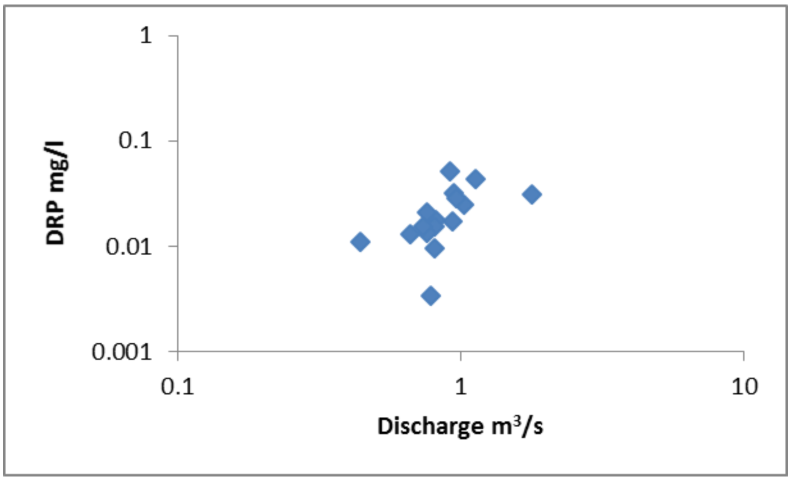


Figure B2.3 Scatter plot of reactive phosphorus concentration against discharge at Ravenstonedale

Date	Flow (m^3/s)	N (mg/l)
01/11/2011	0.82	1.232
03/11/2011	0.67	1.238
21/11/2011	0.44	2.525
24/11/2011	1.78	1.271
06/03/2012	0.94	2.197
14/03/2012	0.81	2.152
19/03/2012	0.81	1.880
21/03/2012	0.76	1.907
02/05/2012	0.78	1.526
09/05/2012	0.74	1.171
16/05/2012	0.92	1.365
21/05/2012	0.76	1.548
23/07/2012	0.95	1.526
26/07/2012	1.03	1.171
31/07/2012	0.97	1.365
06/08/2012	1.13	1.548
16/12/2011	0.79	2.681
25/06/2012	1.34	1.654
19/09/2012	1.02	1.365
10/10/2012	0.95	1.913
07/11/2012	1.03	1.901
20/12/2012	2.17	1.015
14/01/2013	1.16	2.508
30/01/2013	2.82	1.856
27/02/2013	1.11	2.134
26/03/2013	1.20	1.676
10/04/2013	1.13	1.079
26/04/2013	1.49	1.326

Table B2.4 Sampled nitrate concentration and discharge values for Ravenstonedale

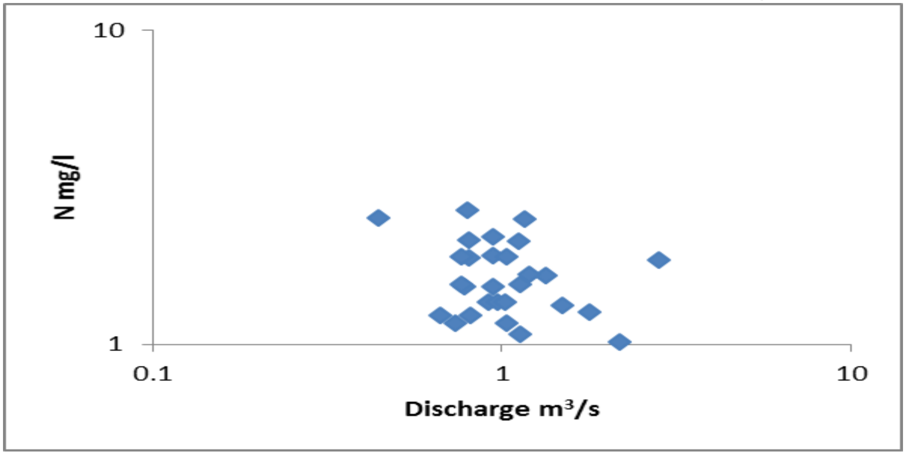


Figure B2.4 Scatter plot of nitrate concentration against discharge at Ravenstonedale

Date	Flow (m^3/s)	SS (mg/l)
01/11/2011	1.21	3.25
03/11/2011	0.87	2.50
21/11/2011	0.40	2.75
24/11/2011	4.10	11.75
06/03/2012	1.58	1.50
14/03/2012	1.43	1.00
19/03/2012	1.44	1.00
21/03/2012	1.39	1.50
02/05/2012	1.42	1.25
09/05/2012	1.32	0.50
16/05/2012	1.66	1.00
21/05/2012	1.35	2.33
23/07/2012	1.67	2.17
26/07/2012	1.80	1.00
31/07/2012	1.70	2.33
06/08/2012	1.97	3.67
16/12/2011	1.17	8.33
25/06/2012	2.26	1.50
19/09/2012	1.81	2.67
10/10/2012	1.68	1.33
07/11/2012	1.80	2.00
20/12/2012	3.97	13.00
14/01/2013	2.04	1.00
30/01/2013	4.59	7.67
27/02/2013	1.95	8.33
26/03/2013	2.09	1.17
10/04/2013	1.99	1.33
26/04/2013	2.57	1.42

Table B3.1 Sampled suspended sediment concentration and discharge values for Smardale

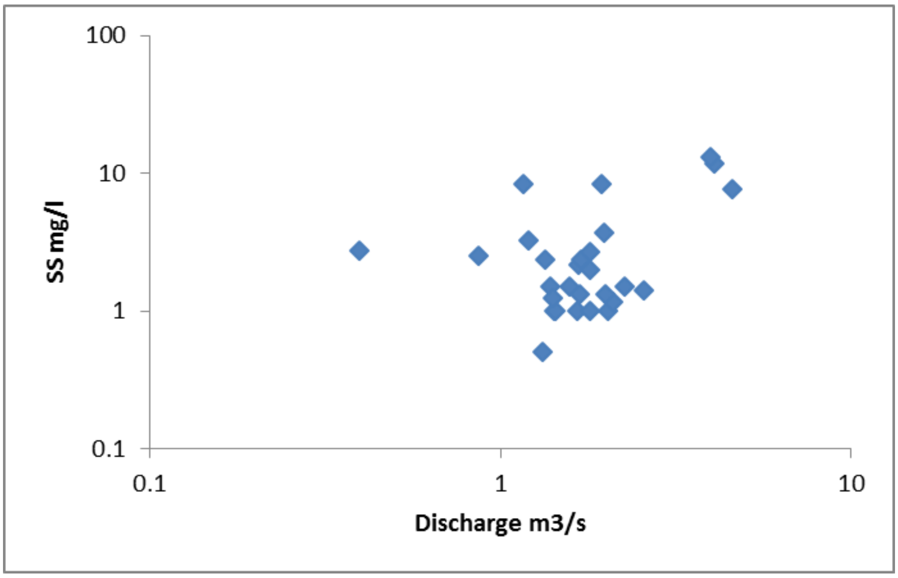


Figure B3.1 Scatter plot of nitrate concentration against discharge at Smardale

Date	Flow (m^3/s)	TP (mg/l)
01/11/2011	1.21	0.042
03/11/2011	0.87	0.040
21/11/2011	0.40	0.020
24/11/2011	4.10	0.089
06/03/2012	1.58	0.033
14/03/2012	1.43	0.057
19/03/2012	1.44	0.012
21/03/2012	1.39	0.021
02/05/2012	1.42	0.009
09/05/2012	1.32	0.005
16/05/2012	1.66	0.104
21/05/2012	1.35	0.042
23/07/2012	1.67	0.025
26/07/2012	1.80	0.013
31/07/2012	1.70	0.028
06/08/2012	1.98	0.028

Table B3.2 Sampled total phosphorus concentration and discharge values for Smardale

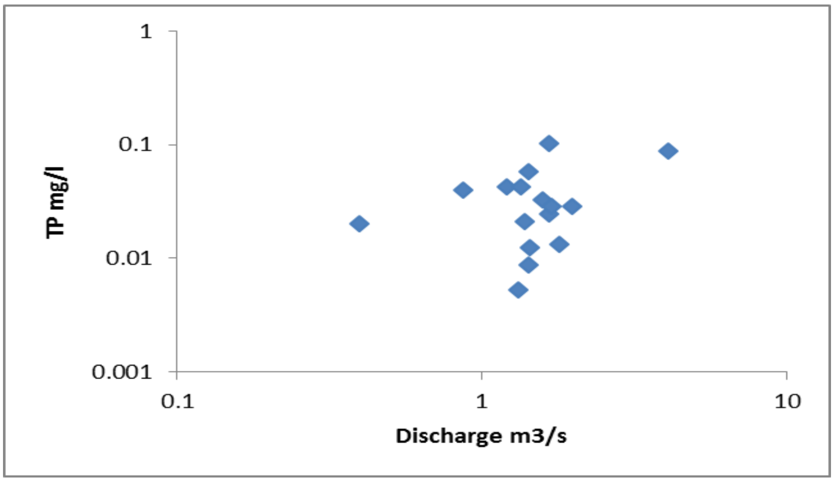


Figure B3.2 Scatter plot of total phosphorus concentration against discharge at Smardale

Date	Flow (m3/s)	DRP (mg/l)
01/11/2011	1.21	0.020
03/11/2011	0.87	0.020
21/11/2011	0.40	0.009
24/11/2011	4.10	0.026
06/03/2012	1.58	0.019
14/03/2012	1.43	0.010
19/03/2012	1.44	0.004
21/03/2012	1.39	0.011
02/05/2012	1.42	0.000
09/05/2012	1.32	0.002
16/05/2012	1.66	0.073
21/05/2012	1.35	0.022
23/07/2012	1.67	0.025
26/07/2012	1.80	0.013
31/07/2012	1.70	0.028
06/08/2012	1.98	0.028

Table B3.3 Sampled reactive phosphorus concentration and discharge values for Smardale

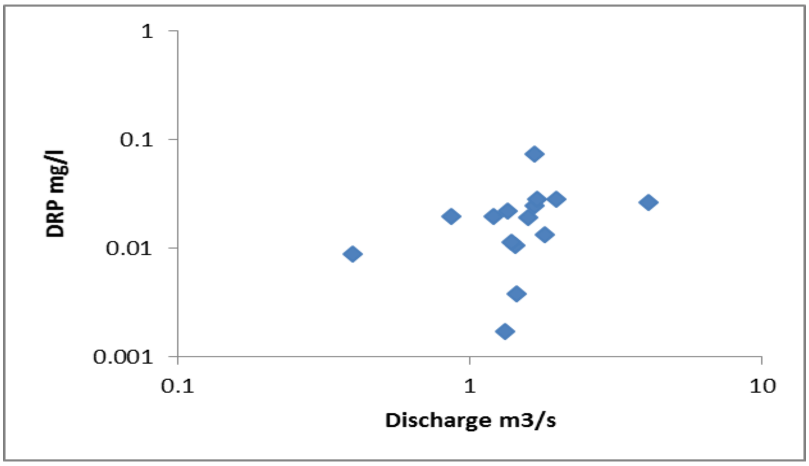


Figure B3.3 Scatter plot of reactive phosphorus concentration against discharge at Smardale

Date	Flow (m3/s)	N (mg/l)
01/11/2011	1.21	2.06
03/11/2011	0.87	2.53
21/11/2011	0.40	3.40
24/11/2011	4.10	1.48
06/03/2012	1.58	3.08
14/03/2012	1.43	2.62
19/03/2012	1.44	2.48
21/03/2012	1.39	2.41
02/05/2012	1.42	2.23
09/05/2012	1.32	1.92
16/05/2012	1.66	1.92
21/05/2012	1.35	1.74
23/07/2012	1.67	2.99
26/07/2012	1.80	2.26
31/07/2012	1.70	1.83
06/08/2012	1.98	1.17
16/12/2011	1.17	3.34
25/06/2012	2.26	2.46
19/09/2012	1.81	1.86
10/10/2012	1.68	2.80
07/11/2012	1.80	2.71
20/12/2012	3.10	2.37
14/01/2013	2.04	3.30
30/01/2013	4.59	2.38
27/02/2013	1.95	3.12
26/03/2013	2.09	2.17
10/04/2013	1.99	2.44
26/04/2013	2.57	3.38

Table B3.4 Sampled nitrate concentration and discharge values for Smardale

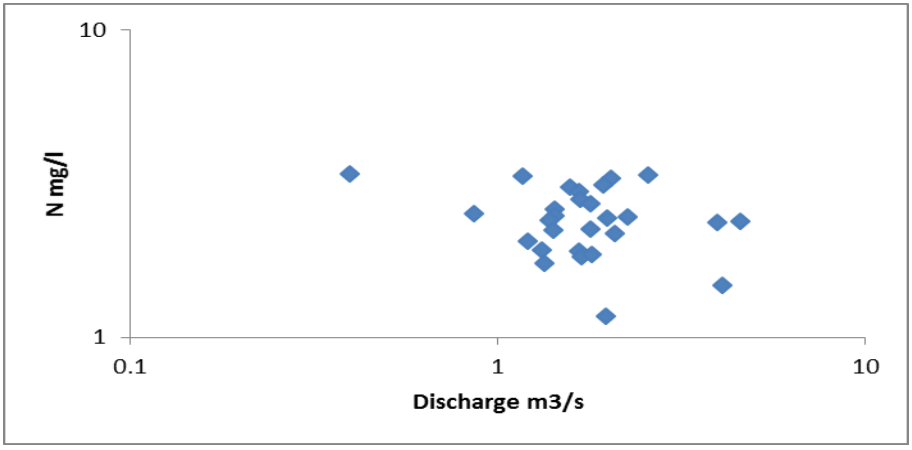


Figure B3.4 Scatter plot of nitrate concentration against discharge at Smardale

Date	**Flow (m3/s)**	**SSC (mg/l)**
01/11/2011	12.00	5.25
03/11/2011	8.03	2.25
21/11/2011	1.89	0.75
24/11/2011	23.10	18.75
16/12/2011	9.81	3.50
06/03/2012	3.81	1.83
14/03/2012	2.34	1.17
19/03/2012	2.14	31.67
21/03/2012	1.83	0.83
02/05/2012	3.08	1.67
09/05/2012	2.27	1.67
16/05/2012	4.27	1.00
21/05/2012	2.67	2.83
25/06/2012	8.03	4.58
23/07/2012	2.84	2.17
26/07/2012	2.67	1.33
31/07/2012	2.74	4.17
06/08/2012	3.99	3.42
19/09/2012	3.87	3.00
10/10/2012	3.21	1.33
07/11/2012	4.23	1.83
20/12/2012	48.9	62.50
30/01/2013	26.9	12.00
27/02/2013	1.87	2.33
26/03/2013	2.05	2.08
10/04/2013	2.62	1.17
26/04/2013	5.75	1.75

Table B4.1 Sampled suspended sediment concentration and discharge values for Great Musgrave

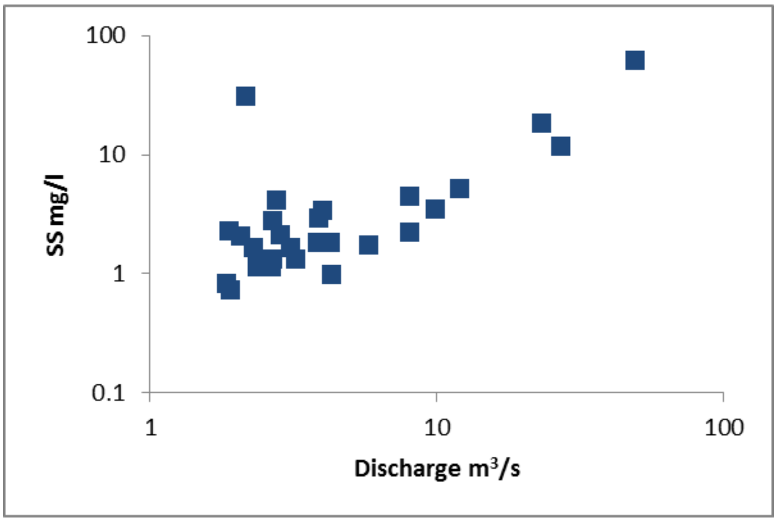


Figure B4.1 Scatter plot of suspended sediment concentration against discharge at Great Musgrave

Date	Flow (m3/s)	TP (mg/l)
01/11/2011	12.00	0.040
03/11/2011	8.03	0.018
21/11/2011	1.89	0.018
24/11/2011	23.10	0.077
06/03/2012	3.81	0.031
14/03/2012	2.34	0.065
19/03/2012	2.14	0.012
21/03/2012	1.83	0.019
02/05/2012	3.08	0.039
09/05/2012	2.27	0.033
16/05/2012	4.27	0.042
21/05/2012	2.67	0.067
23/07/2012	2.84	0.030
26/07/2012	2.67	0.056
31/07/2012	2.74	0.048
06/08/2012	3.99	0.050

Table B4.2 Sampled total phosphorus concentration and discharge values for Great Musgrave

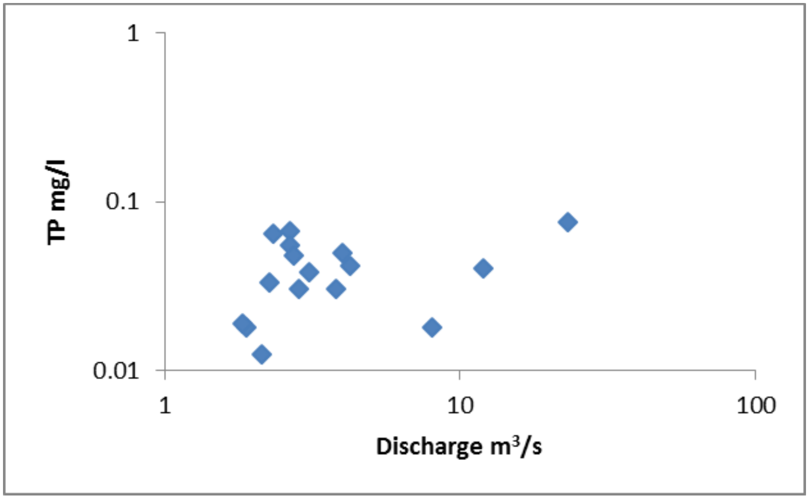


Figure B4.2 Scatter plot of total phosphorus concentration against discharge at Great Musgrave

Date	Flow (m3/s)	RP (mg/l)
01/11/2011	12.00	0.013
03/11/2011	8.03	0.018
21/11/2011	1.89	0.011
24/11/2011	23.10	0.018
06/03/2012	3.81	0.017
14/03/2012	2.34	0.025
19/03/2012	2.14	0.002
21/03/2012	1.83	0.013
02/05/2012	3.08	0.025
09/05/2012	2.27	0.022
16/05/2012	4.27	0.029
21/05/2012	2.67	0.034
23/07/2012	2.84	0.027
26/07/2012	2.67	0.038
31/07/2012	2.74	0.032
06/08/2012	3.99	0.027

Table B4.3 Sampled reactive phosphorus concentration and discharge values for Great Musgrave

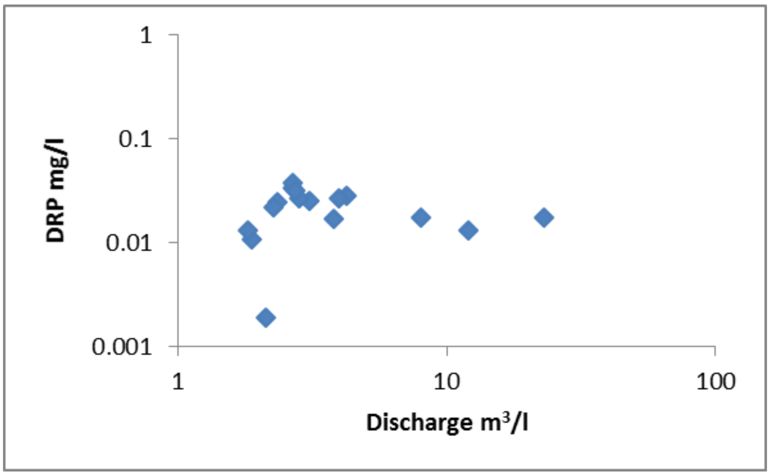


Figure B4.3 Scatter plot of reactive phosphorus concentration against discharge at Great Musgrave

Date	Flow (m^3/s)	N (mg/l)
01/11/2011	12.00	1.666
03/11/2011	8.03	3.039
21/11/2011	1.89	5.083
24/11/2011	23.10	1.425
06/03/2012	3.81	3.310
14/03/2012	2.34	4.286
19/03/2012	2.14	4.119
21/03/2012	1.83	4.799
02/05/2012	3.08	4.026
09/05/2012	2.27	3.047
16/05/2012	4.27	2.828
21/05/2012	2.67	3.375
23/07/2012	2.84	4.726
26/07/2012	2.67	4.198
31/07/2012	2.74	3.049
06/08/2012	3.99	2.015
16/12/2011	9.81	5.238
25/06/2012	8.03	2.283
19/09/2012	3.87	2.485
10/10/2012	3.21	5.138
07/11/2012	4.23	2.869
20/12/2012	48.9	1.352
30/01/2013	26.9	2.849
27/02/2013	1.87	5.334
26/03/2013	2.05	4.047
10/04/2013	2.62	3.015
26/04/2013	5.75	2.523

Table B4.4 Sampled nitrate concentration and discharge values for Great Musgrave

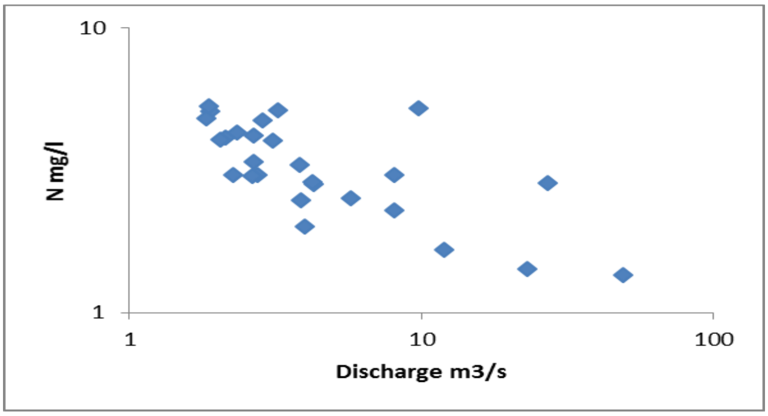


Figure B4.4 Scatter plot of nitrate concentration against discharge at Great Musgrave

Date	Flow (m^3/s)	SSC (mg/l)
11/1/2011	14.08	10.00
11/3/2011	9.68	5.75
11/21/2011	2.83	2.75
11/24/2011	27.95	55.25
12/16/2011	11.64	3.00
3/6/2012	6.81	1.50
3/14/2012	4.61	1.33
3/19/2012	4.23	2.17
3/21/2012	3.74	2.00
5/2/2012	5.53	1.92
5/9/2012	4.43	1.42
5/16/2012	7.25	1.67
5/21/2012	5.22	2.50
6/25/2012	12.65	5.33
7/23/2012	5.65	2.67
7/26/2012	5.53	3.83
7/31/2012	5.49	10.00
8/6/2012	7.12	17.33
9/19/2012	6.74	7.67
10/10/2012	6.25	4.83
11/7/2012	8.24	3.00
12/20/2012	54.37	91.67
1/30/2013	33.86	17.67
2/27/2013	3.39	3.00
3/26/2013	3.80	1.50
4/10/2013	4.33	1.00
4/26/2013	8.83	2.08

Table B5.1 Sampled suspended sediment concentration and discharge values for Appleby

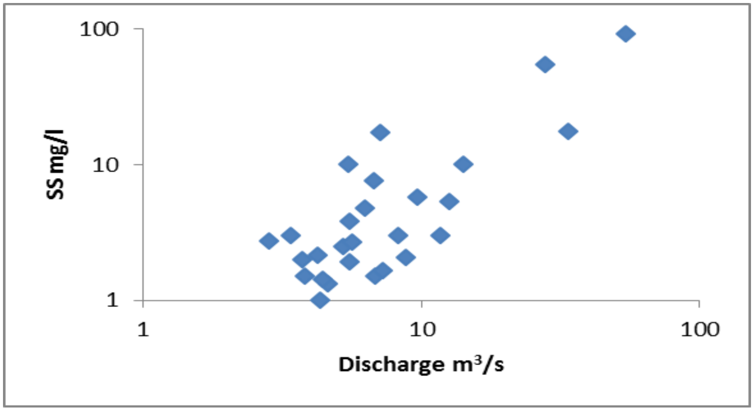


Figure B5.1 Scatter plot of suspended sediment concentration against discharge at Appleby

Date	Flow (m^3/s)	TP (mg/l)
01/11/2011	14.08	0.048
03/11/2011	9.68	0.046
21/11/2011	2.83	0.026
24/11/2011	27.95	0.165
06/03/2012	6.81	0.033
14/03/2012	4.61	0.034
19/03/2012	4.23	0.018
21/03/2012	3.74	0.040
02/05/2012	5.53	0.039
09/05/2012	4.43	0.060
16/05/2012	7.25	0.074
21/05/2012	5.22	0.047
23/07/2012	5.65	0.071
26/07/2012	5.53	0.035
31/07/2012	5.49	0.050
06/08/2012	7.12	0.092

Table B5.2 Sampled total phosphorus concentration and discharge values for Appleby

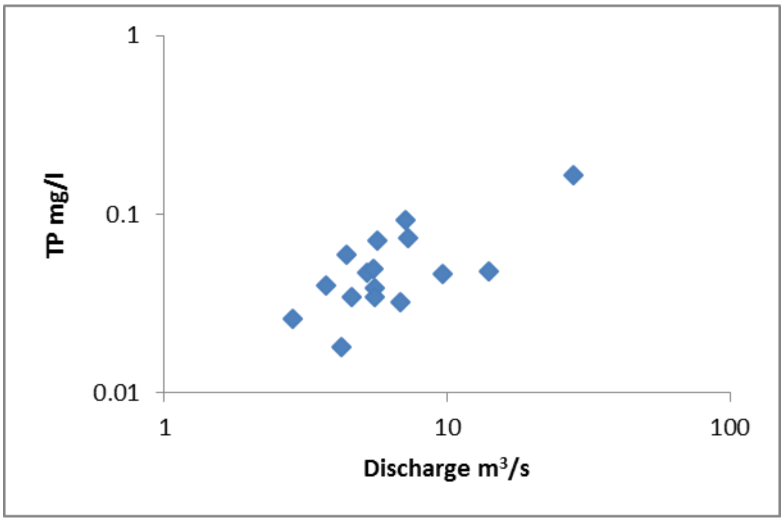


Figure B5.2 Scatter plot of total phosphorus concentration against discharge at Appleby

Date	Flow (m^3/s)	RP (mg/l)
01/11/2011	14.08	0.015
03/11/2011	9.68	0.018
21/11/2011	2.83	0.007
24/11/2011	27.95	0.024
06/03/2012	6.81	0.019
14/03/2012	4.61	0.032
19/03/2012	4.23	0.011
21/03/2012	3.74	0.030
02/05/2012	5.53	0.027
09/05/2012	4.43	0.046
16/05/2012	7.25	0.059
21/05/2012	5.22	0.017
23/07/2012	5.65	0.057
26/07/2012	5.53	0.015
31/07/2012	5.49	0.028
06/08/2012	7.12	0.034

Table B5.3 Sampled reactive phosphorus concentration and discharge values for Appleby

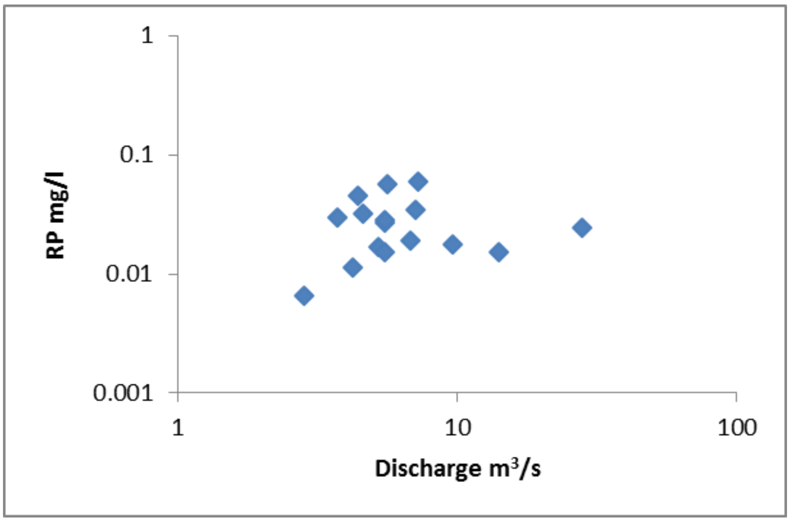


Figure B5.3 Scatter plot of reactive phosphorus concentration against discharge at Appleby

Date	Flow (m^3/s)	N (mg/l)
01/11/2011	14.08	2.726
03/11/2011	9.68	3.743
21/11/2011	2.83	5.942
24/11/2011	27.95	1.751
16/12/2011	11.64	5.993
06/03/2012	6.81	4.303
14/03/2012	4.61	5.088
19/03/2012	4.23	5.053
21/03/2012	3.74	5.715
02/05/2012	5.53	3.866
09/05/2012	4.43	3.836
16/05/2012	7.25	3.156
21/05/2012	5.22	3.691
25/06/2012	12.65	2.370
23/07/2012	5.65	4.919
26/07/2012	5.53	4.728
31/07/2012	5.49	3.726
06/08/2012	7.12	2.592
19/09/2012	6.74	2.903
10/10/2012	6.25	5.692
07/11/2012	8.24	3.214
20/12/2012	54.37	1.546
30/01/2013	33.86	3.065
27/02/2013	3.39	6.800
26/03/2013	3.80	5.127
10/04/2013	4.33	4.300
26/04/2013	8.83	3.353

Table B5.4 Sampled reactive nitrate concentration and discharge values for Appleby

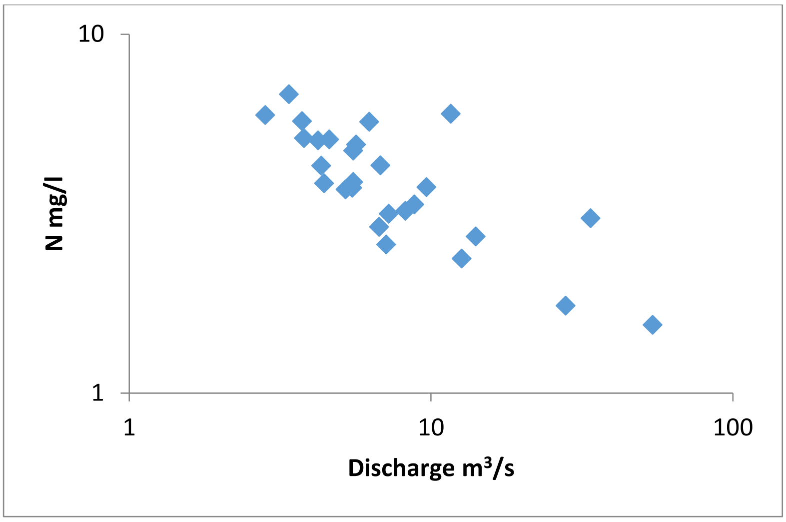


Figure B5.4 Scatter plot of nitrate concentration against discharge at Appleby

Date	Flow (m^3/s)	SSC (mg/l)
01/11/2011	21.90	5.00
03/11/2011	25.50	40.25
21/11/2011	5.35	1.25
24/11/2011	42.00	36.25
16/12/2011	27.75	3.83
06/03/2012	8.78	2.00
14/03/2012	5.56	1.33
19/03/2012	5.28	2.33
21/03/2012	4.56	1.33
02/05/2012	7.15	1.92
09/05/2012	5.61	24.50
16/05/2012	10.30	2.33
21/05/2012	6.57	3.00
25/06/2012	19.60	7.17
23/07/2012	7.19	2.83
26/07/2012	7.32	1.33
31/07/2012	6.80	3.33
06/08/2012	9.48	9.67
19/09/2012	8.31	2.83
10/10/2012	9.60	1.67
07/11/2012	13.50	3.50
20/12/2012	162.00	98.83
30/01/2013	62.40	18.25
27/02/2013	4.84	2.50
26/03/2013	5.33	2.42
10/04/2013	5.17	1.67

Table B6.1 Sampled suspended sediment concentration and discharge values for Temple Sowerby

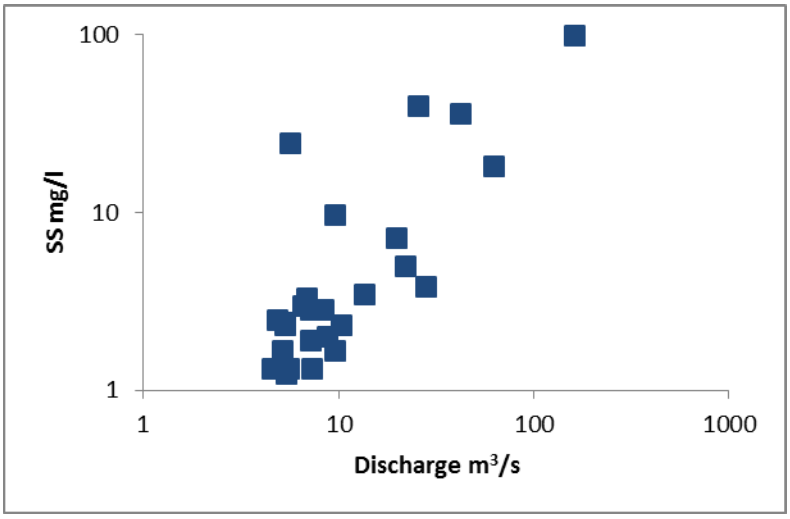


Figure B6.1 Scatter plot of suspended sediment concentration against discharge at Temple Sowerby

Date	Flow (m^3/s)	TP (mg/l)
01/11/2011	21.90	0.046
03/11/2011	25.50	0.248
21/11/2011	5.35	0.063
24/11/2011	42.00	0.121
06/03/2012	8.78	0.029
14/03/2012	5.56	0.027
19/03/2012	5.28	0.024
21/03/2012	4.56	0.021
02/05/2012	7.15	0.046
09/05/2012	5.61	0.019
16/05/2012	10.30	0.101
21/05/2012	6.57	0.037
23/07/2012	7.19	0.048
26/07/2012	7.32	0.075
31/07/2012	6.80	0.042
06/08/2012	9.48	0.158

Table B6.2 Sampled total phosphorus concentration and discharge values for Temple Sowerby

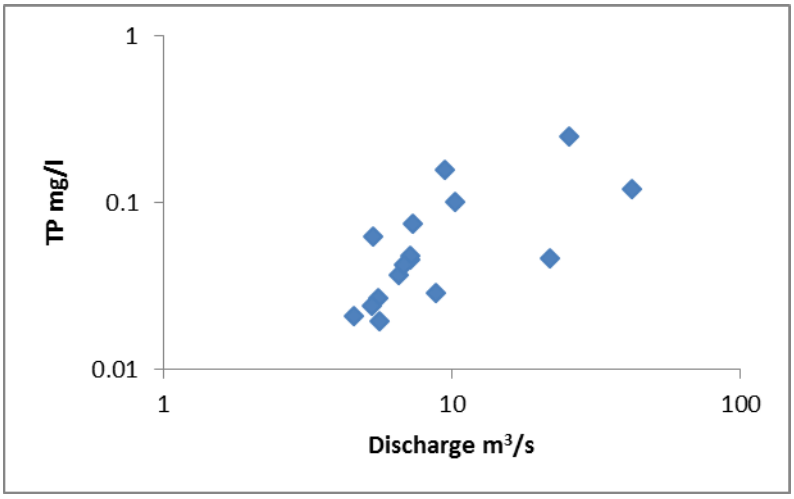


Figure B6.2 Scatter plot of total phosphorus concentration against discharge at Temple Sowerby

Date	Flow (m^3/s)	RP (mg/l)
01/11/2011	21.90	0.037
03/11/2011	25.50	0.096
21/11/2011	5.35	0.033
24/11/2011	42.00	0.026
06/03/2012	8.78	0.010
14/03/2012	5.56	0.015
19/03/2012	5.28	0.011
21/03/2012	4.56	0.015
02/05/2012	7.15	0.029
09/05/2012	5.61	0.007
16/05/2012	10.3	0.075
21/05/2012	6.57	0.017
23/07/2012	7.19	0.034
26/07/2012	7.32	0.053
31/07/2012	6.80	0.025
06/08/2012	9.48	0.021

Table B6.3 Sampled reactive phosphorus concentration and discharge values for Temple Sowerby

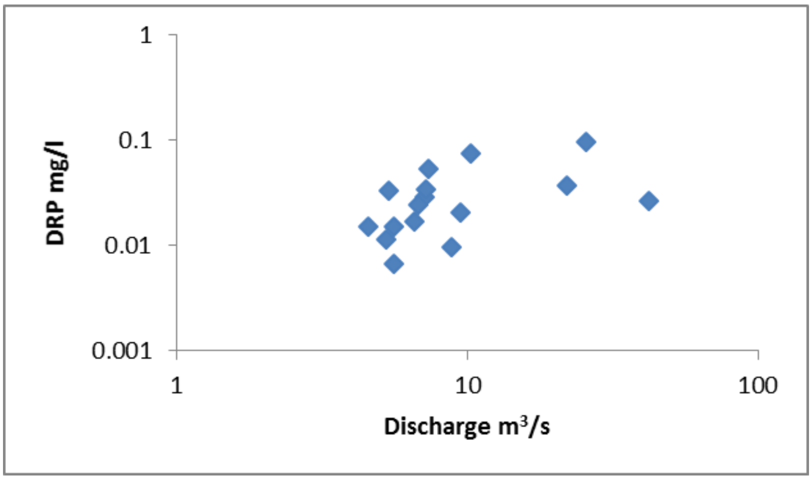


Figure B6.3 Scatter plot of reactive phosphorus concentration against discharge at Temple Sowerby

Date	Flow (m^3/s)	N (mg/l)
01/11/2011	21.90	4.550
03/11/2011	25.50	5.263
21/11/2011	5.35	7.762
24/11/2011	42.00	5.697
06/03/2012	8.78	5.384
14/03/2012	5.56	6.653
19/03/2012	5.28	6.531
21/03/2012	4.56	7.370
02/05/2012	7.15	5.005
09/05/2012	5.61	5.801
16/05/2012	10.30	4.245
21/05/2012	6.57	4.995
23/07/2012	7.19	6.152
26/07/2012	7.32	5.893
31/07/2012	6.80	5.154
06/08/2012	9.48	4.276
16/12/2011	27.75	7.901
25/06/2012	19.60	3.518
19/09/2012	8.31	3.711
10/10/2012	9.60	7.386
07/11/2012	13.50	4.602
20/12/2012	162.00	2.501
30/01/2013	62.40	3.939
27/02/2013	4.84	8.931
26/03/2013	5.33	6.902
10/04/2013	5.17	5.736

Table B6.4 Sampled nitrate concentration and discharge values for Temple Sowerby

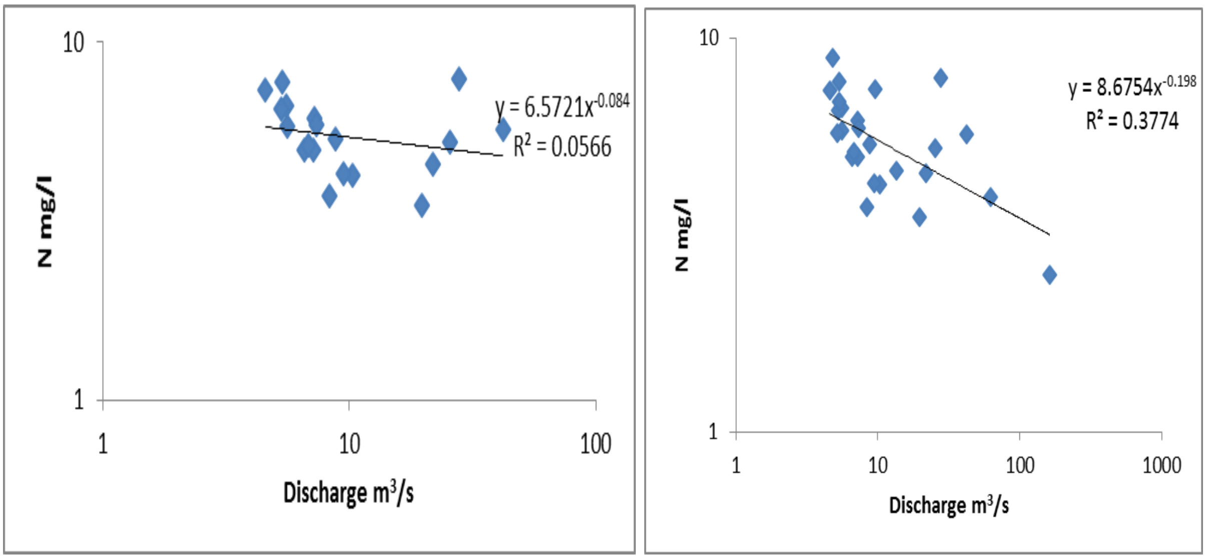


Figure B6.4 Scatter plot of nitrate concentration against discharge at Temple Sowerby after seasonal campaign in 2012 and at the end of the field work in April 2013 respectively

Date	Flow (m^3/s)	SSC (mg/l)
01/11/2011	46.80	4.00
03/11/2011	39.60	1.00
21/11/2011	20.40	0.25
24/11/2011	40.80	3.25
16/12/2011	78.20	4.33
06/03/2012	26.30	2.67
14/03/2012	20.00	1.67
19/03/2012	19.00	1.83
21/03/2012	17.00	2.17
02/05/2012	21.50	1.42
09/05/2012	19.80	2.33
16/05/2012	33.80	4.58
21/05/2012	22.60	2.17
25/06/2012	78.10	6.83
23/07/2012	24.20	2.50
26/07/2012	26.50	1.17
31/07/2012	24.20	3.00
06/08/2012	32.60	9.17
19/09/2012	28.10	3.42
10/10/2012	34.80	1.17
07/11/2011	46.10	1.33
20/12/2012	209.00	43.00
30/01/2013	142.00	30.83
27/02/2013	18.70	2.17
26/03/2013	18.20	1.50
10/04/2013	15.80	1.17

Table B7.1 Sampled suspended sediment concentration and discharge values for Great Corby

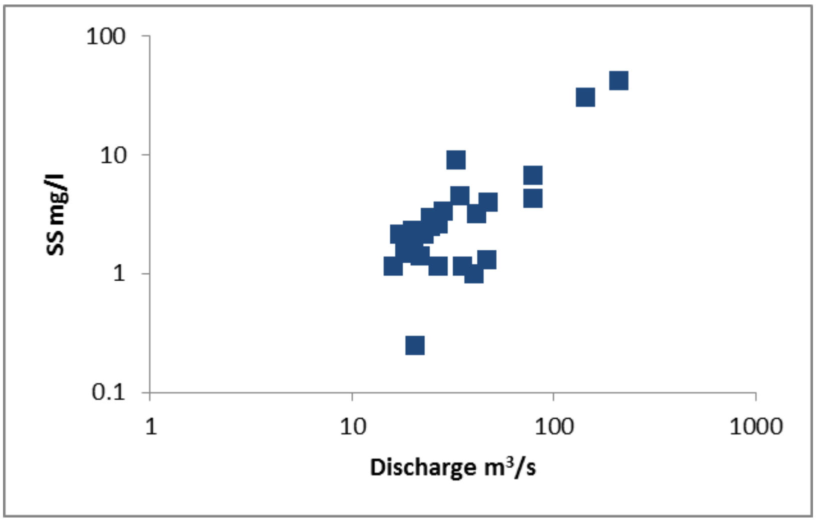


Figure B7.1 Scatter plot of suspended sediment concentration against discharge at Great Corby

Date	Flow (m3/s)	TP mg/l
01/11/2011	46.80	0.046
03/11/2011	39.60	0.034
21/11/2011	20.40	0.036
24/11/2011	40.80	0.044
06/03/2012	26.30	0.042
14/03/2012	20.00	0.050
19/03/2012	19.00	0.032
21/03/2012	17.00	0.031
02/05/2012	21.50	0.025
09/05/2012	19.80	0.032
16/05/2012	33.80	0.083
21/05/2012	22.60	0.053
23/07/2012	24.20	0.063
26/07/2012	26.50	0.086
31/07/2012	24.20	0.037
06/08/2012	32.60	0.073

Table B7.2. Sampled total phosphorus concentration and discharge values for Great Corby

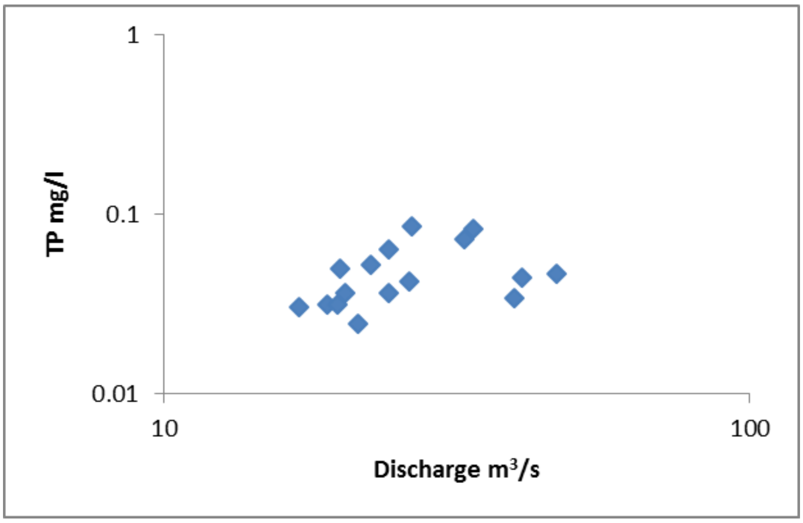


Figure B7.2 Scatter plot of total phosphorus concentration against discharge at Great Corby

Date	Flow (m^3/s)	RP (mg/l)
01/11/2011	46.80	0.026
03/11/2011	39.60	0.015
21/11/2011	20.40	0.022
24/11/2011	40.80	0.024
06/03/2012	26.30	0.021
14/03/2012	20.00	0.021
19/03/2012	19.00	0.019
21/03/2012	17.00	0.019
02/05/2012	21.50	0.008
09/05/2012	19.80	0.016
16/05/2012	33.80	0.059
21/05/2012	22.60	0.032
23/07/2012	24.20	0.049
26/07/2012	26.50	0.057
31/07/2012	24.20	0.028
06/08/2012	32.60	0.030

Table B7.3 Sampled reactive phosphorus concentration and discharge values for Great Corby

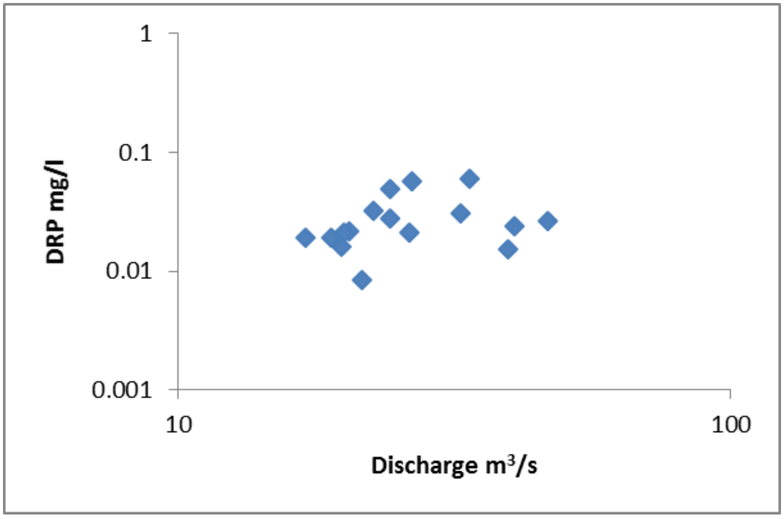


Figure B7.3 Scatter plot of reactive phosphorus concentration against discharge at Great Corby

Date	Flow (m^3/s)	N (mg/l)
01/11/2011	46.80	5.306
03/11/2011	39.60	5.229
21/11/2011	20.40	8.329
24/11/2011	40.80	8.365
06/03/2012	78.20	7.383
14/03/2012	26.30	7.833
19/03/2012	20.00	9.401
21/03/2012	19.00	10.61
02/05/2012	17.00	6.826
09/05/2012	21.50	8.6475
16/05/2012	19.80	4.742
21/05/2012	33.80	7.215
23/07/2012	22.60	7.518
26/07/2012	78.10	7.022
31/07/2012	24.20	7.103
06/08/2012	26.50	4.978
16/12/2011	24.20	7.564
25/06/2012	32.60	3.664
19/09/2012	28.10	4.993
10/10/2012	34.80	7.203
07/11/2012	46.10	5.195
20/12/2012	209.00	4.820
30/01/2013	142.00	3.839
27/02/2013	18.70	10.90
26/03/2013	18.20	9.929
10/04/2013	15.80	9.277

Table B7.4 Sampled nitrate concentration and discharge values for Great Corby

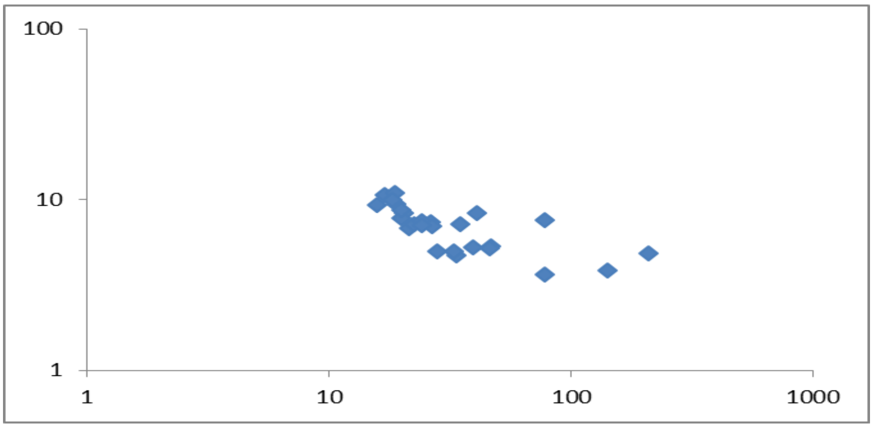


Figure B7.4 Scatter plot of nitrate concentration against discharge at Great Corby

Date	Flow (m^3/s)	SSC (mg/l)
01/11/2011	0.16	9.75
03/11/2011	0.19	16.25
21/11/2011	0.11	3.75
24/11/2011	0.11	16.25
06/03/2012	0.21	6.50
14/03/2012	0.12	2.50
19/03/2012	0.11	4.17
21/03/2012	0.10	6.00
02/05/2012	0.10	5.08
09/05/2012	0.09	3.33
16/05/2012	0.15	3.83
21/05/2012	0.12	6.50
23/07/2012	0.12	2.67
26/07/2012	0.11	3.25
31/07/2012	0.09	4.00
06/08/2012	0.09	3.17
16/12/2011	1.81	6.00
25/06/2012	0.14	3.33
19/09/2012	0.14	2.00
10/10/2012	0.19	2.08
07/11/2012	0.18	1.92
20/12/2012	0.47	4.33
14/01/2013	0.17	3.67
30/01/2013	0.74	7.33
27/02/2013	0.12	6.00
26/03/2013	0.11	2.75
10/04/2013	0.08	1.92
26/04/2013	0.14	2.58

Table B8.1 Sampled suspended sediment concentration and discharge values at Blind Beck

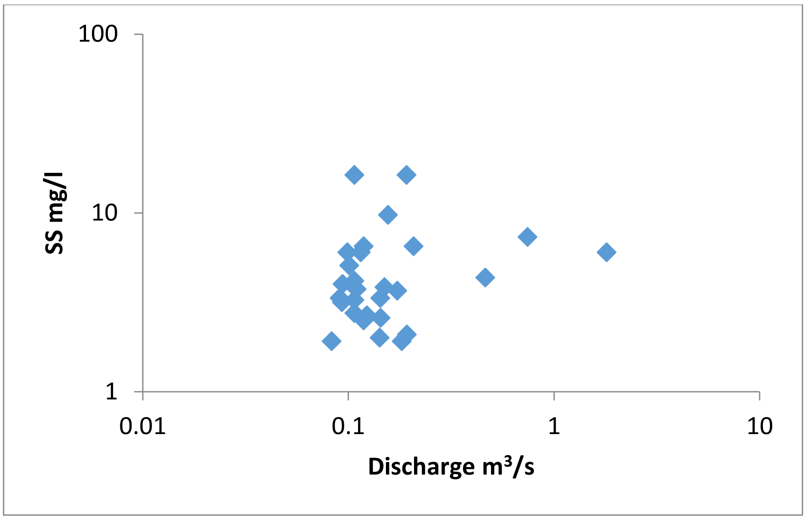


Figure B8.1Scatter plot of suspended sediment concentration against discharge at Blind Beck

Date	Flow (m^3/s)	TP (mg/l)
01/11/2011	0.16	0.105
03/11/2011	0.19	0.107
21/11/2011	0.11	0.040
24/11/2011	0.11	0.133
06/03/2012	0.21	0.038
14/03/2012	0.12	0.038
19/03/2012	0.11	0.024
21/03/2012	0.10	0.017
02/05/2012	0.10	0.016
09/05/2012	0.09	0.153
16/05/2012	0.15	0.076
21/05/2012	0.12	0.035
23/07/2012	0.12	0.029
26/07/2012	0.11	0.019
31/07/2012	0.09	0.023
06/08/2012	0.09	0.037

Table B8.2 Sampled total phosphorus concentration and discharge values for Blind Beck

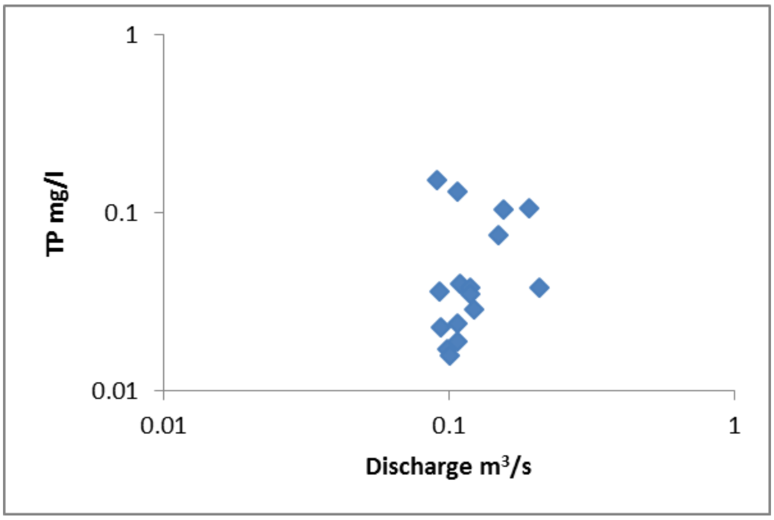


Figure B8.2 Scatter plot of total phosphorus concentration against discharge at Blind Beck

Date	Flow (m^3/s)	RP (mg/l)
01/11/2011	0.16	0.046
03/11/2011	0.19	0.033
21/11/2011	0.11	0.024
24/11/2011	0.11	0.050
06/03/2012	0.21	0.019
14/03/2012	0.12	0.006
19/03/2012	0.11	0.013
21/03/2012	0.10	0.017
02/05/2012	0.10	0.010
09/05/2012	0.09	0.066
16/05/2012	0.15	0.063
21/05/2012	0.12	0.024
23/07/2012	0.12	0.019
26/07/2012	0.11	0.011
31/07/2012	0.09	0.026
06/08/2012	0.09	0.004

Table B8.3 Sampled reactive phosphorus concentration and discharge values for Blind Beck

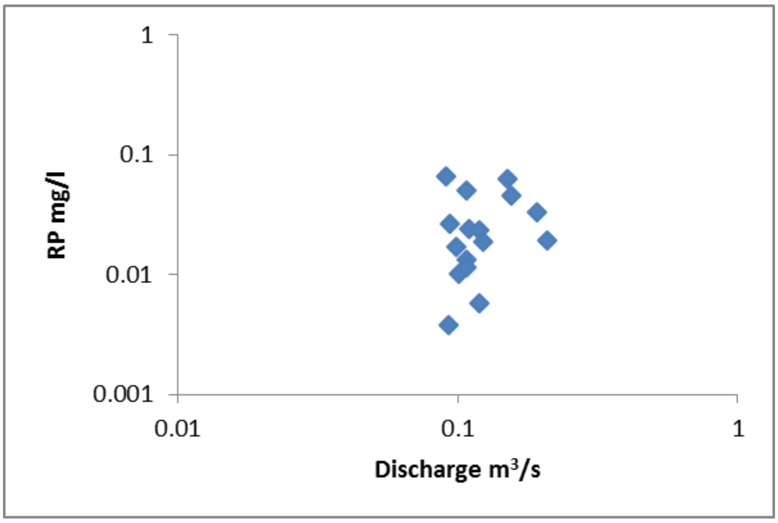


Figure B8.3 Scatter plot of reactive phosphorus concentration against discharge at Blind Beck

Date	Flow (m3/s)	N mg/l
01/11/2011	0.16	6.411
03/11/2011	0.19	5.467
21/11/2011	0.11	18.48
24/11/2011	0.11	8.746
06/03/2012	0.21	11.50
14/03/2012	0.12	16.60
19/03/2012	0.11	18.40
21/03/2012	0.10	20.09
02/05/2012	0.10	15.99
09/05/2012	0.09	13.51
16/05/2012	0.15	10.14
21/05/2012	0.12	13.71
23/07/2012	0.12	11.01
26/07/2012	0.11	11.25
31/07/2012	0.09	17.63
06/08/2012	0.09	10.38
16/12/2011	1.81	10.27
25/06/2012	0.14	9.447
19/09/2012	0.14	9.848
10/10/2012	0.19	10.73
07/11/2012	0.18	7.892
20/12/2012	0.47	6.456
14/01/2013	0.17	10.03
30/01/2013	0.74	5.399
27/02/2013	0.12	9.811
26/03/2013	0.11	10.84
10/04/2013	0.08	8.875
26/04/2013	0.14	10.96

Table B8.4 Sampled nitrate concentration and discharge values for Blind Beck

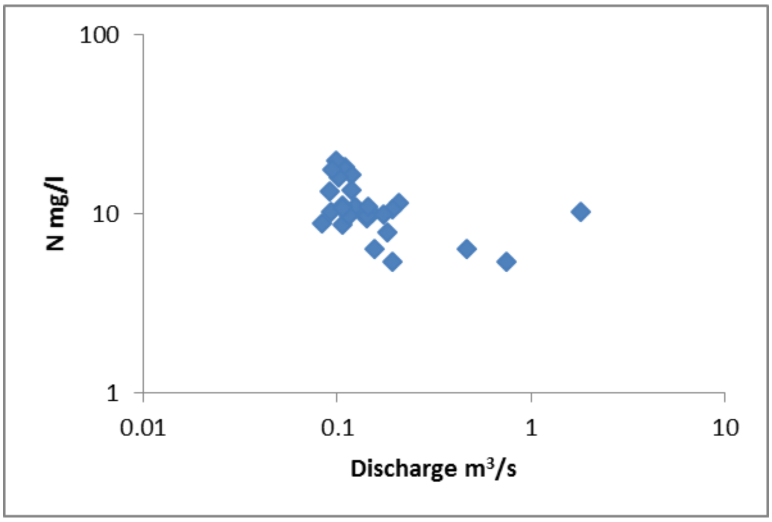


Figure B8.4 Scatter plot of nitrate concentration against discharge at Blind Beck

Dates	Flow m3/s	SS mg/l
01/11/2011	2.85	5.50
03/11/2011	2.70	1.50
21/11/2011	0.56	0.00
24/11/2011	9.63	16.00
06/03/2012	1.33	1.67
14/03/2012	0.70	0.00
19/03/2012	0.63	2.50
21/03/2012	0.55	1.67
02/05/2012	0.89	0.75
09/05/2012	2.94	1.33
16/05/2012	1.18	1.17
21/05/2012	0.77	1.67
23/07/2012	0.86	0.75
26/07/2012	0.87	1.17
31/07/2012	0.80	3.83
06/08/2012	2.63	2.17
16/12/2011	2.48	1.67
25/06/2012	1.89	1.17
19/09/2012	1.09	2.17
10/10/2012	0.99	0.67
07/11/2012	1.54	1.00
20/12/2012	10.85	17.83
14/01/2013	0.786	0.33
30/01/2013	8.21	8.50
27/02/2013	0.50	1.67
26/03/2013	0.58	1.58
10/04/2013	1.04	1.17
26/04/2013	1.87	1.58

Table B9.1 Sampled suspended sediment concentration and discharge values for Kirkby Stephen

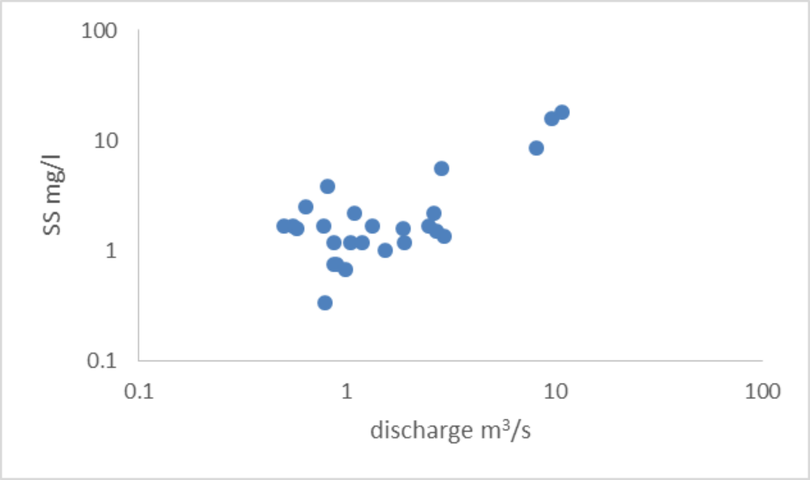


Figure B9.1 Scatter plot of suspended sediment concentration against discharge at Kirkby Stephen

Dates	Flow m3/s	TP mg/l
01/11/2011	2.85	0.024
03/11/2011	2.70	0.014
21/11/2011	0.56	0.012
24/11/2011	9.63	0.056
06/03/2012	1.33	0.027
14/03/2012	0.70	0.019
19/03/2012	0.63	0.018
21/03/2012	0.55	0.015
02/05/2012	0.89	0.040
09/05/2012	2.94	0.010
16/05/2012	1.18	0.090
21/05/2012	0.77	0.033
23/07/2012	0.86	0.033
26/07/2012	0.87	0.086
31/07/2012	0.80	0.031
06/08/2012	2.63	0.035

Table B9.2 Sampled total phosphorus concentration and discharge values for Kirkby Stephen

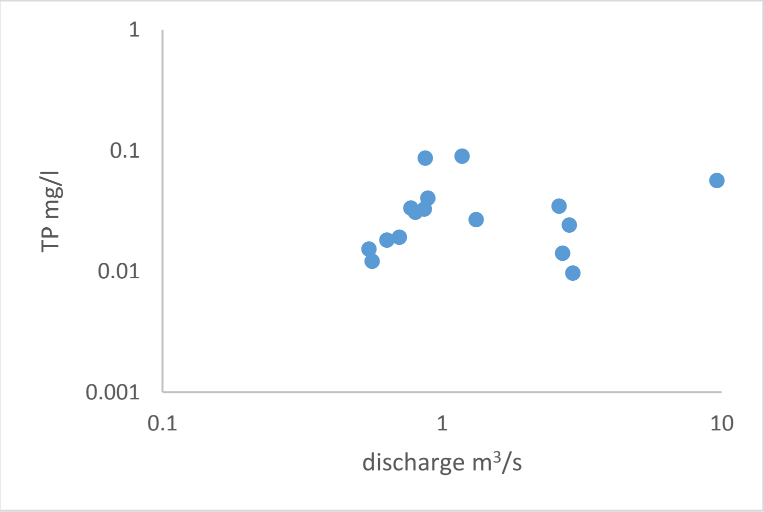


Figure B9.2 Scatter plot of total phosphorus concentration against discharge at Kirkby Stephen

Dates	Flow m3/s	RP mg/l
11/1/2011	2.85	0.011
11/3/2011	2.70	0.002
11/21/2011	0.56	0.002
11/24/2011	9.63	0.015
3/6/2012	1.33	0.019
3/14/2012	0.70	0.010
3/19/2012	0.63	0.013
3/21/2012	0.55	0.010
5/2/2012	0.89	0.031
5/9/2012	2.94	0.003
5/16/2012	1.18	0.070
5/21/2012	0.77	0.019
7/23/2012	0.86	0.027
7/26/2012	0.87	0.070
7/31/2012	0.80	0.017
8/6/2012	2.63	0.013

Table B9.3 Sampled reactive phosphorus concentration and discharge values for Kirkby Stephen

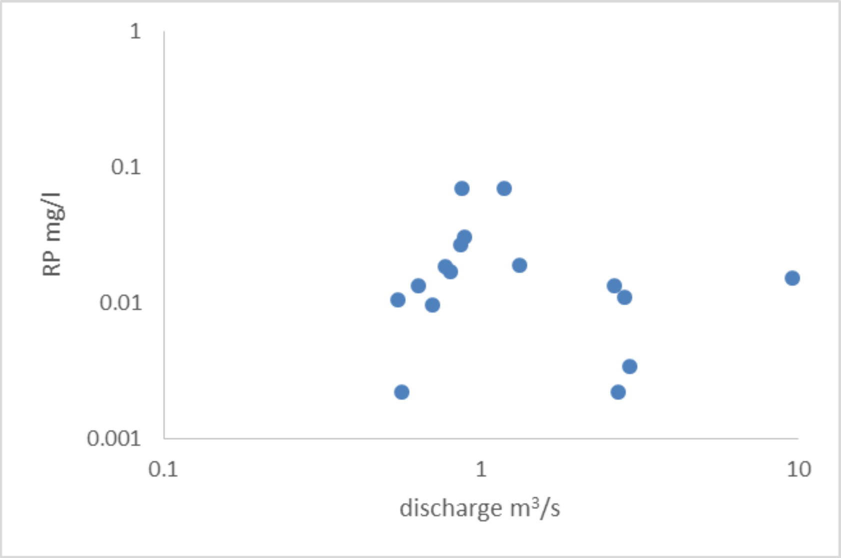


Figure B9.3 Scatter plot of reactive phosphorus concentration against discharge at Kirkby Stephen

Dates	Flow m3/s	N mg/l
11/1/2011	2.85	1.182
11/3/2011	2.70	1.596
11/21/2011	0.56	3.052
11/24/2011	9.63	1.222
3/6/2012	1.33	2.321
3/14/2012	0.70	2.640
3/19/2012	0.63	2.317
3/21/2012	0.55	2.628
5/2/2012	0.89	2.635
5/9/2012	2.94	1.884
5/16/2012	1.18	1.592
5/21/2012	0.77	2.281
7/23/2012	0.86	2.677
7/26/2012	0.87	2.283
7/31/2012	0.80	1.385
8/6/2012	2.63	0.763
12/16/2011	2.48	4.085
6/25/2012	1.89	1.565
9/19/2012	1.09	1.446
10/10/2012	0.99	3.110
11/7/2012	1.54	2.171
12/20/2012	10.85	1.496
1/14/2013	0.786	3.397
1/30/2013	8.21	2.296
2/27/2013	0.50	2.777
3/26/2013	0.58	2.746
4/10/2013	1.04	1.967
4/26/2013	1.87	1.911

Table B9.4 Sampled nitrate concentration and discharge values for Kirkby Stephen

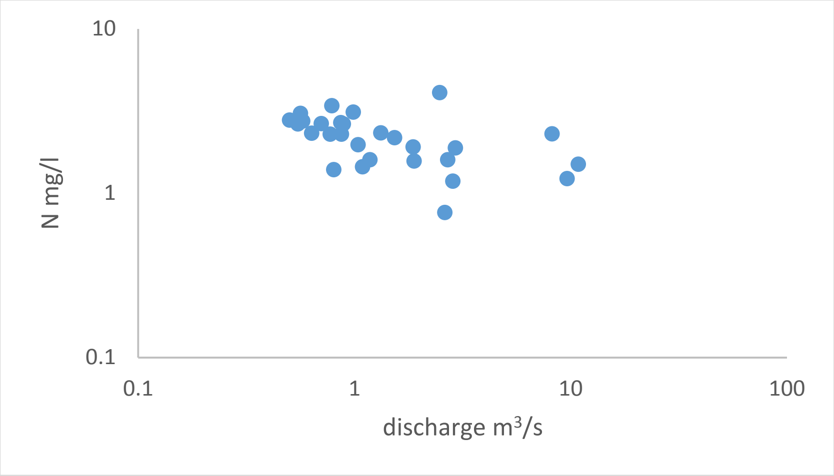


Figure B9.4 Scatter plot of nitrate concentration against discharge at Kirkby Stephen

Site	a	b	R^2 value
Gais Gill	2. 262	0.408	0.04
Ravenstonedale	2.988	1.009	0.45
Smardale	1.624	0.929	0.54
Great Musgrave	0.670	1.005	0.71
Appleby	0.328	1.265	0.64
Temple Sowerby	0.274	1.117	0.75
Great Corby	0.025	1.361	0.69
Blind Beck	6.003	0.192	0.05
Kirkby Stephen	1.247	0.964	0.72

Table B10 Suspended sediment concentration-discharge rating coefficients for the CHASM sites

Site	a	b	R^2 value
Gais Gill	0.067	0.608	0.05
Ravenstonedale	0.046	0.884	0.24
Smardale	0.023	0.465	0.07
Great Musgrave	0.026	0.252	0.11
Appleby	0.014	0.670	0.48
Temple Sowerby	0.009	0.799	0.46
Great Corby	0.010	0.472	0.15
Blind Beck	0.343	0.984	0.11
Kirkby Stephen	0.027	0.097	0.01

Table B11 Total phosphorus concentration-discharge rating coefficients for the CHASM sites

Site	a	b	R^2 value
Gais Gill	0.016	0.325	0.01
Ravenstonedale	0.022	1.218	0.28
Smardale	0.012	0.568	0.09
Great Musgrave	0.018	0.054	0.003
Appleby	0.019	0.124	0.01
Temple Sowerby	0.008	0.549	0.23
Great Corby	0.006	0.434	0.07
Blind Beck	0.135	0.886	0.08
Kirkby Stephen	0.014	-0.217	0.03

Table 12 Reactive phosphorus concentration-discharge rating coefficients for the CHASM sites

Site	a	b	R^2 value
Gais Gill	0.500	0.452	0.24
Ravenstonedale	1.615	-0.197	0.07
Smardale	2.560	-0.142	0.07
Great Musgrave	5.123	-0.317	0.51
Appleby	8.595	-0.407	0.61
Temple Sowerby	8.675	-0.198	0.38
Great Corby	22.08	-0.340	0.53
Blind Beck	6.780	-0.248	0.23
Kirkby Stephen	2.220	-0.213	0.25

Table 13 Nitrate concentration-discharge rating coefficients for the CHASM sites

Appendix C – Demonstration Test Catchment

Nutrient rating curves for the Dacre Beck

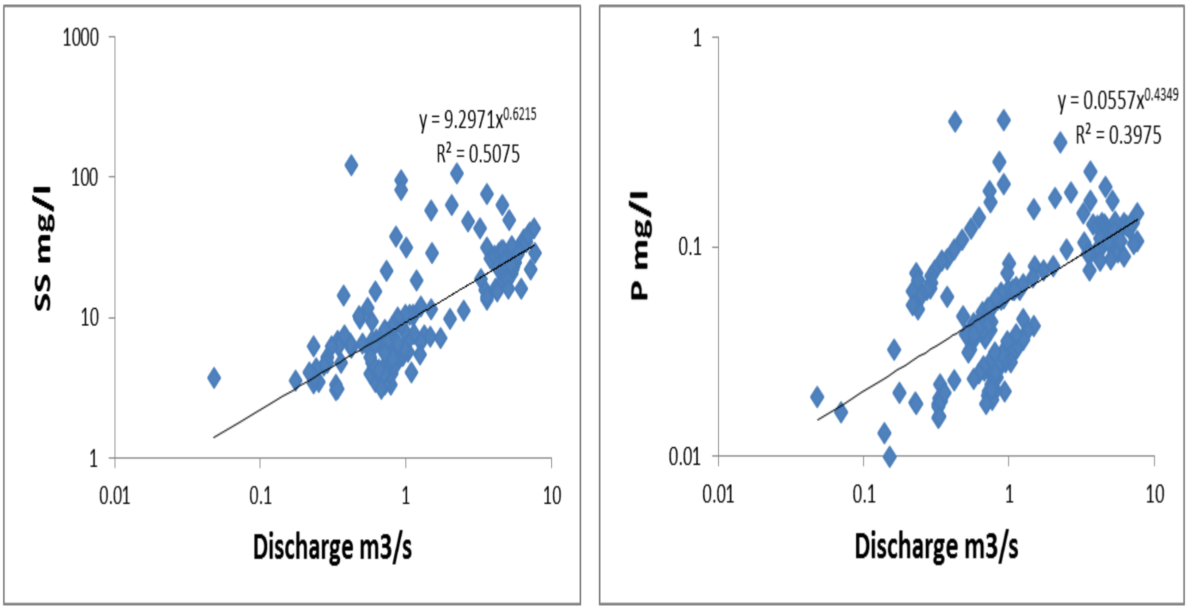


Figure C1.1 Scatter plot of suspended sediment and total phosphorus concentrations against discharge at Dacre

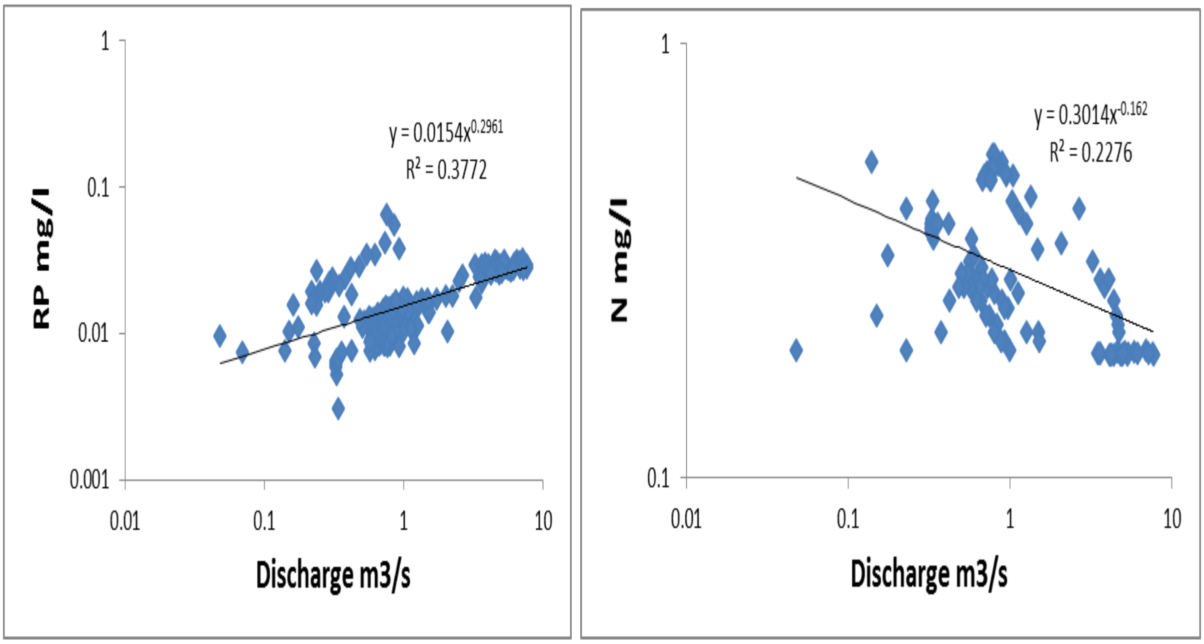


Figure C1.2 Scatter plot of reactive phosphorus and nitrate concentrations against discharge at Dacre

Seasonal pattern of nutrient concentration in Dacre Beck

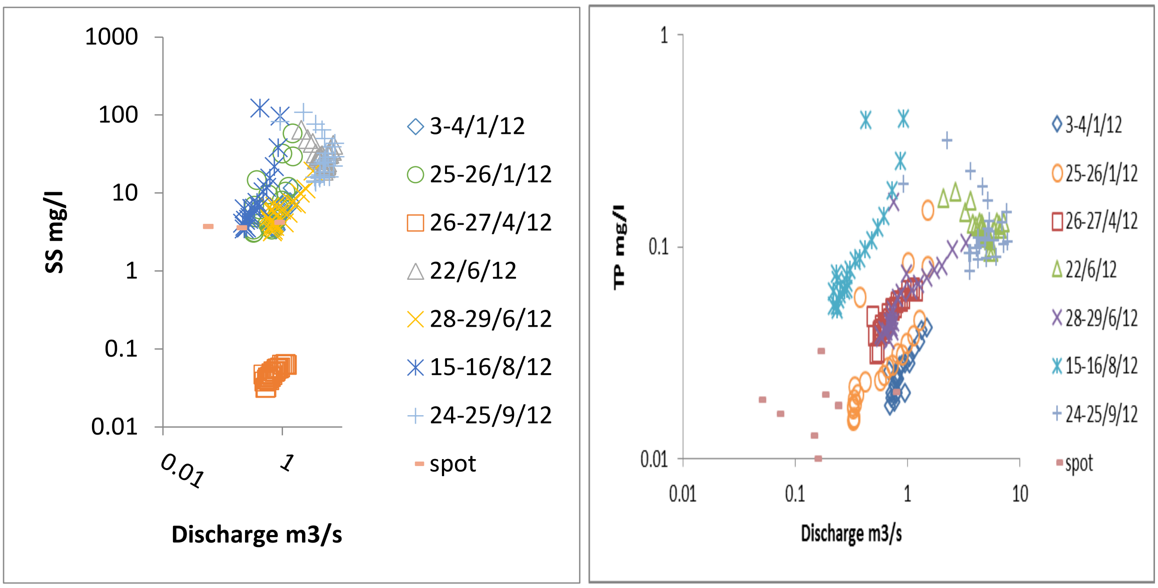


Figure C2.1 Seasonal pattern of suspended sediment and total phosphorus concentrations against discharge at Dacre

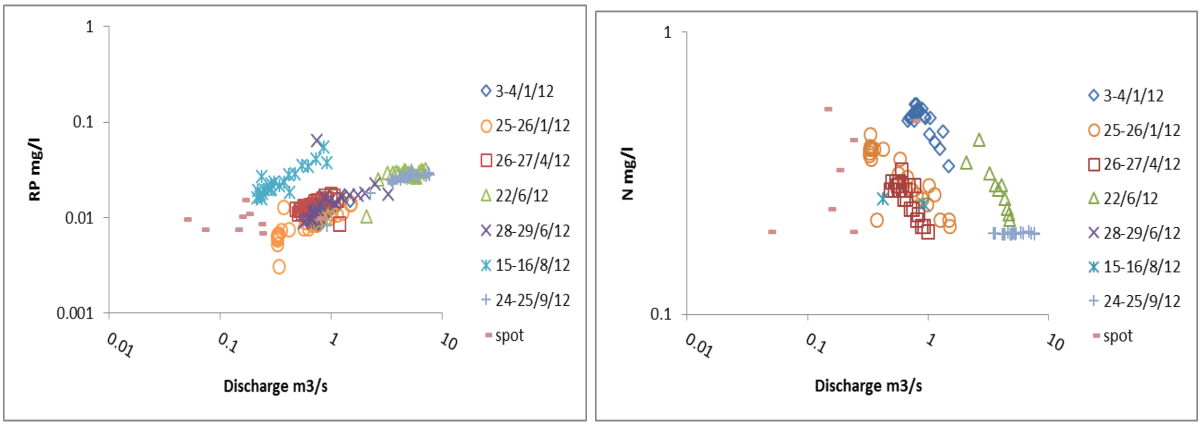


Figure C2.2 Seasonal pattern of reactive p and nitrate concentrations against discharge at Dacre

Nutrient rating curves for the Pow Beck

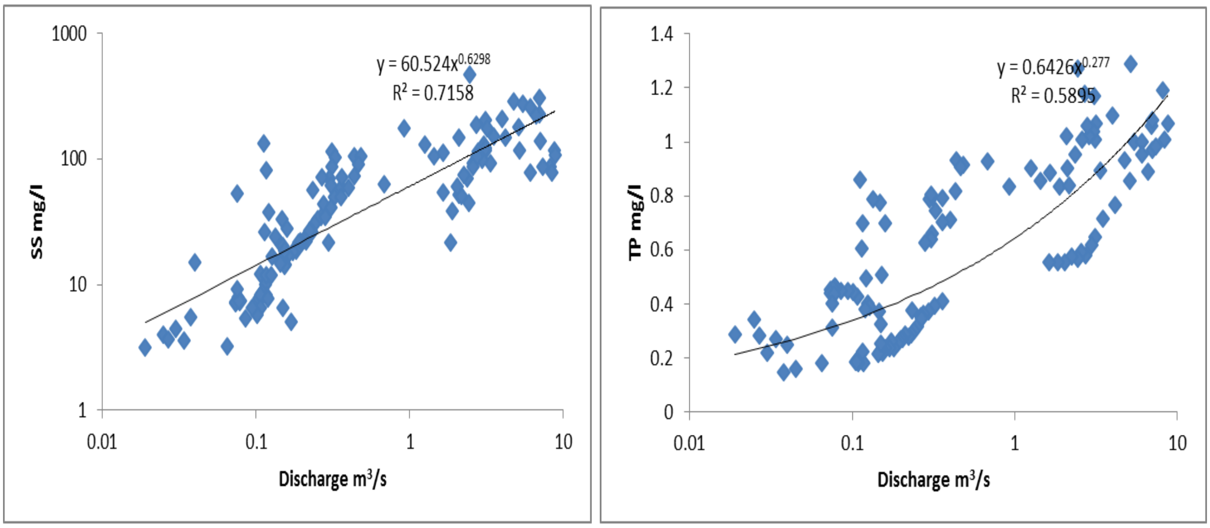


Figure C3.1 Scatter plot of suspended sediment and total phosphorus concentrations against discharge at Pow Beck

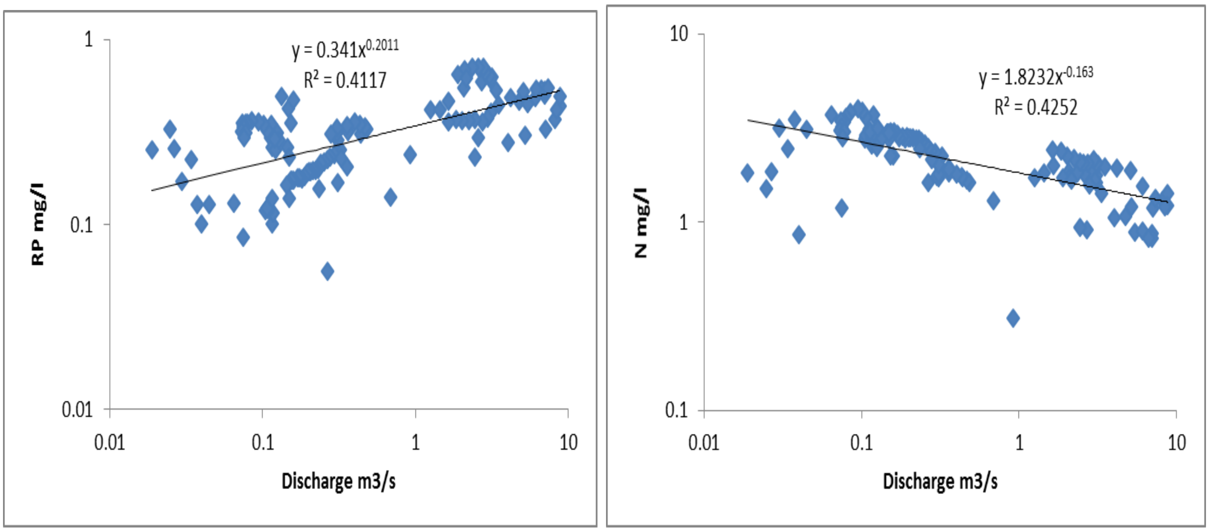


Figure C3.2 Scatter plot of reactive phosphorus and nitrate concentrations against discharge at Pow Beck

Seasonal pattern of nutrient concentration in Pow Beck

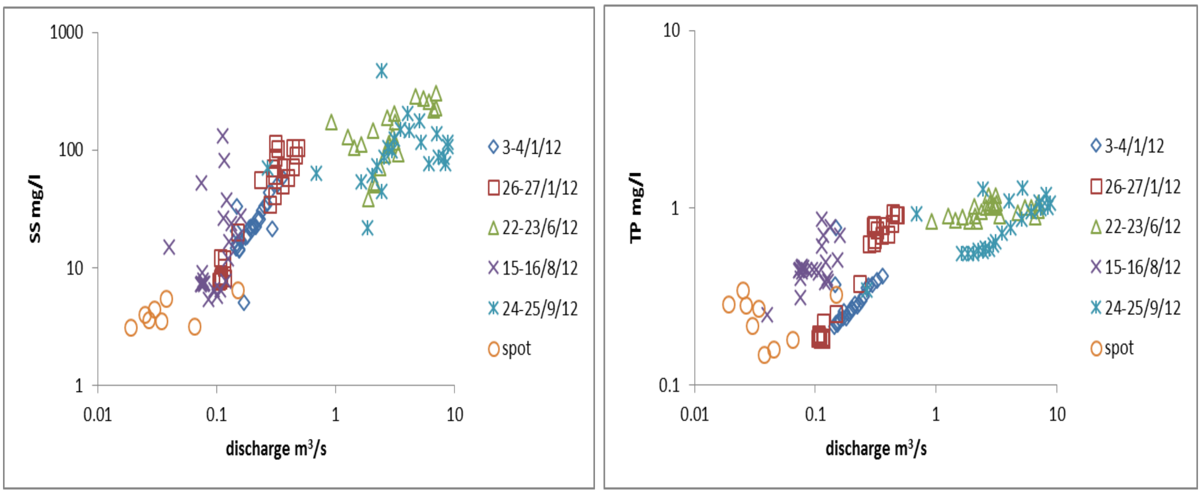


Figure C4.1 Seasonal pattern of suspended sediment and total phosphorus concentrations against discharge at Pow Beck

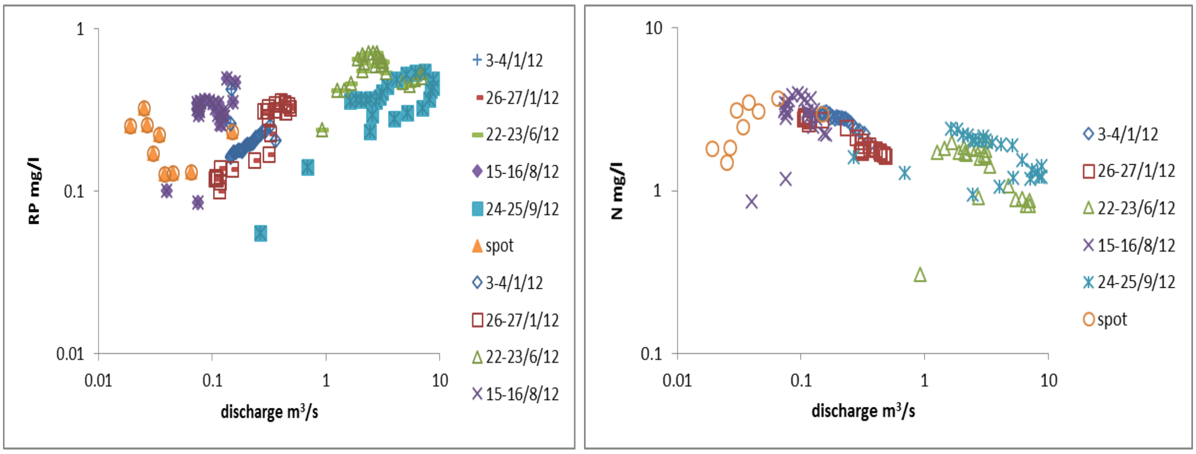


Figure C4.2 Seasonal pattern of reactive phosphorus and nitrate concentrations against discharge at Pow Beck

Seasonal pattern of nutrient concentration in Morland Beck

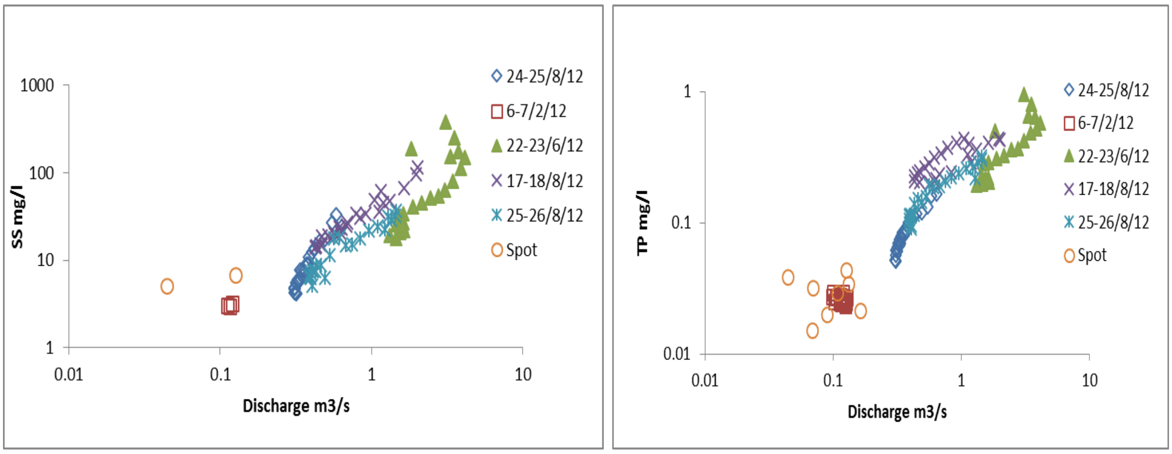


Figure C5.1 Seasonal pattern of suspended sediment and total phosphorus concentrations against discharge at Morland Beck

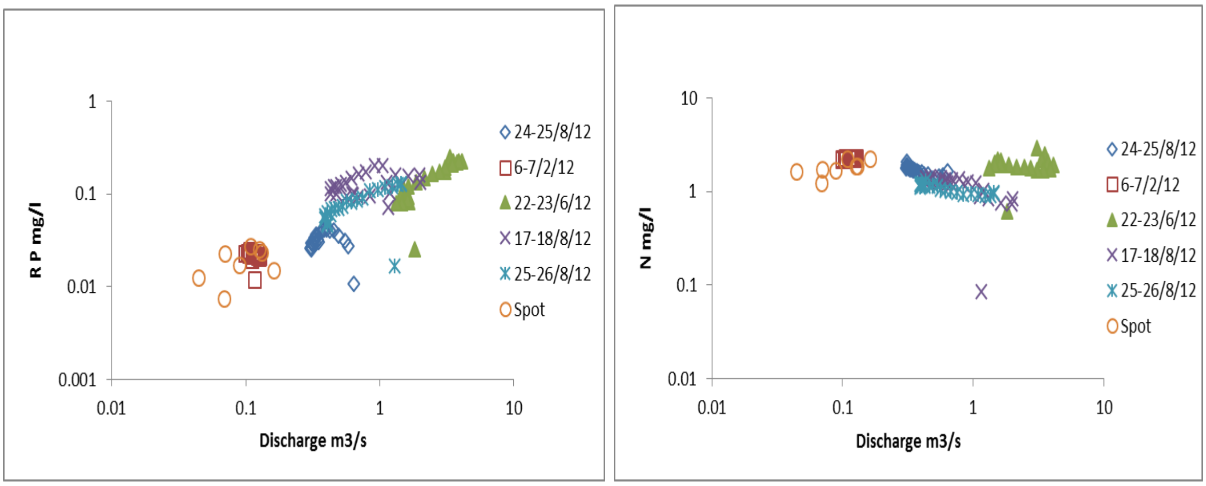


Figure C5.2 Seasonal pattern of reactive phosphorus and nitrate concentrations against discharge at Morland Beck

Comparison of data from auto sampler with the continuous monitoring equipment at Dacre

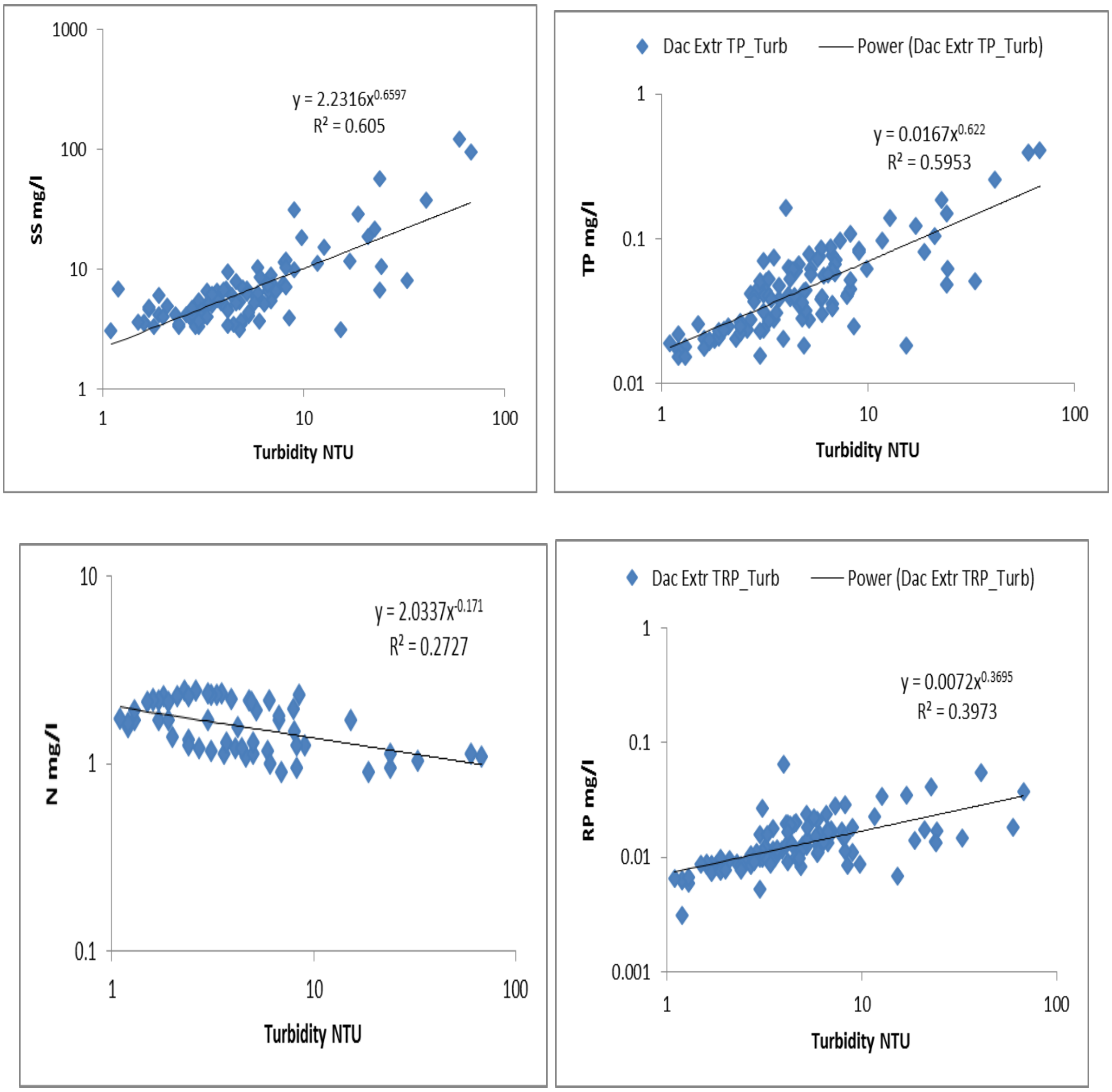


Figure C6.1 Comparison of nutrient and sediment data from the auto sampler with the data that correspond in data in the continuous monitoring equipment at Dacre

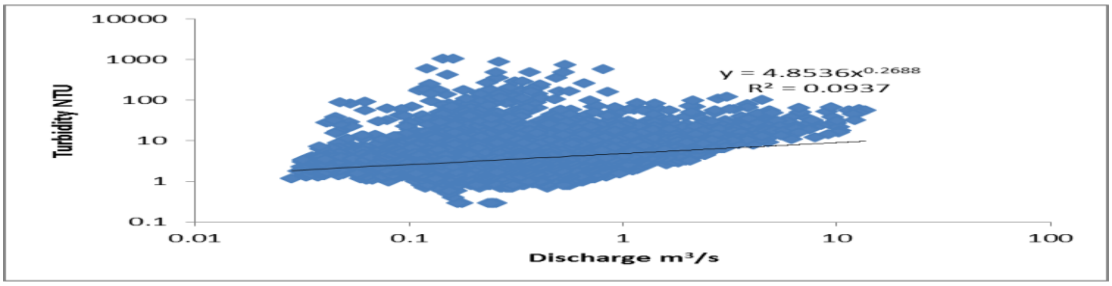


Figure C6.2 High resolution turbidity-flow curve at Dacre Beck

Appendix D – One year Flow Duration Curves (FDC) from 01/10/11 – 31/01/2012

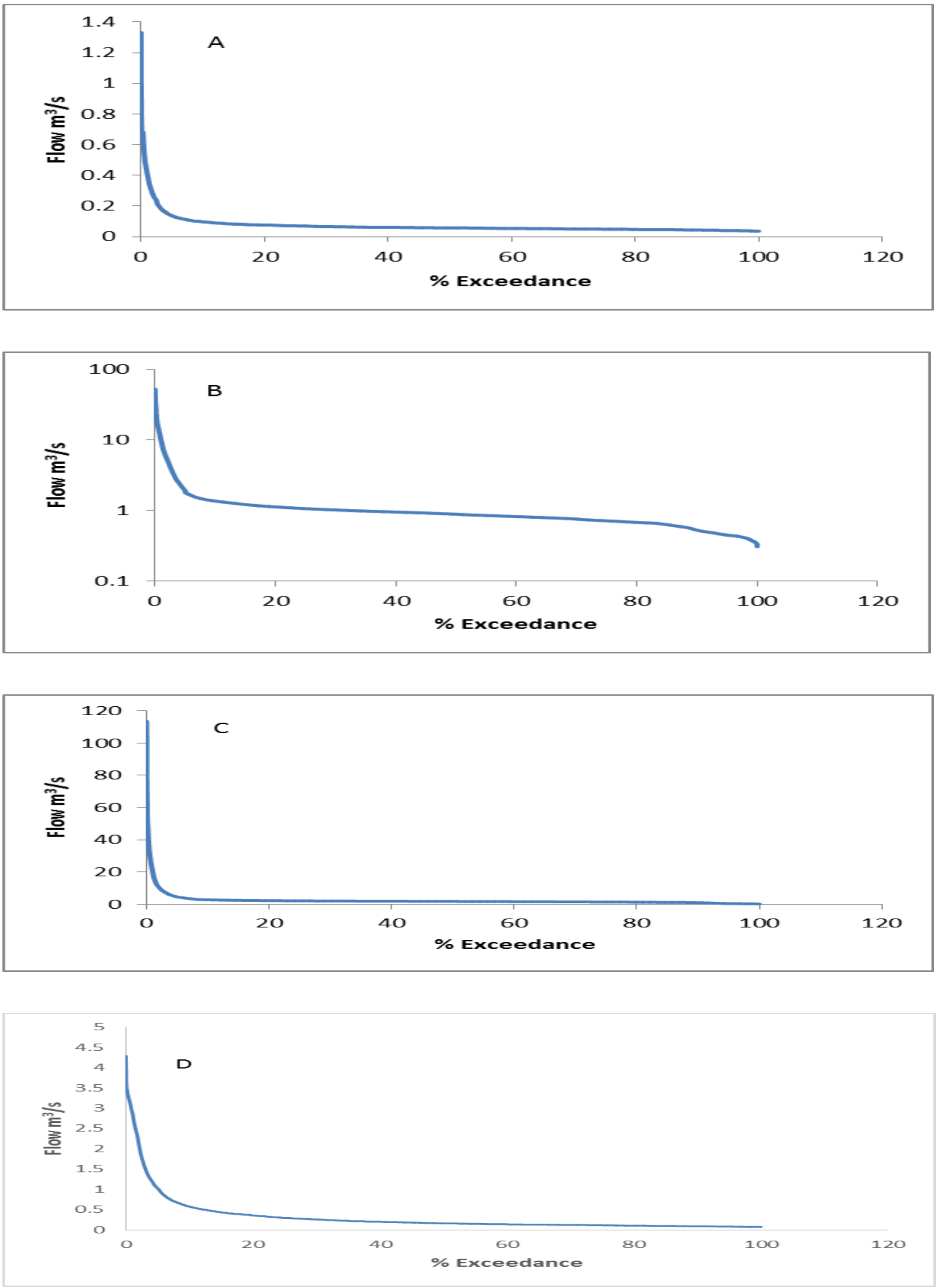


Figure D1.1 Flow duration curves for A. Gais Gill B. Ravenstonedale C. Smardale D. Blind Beck

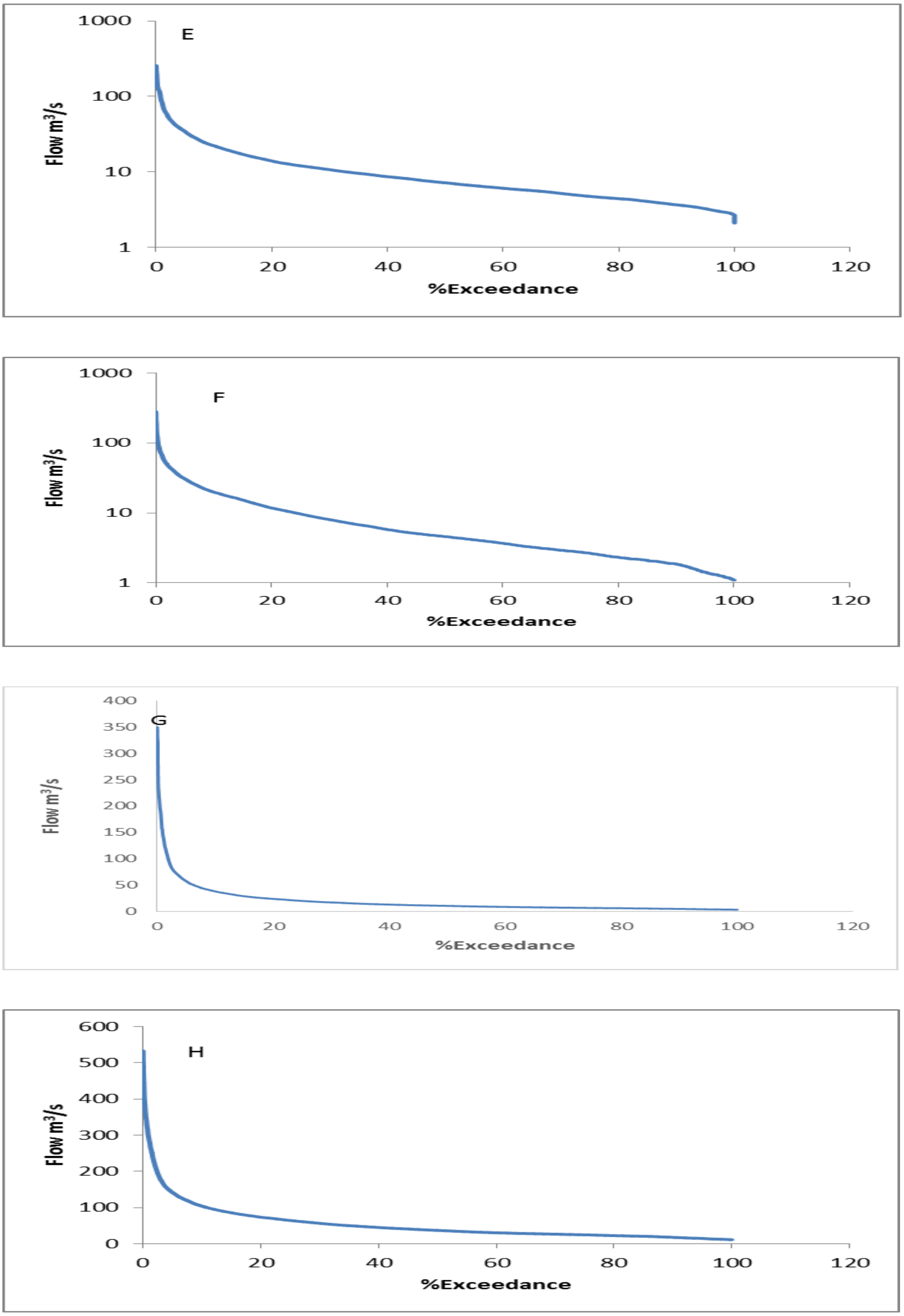
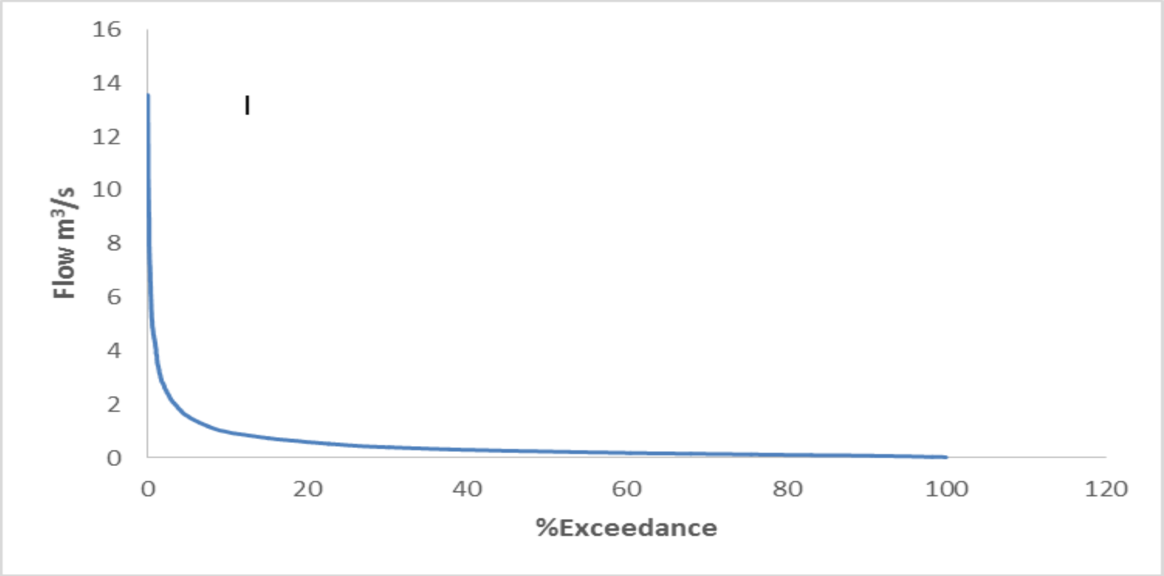


Figure D1.2 Flow duration curves for E. Appleby F. Great Musgrave G. Temple Sowerby H. Great Corby



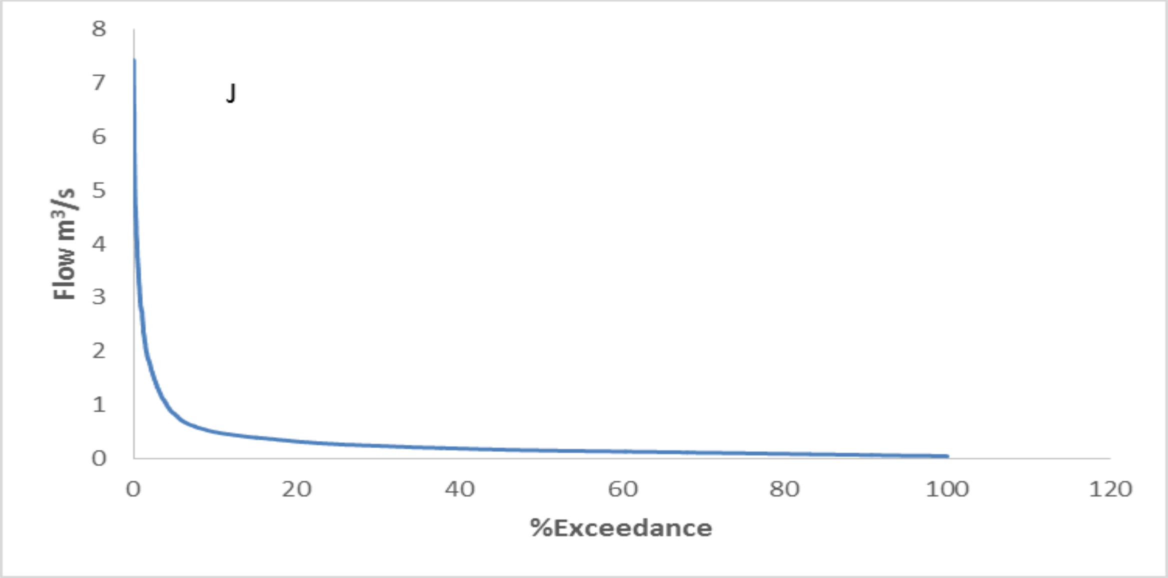


Figure D1.3 Flow duration curves for I. Dacre and J. Morland

Appendix E – Load and Yield

FDC method – Temple Sowerby

Time interval (%)	Interval midpoint (%)	Interval ∆P (%)	Discharge Q m3/s	Concentration C mg/l	Q * ∆P m3/s	Sediment load Qs * ∆P (tons/year)
0.00-0.02	0.01	0.02	347	188.4945	0.0694	413.716
0.02-0.1	0.06	0.08	329	177.6063	0.2632	1478.388
0.1-0.5	0.3	0.4	254	133.0301	1.016	4274.524
0.5-1.5	1	1	155	76.62157	1.55	3756.013
1.5-5.0	3.25	3.5	86.55	39.96482	3.02925	3828.752
5.0 -15	10	10	43.15	18.3664	4.315	2506.393
15-25	20	10	24.45	9.737737	2.445	752.9761
25-35	30	10	17.1	6.531414	1.71	353.2219
35-45	40	10	12.95	4.788019	1.295	196.0965
45-55	50	10	10.305	3.709584	1.0305	120.8975
55-65	60	10	8.365	2.938631	0.8365	77.74192
65-75	70	10	6.94	2.385333	0.694	52.35436
75-85	80	10	5.765	1.938936	0.5765	35.35143
85-95	90	10	4.46	1.455652	0.446	20.53226
95-98.5	96.75	3.5	3.51	1.113932	0.12285	4.327908
Total						17871.29

Table E 1.1 Specific suspended sediment yield at Temple Sowerby

Time interval (%)	**Interval midpoint (%)**	**Interval ∆P (%)**	**Discharge Q m3/s**	**Concentration C mg/l**	**Q * ∆P m3/s**	**Phosphorus load Qs * ∆P (tons/year)**
0.00-0.02	0.01	0.02	347	0.976173	0.0694	2.142548
0.02-0.1	0.06	0.08	329	0.935483	0.2632	7.786929
0.1-0.5	0.3	0.4	254	0.76072	1.016	24.44348
0.5-1.5	1	1	155	0.512594	1.55	25.12751
1.5-5.0	3.25	3.5	86.55	0.321735	3.02925	30.82324
5.0 -15	10	10	43.15	0.184451	4.315	25.17136
15-25	20	10	24.45	0.117137	2.445	9.057656
25-35	30	10	17.1	0.088019	1.71	4.760094
35-45	40	10	12.95	0.070482	1.295	2.88664
45-55	50	10	10.305	0.058718	1.0305	1.913652
55-65	60	10	8.365	0.049701	0.8365	1.314857
65-75	70	10	6.94	0.042809	0.694	0.939602
75-85	80	10	5.765	0.03691	0.5765	0.672964
85-95	90	10	4.46	0.030065	0.446	0.424066
95-98.5	96.75	3.5	3.51	0.024826	0.12285	0.096455
Total						137.5611

Table E1.2 Specific total phosphorus yield at Temple Sowerby

Time interval (%)	Interval midpoint (%)	Interval ∆P (%)	Discharge Q m3/s	Concentration C mg/l	Q * ∆P m3/s	Nitrogen load Qs * ∆P (tons/year)
0.00-0.02	0.01	0.02	347	2.72461	0.0694	5.980094
0.02-0.1	0.06	0.08	329	2.753498	0.2632	22.92001
0.1-0.5	0.3	0.4	254	2.898227	1.016	93.12588
0.5-1.5	1	1	155	3.195978	1.55	156.6678
1.5-5.0	3.25	3.5	86.55	3.586829	3.02925	343.6292
5.0 -15	10	10	43.15	4.116834	4.315	561.8086
15-25	20	10	24.45	4.606916	2.445	356.2324
25-35	30	10	17.1	4.944886	1.71	267.4217
35-45	40	10	12.95	5.224685	1.295	213.9805
45-55	50	10	10.305	5.466458	1.0305	178.1551
55-65	60	10	8.365	5.696935	0.8365	150.7133
65-75	70	10	6.94	5.911536	0.694	129.749
75-85	80	10	5.765	6.132693	0.5765	111.8136
85-95	90	10	4.46	6.452399	0.446	91.01235
95-98.5	96.75	3.5	3.51	6.765793	0.12285	26.28682

Table E1.3 Specific nitrate yield at Temple Sowerby

Load and Specific yield - Approximate method - Ravenstonedale

Date	tons/yr	tons/yr/km2
01/11/2011	167.7443	6.451704
03/11/2011	84.37817	3.245314154
21/11/2011	3.494673	0.1344105
24/11/2011	646.2931	24.85742781
06/03/2012	54.38618	2.091776077
14/03/2012	21.24213	0.817005
19/03/2012	46.73269	1.797411
21/03/2012	28.11551	1.081365923
02/05/2012	51.6558	1.986761538
09/05/2012	34.96254	1.344713192
16/05/2012	58.12859	2.235714923
21/05/2012	40.16502	1.544808462
23/07/2012	49.86366	1.917833077
26/07/2012	91.93678	3.536030077
31/07/2012	69.02375	2.654759423
06/08/2012	130.9211	5.035426846
16/12/2011	50.19046	1.930402385
25/06/2012	127.04164	4.886217
19/09/2012	67.07347	2.579749038
10/10/2012	44.87729	1.726049769
07/11/2012	38.00391	1.461688846
20/12/2012	399.5945	15.36901962
14/01/2013	67.37392	2.591304692
30/01/2013	624.74	24.02846169
27/02/2013	105.4095	4.054209923
26/03/2013	72.80042	2.800016019
10/04/2013	65.40257	2.515483385
26/04/2013	102.1678	3.9295305
Avg	119.4186	4.593021245

Table E2.1 Calculated suspended sediment load and yield at Ravenstonedale

Date	tons/yr	tons/yr/km2
01/11/2011	1.248717	0.048027573
03/11/2011	1.148292	0.044165062
21/11/2011	0.4227427	0.016259335
24/11/2011	4.305599	0.165599975
06/03/2012	1.0213722	0.039283546
14/03/2012	1.218944	0.04688246
19/03/2012	0.511956	0.019690633
21/03/2012	0.46096	0.017729248
02/05/2012	0.305086	0.011734081
09/05/2012	0.737477	0.02836449
16/05/2012	1.992455	0.076632872
21/05/2012	1.059018	0.040731459
23/07/2012	1.379778	0.053068402
26/07/2012	1.434109	0.05515804
31/07/2012	1.532682	0.058949308
06/08/2012	2.950322	0.113473912
Avg	1.358094	0.0522344

Table E2.2 Calculated total phosphorus load and yield at Ravenstonedale

Date	tons/yr	tons/yr/km2
01/11/2011	0.452751	0.017413506
03/11/2011	0.27756	0.010675376
21/11/2011	0.1532751	0.005895197
24/11/2011	1.72542	0.066362317
06/03/2012	0.509614	0.019600532
14/03/2012	0.389243	0.014970888
19/03/2012	0.243277	0.009356805
21/03/2012	0.321995	0.012384416
02/05/2012	0.084121	0.003235439
09/05/2012	0.355853	0.013686648
16/05/2012	1.479099	0.05688842
21/05/2012	0.511005	0.019654052
23/07/2012	0.965653	0.037140492
26/07/2012	0.800888	0.030803376
31/07/2012	0.873663	0.033602423
06/08/2012	1.559203	0.059969355
Avg	0.668914	0.025727453

Table E2.3 Calculated total phosphorus load and yield at Ravenstonedale

Date	tons/yr	tons/yr/km2
01/11/2011	31.78109	1.222349766
03/11/2011	26.1045	1.004019066
21/11/2011	35.28921	1.357277229
24/11/2011	71.40134	2.746205394
06/03/2012	65.17442	2.506708386
14/03/2012	54.85568	2.109833712
19/03/2012	47.92225	1.84316328
21/03/2012	45.95682	1.767569842
02/05/2012	37.83684	1.455263092
09/05/2012	27.29409	1.049772765
16/05/2012	39.65823	1.525316506
21/05/2012	37.29322	1.434354657
23/07/2012	65.17679	2.506799615
26/07/2012	50.13259	1.928176401
31/07/2012	35.96904	1.383424633
06/08/2012	14.63936	0.563052275
16/12/2011	67.26777	2.587221796
25/06/2012	70.021118	2.693119937
19/09/2012	43.93044	1.68963243
10/10/2012	57.23351	2.201288806
07/11/2012	61.90837	2.38109113
20/12/2012	69.49519	2.672892069
14/01/2013	92.16753	3.544904819
30/01/2013	165.6453	6.370974986
27/02/2013	74.96369	2.883218957
26/03/2013	63.64022	2.44770096
10/04/2013	38.47455	1.479790271
26/04/2013	62.50311	2.403965851
Avg	55.49058	2.134253165

Table E2.3 Calculated total phosphorus load and yield at Ravenstonedale

Appendix F - Bank-side continuous monitoring analyser

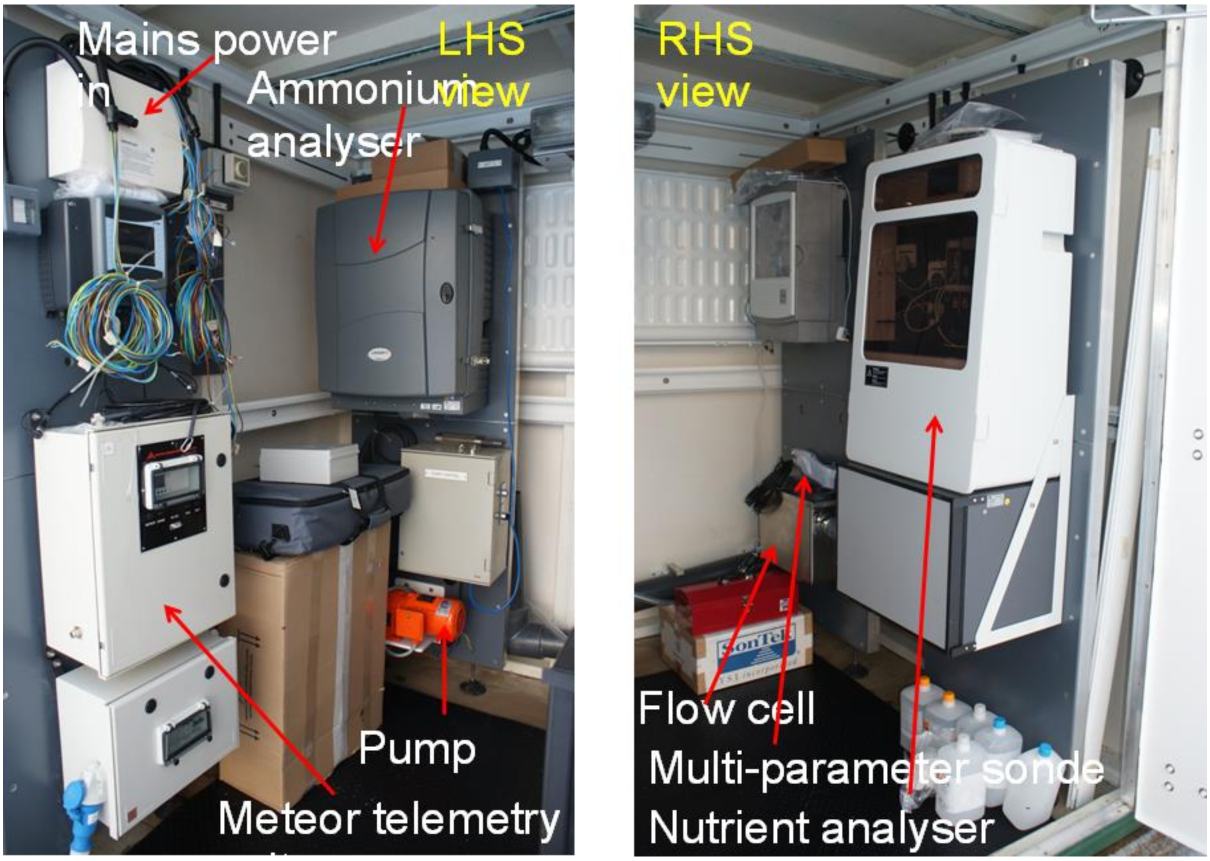


Plate F1 – Picture showing the components of the continuous monitoring device (Lecture note, Newcastle University)

References

Allen, D.J., Newell, A.J. and Butcher, A.S. (2010) *Preliminary reveiw of the geology and hydro geology of the Eden DTC sub-catchments* (OR//10/063). [Online]. Available at: http://nora.nerc.ac.uk/12788/1/OR10063.

Anderson, H.E., Perdersen, M.L., Lorgensen, O. and Kronvang, B. (2001) 'Analysis of the hydrology and flow of nitrogen in 17 Danish catchments', *Water Science and Technology*, 44(7), pp. 63-68.

Ankers, C., Walling, D.E. and Smith, R.P. (2003) 'The influence of catchment characteristics on suspended sediment properties', *Hydrobiologia*, 494(1-3), pp. 159-167.

Anthony, S., Quinn, P. and Lord, E.I. (1996) 'Catchment scale modelling of nitrate leaching', *Aspects of Applied Biology*, 46, pp. 23 - 32.

Anthony, S.G., Silgram M., Colins, A.L. and Fawcett, L.E. (2009) 'Modelling nitrate river water quality for policy support', *International Journal of River Basin Management*, 7, pp. 259 -275.

APHA (1992) *Standard Methods for the Examination of Water and Wastewater*. Washington DC, USA: American Public Health Association.

Armstrong, A.C. and Burt, T.P. (1993) 'Nitrate losses from agricultural land', in Burt, T.P., Heathwaite, A.L. and Trudgill, S.T. (eds.) *Nitrate: processes, patterns and management*. Chichester, UK: John Wiley and Sons Ltd, pp. 239-268.

Arnold, J.G., Srinivasan, R., Muttiah, R.S. and Williams, J.R. (1998) 'Large area hydrologic modeling and assessment part 1: model development 1. JAWRA', *J. Am. Water Resour. Assoc.*, 34, pp. 73 - 89.

Asadi, M.E., Clemente, R.S., Das Gupta, A., Loof, R. and Hansen, G.K. (2002) 'Impacts of fertigation via sprinkler irrigation on nitrate leaching and corn yield in an acid-sulphate soil in Thailand', *Agricultural Water Management*, 52(3), pp. 197-213.

Asselman, N.E.M. (2000) 'Fitting and interpretation of sediment rating curves.', *Journal of Hydrology*, 234(3 - 4), pp. 228 - 248.

Bai, X., Ding, S., Fan, C., Liu, T., Shi, D. and Zhang, L. (2009) 'Organic phosphorus species in surface sediments of a large, shallow, eutrophic lake, Lake Taihu, China', *Environ Pollut*, 157(8-9), pp. 2507-13.

Baldwin, D.S., Mitchell, A.M. and Olley, J.M. (2002) 'Pollutants-sediment intereactions: sorption, reactivity and transport of phosphorus ', in Haygarth, P.M. and Jarvis, S.C. (eds.) *Agriculture, Hydrology and Water Quality*. Wallingford, UK: CAB International, pp. 265-280.

Ballantine, D.J., Walling, D.E., Collins, A.L. and Leeks, G.J.L. (2008) 'The phosphorus content of fluvial suspended sediment in three lowland groundwater-dominated catchments', *Journal of Hydrology* 357, pp. 140-151.

Barber, N.J. (2008) *The application of a farm integrated runoff management (FIRM) plan to Sykeside farm, Cumbria: A scoping study*. Unpublished MSc thesis.

Barber, N.J. (2013) *Sediment, nutrient and runoff mangement and mitigation in rural catchments*. Unpublished PhD thesis. Newcastle University.

Barber, N.J. (2014) *EdenDTC* Available at: 46. https://www.flickr.com/photos/128904906@N07/15628898076/in/pool-eden_dtc.

Baron, J.S., Hartman, M.D., Band, L.E. and Lammers, R.B. (2000a) 'Sensitivity of a high-elevation Rocky Mountain watershed to altered climate and CO2', *Water Resources Research*, 36(1), pp. 89-99.

Baron, J.S., Rueth, H.M., Wolfe, A.M., Nydick, K.R., Allstott, E.J., Minear, J.T. and Moraska, B. (2000b) 'Ecosystem responses to nitrogen deposition in the Colorado Front Range', *Ecosystems*, 3(4), pp. 352-368.

Beasley, D.B., Huggins, L.F. and Monke, E.J. (1980) 'Answers - a Model for Watershed Planning', *Transactions of the Asae*, 23(4), pp. 938-944.

Beven, K.J. (1986) 'Hillslope runoff processes and flood frequency characteristics', *Hillslope Processes* 16, pp. 187-202.

Beven, K., Lamb, R., Quinn, P., Romanowicz, R., Freer, J. and (eds.) (1995) *TOPMODEL*. Highland Ranch, CO: Water Resources Publications.

Beven, K.J. (2000) 'Uniqueness of place and process representations in hydrological modelling', *Hydrology and Earth System Sciences*, 4(2), pp. 203-213.

Beven, K., Heathwaite, A.L., Haygarth, P., Walling, D.E., Brazier, R.E. and Withers, P. (2005) 'On the concept of delivery of sediment and nutrients to stream channels', *Hydrol. Process*, 19, pp. 551-556.

Beven, K.J. (2011) *Rainfall-Runoff modelling*. Chichester: Wiley-Blackwell.

Birkinshaw, S.J. and Ewen, J. (2000) 'Nitrogen transformation component for SHETRAN catchment nitrate transport modelling', *Journal of Hydrology*, 230(1–2), pp. 1-17.

Bloschl, G. (2001) 'Scaling in Hydrology', *Hydrological Processes*, 15, pp. 709-711.

Bloschl, G. and Sivapalan, M. (1995) 'Scale Issues in Hydrological Modeling - a Review', *Hydrological Processes*, 9(3-4), pp. 251-290.

Boorman, D.B., Hollis, J.M. and Lilly, A. (1995) *Hydrology of soil types: a hydrological classification of the soils of the United Kingdom' Institute of Hydrology* (126). Wallingford, UK.

Bowes, M.J., House, W.A. and Hodgkinson, R.A. (2003) 'Phosphorus dynamics along a river continuum', *Science of the Total Environment* 313, pp. 119-212.

Bowes, M.J., Smith, J.T., Jarvie, H.P. and Neal C. (2008) 'Modelling of phosphorus inputs to rivers from diffuse and point sources', *Sci. Total Environment*, 395, pp. 125 - 138.

Bowes, M.J., Jarvie, H.P., Halliday, S.J., Skeffington, R.A., Wade, A.J., Loewenthal, M., Gozzard, E., Newman, J.R. and Palmer-Felgate, E.J. (2015) 'Characterising phosphorus and nitrate inputs to a rural river using high-frequency concentration-flow relationships', *Science of The Total Environment*, 511, pp. 608 - 620.

Brazier, R.E., Rowan, J.S., Anthony, S.G. and Quinn, P.F. (2001) ''MIRSED' towards an MIR approach to modelling hillslope soil erosion', *Catena*, 42, pp. 59 - 79.

British Standard 7755 Section 3.2 (1995) *Determination of pH*.

British Standard 7755 Section 3.6 (1995) *Determination of phosphorus - spectrometric determination of phosphrus soluble in sodium hydrogen carbonate solution*.

British Standard section 3.8 (1995) *Determination of organic carbon and total carbon after dry combustion (elementary analysis)*.

British Standard EN 1189 (1997) *BS EN 1189:1997: Determination of phophorus: Ammonium molybdate spectrometric method*.

British Standard ISO11277 (2009) *Determination of partcile size distribution in mineral soil material - method by sieving and sedimentation*.

Brownlie, W., May, L., McDonald, C., Roaf, S. and Spears B.M. (2014) 'Assessment of a novel development policy for the control of phosphorus losses from private sewage systems to the Loch Leven catchment, Scotland, UK', *Environmental Science & Policy*, 38, pp. 207 - 216.

Burkett, V.R., Wilcox, D.A., Stottlemyer, R., Barrow, W., Fagre, D., Baron, J., Price, J., Nielsen, J.L., Allen, C.D., Peterson, D.L., Ruggerone, G. and Doyle, T. (2005) 'Nonlinear dynamics in ecosystem response to climatic change: Case studies and policy implications', *Ecological Complexity*, 2(4), pp. 357-394.

Burt, T.P., Heathwaite, A.L. and Trudgill, S.T. (1993) *Nitrate: Processes, Patterns and Management' Wiley*. Chischester: Wiley.

Cammeraat, L.H. (2002) 'A review of two strongly contrasting geomorphological systems within the context of scale', *Earth Surface Processes and Landforms*, 27(11), pp. 1201-1222.

Canter, L.W. (1997) *Nitrates in groundwater*. USA: CRC Press

Carpenter, S.R., Ludwig, D. and Brock, W.A. (1999) 'Management of eutrophication for lakes subject to potentially irreversible change', *Ecological Applications*, 9(3), pp. 751-771.

Cassidy, R. and Jordan, P. (2011) 'Limitations of instaneous water quality sampling in surface-water catchments: Comparison with near-continuous phophorus time-series data', *Journal of Hydrology*, 405, pp. 182 - 193.

CEH (2000) *Land cover map*. Available at: http://www.ceh.ac.uk/landcovermap2000.html (Accessed: 17/12/2014).

CEH (2014) *National Flow Archive*. Available at: http://www.ceh.ac.uk/data/nrfa/data/search.html (Accessed: 17/12/2014).

Chadwick, R.A., Holliday, D.W., Holloway, S. and Hubert, A.G. (1995) *The structure and evolution of the Northumberland-Solway Basin and adjacent areas.* (ISBN 0118845012).

Clark, M.P., Rupp, D.E., Woods, R.A., Tromp-van Meerveld, H.J., Peters, N.E. and Freer, J.E. (2009) 'Consistency between hydrological models and field observations: linking processes at the hillslope scale to hydrological responses at the watershed scale', *Hydrological Processes*, 23(2), pp. 311-319.

Clement, J.C., Aquillina, L., Bour, O., Kristelle, P., Burt, T.P. and Pinay, G. (2003) 'Hydrological flowpaths and nitrate removal rates within a riparian floodplain along a fourth-order stream in Brittany (France)', *Hydrol. Processes* 17, pp. 1177-1195.

Clemente, R., Walker, D.J., Roig, A. and Bernal, M.P. (2003) 'Heavy metal bioavailability in a soil affected by mineral sulphides contamination following the mine spillage at Aznalcollar (Spain)', *Biodegradation*, 14(3), pp. 199-205.

Cooke, S.E., Ahmed, S.M. and MacAlpine, N.D. (2005) *Introductory guide to surface water quality monitoring in agriculture.* Edmonton, Alberta: Conservation and Development Branch, Alberta Agriculture, Food and Rural Development.

Correll, D.L., Jordan, T.E. and Weller, D.E. (1992) 'Nutrient Flux in a Landscape - Effects of Coastal Land-Use and Terrestrial Community Mosaic on Nutrient Transport to Coastal Waters', *Estuaries*, 15(4), pp. 431-442.

Daniels, R.B. and Gilliam, J.W. (1996) 'Sediment and chemical load reduction by grass and riparian filters', *Soil Science Society of American Journal* 60, pp. 246-251.

Davison, P.S., Withers, P.J.A., Lord, E.I., Betson, M.J. and Stromqvist, J. (2008). 'PSYCHIC - a process-based model of phosphorus and sediment mobilisation and delivery within agricultural catchments. Part 1: model description and parameterisation', *J. Hydrol.*, 350, pp. 290 - 302.

De Roo, A.P.J. and Jetten, V.G. (1999) 'Calibrating and validating the LISEM model for two data sets from the Netherlands and South Africa', *Catena*, 37(3-4), pp. 477-493.

Defra (2012) *Annual average, highest and lowest mean concentrations of water quality: Nitrates by region - 1980 to 2011*. Available at: http://www.defra.gov.uk/statistics/environment/inland-water/ (Accessed: 11/09/2014).

Demars, B.O.L. and Harper, D.M. (2005) 'Water column and sediment phosphorus in a calcareous lowland river and their differential response to point source control measures', *Water, Air and Soil Pollution* 167, pp. 273-293.

Dillon, P.J. and Kirchner, W.B. (1975) 'The effects of geology and land use on the export of phosphorus from watersheds', *Water Research* 9, pp. 135-148.

Dooge, J.C.I. (1982) 'Parameterization of hydrological processes', in Eagleson, P.S. (ed.) *Land Surface Processes in Atmospheric General Circulation Models*. London: Cambridge University Press, pp. 243-288.

Dooge, J.C.I. (1986) 'Looking for Hydrologic Laws', *Water Resources Research*, 22(9), pp. S46-S58.

EA (2000) *Aquatic eutrophication in England and Wales: a management strategy*. Bristol.

EA (2003) *Investigation of rising nitrate concentrations in groundwater in the Eden Valley, Cumbria: Scoping study*. Olton, UK: Environment Agency, Science Group - Air, Land, Water.

EdenDTC (2011) *A National Demonstration Test Catchment*. Available at: http://www.edendtc.org.uk/category/catchment-info/ (Accessed: 11/12/2014).

Eden Demonstration Test Catchment (2014a) *Morland catchment*. Available at: http://www.edendtc.org.uk/conceptual-model-2/store/farm/morland-catchment/.

Eden Demonstration Test Catchment (2014b) *Soil Science video by Phil Haygarth*. Available at: http://www.edendtc.org.uk/2014/03/soil-science-video-by-phil-haygarth/ (Accessed: 20 March 2014).

Eden River Trust (2014) *The River Eden catchment*. Available at: http://trust.edenriverstrust.org.uk/map.html (Accessed: 17/12/2014).

Elementar Analysensysteme GMbH (2005) 'Vario Max CNS Macro Elementar Analyzer'. Hanau Germany.

Ewen, J., Parkin, G. and O'Connell, P.E. (2000) 'Shetran: Distributed River Basin Flow and Transport Modeling System', *Journal of Hydrologic Engineering*, 5(3), pp. 250-258.

FAO (1992) *FAO corporate document repository*.

Fenn, M.E., Baron, J.S., Allen, E.B., Rueth, H.M., Nydick, K.R., Geiser, L., Bowman, W.D., Sickman, J.O., Meixner, T., Johnson, D.W. and Neitlich, P. (2003) 'Ecological effects of nitrogen deposition in the western United States', *Bioscience*, 53(4), pp. 404-420.

Feng, X.H., Kirchner, J.W. and Neal, C. (2004) 'Measuring catchment-scale chemical retardation using spectral analysis of reactive and passive chemical tracer time series', *J. Hydrol.*, 292, pp. 296 - 307.

Foster, S.S.D. (1993) 'The Chalk aquifer –its vulnerability to pollution', in Downing, R.A., Price, M. and Jones, G.P. (eds.) *The hydrogeology of the chalk of north-west Europe*. Oxford: Clarendon Press, pp. 1-13.

Fowler, D., Cape, J.N. and Unsworth, M.H. (1989) 'Deposition of atmospheric pollutants on forests', *Philosophical Transactions of the Royal Society of London Series B-Biological Sciences* 324, pp. 247-265.

Fragala, F.A. (2009) *Assessment of local recharge through glacial and alluvial deposits in the upper Eden valley*. Unpublished PhD thesis. Newcastle University.

Gall, H.E., Sassman, S.A., Jenkinson, B., Lee, L.S. and Jafvert, C.T. (2015) 'Comparison of export dynamics of nutrients and animal-borne estrogens from a tile-drained midwestern agroecosystem', *Water Research*, 72, pp. 162 - 173.

Galloway, J.N., Schlesinger, W.H., Levy, H., Michaels, A. and Schnoor, J.L. (1995) 'Nitrogen-Fixation - Anthropogenic Enhancement-Environmental Response', *Global Biogeochemical Cycles*, 9(2), pp. 235-252.

Gassman, P.W., Reyes, M.R., Green, C.H. and Arnold, J.G. (2007) 'The soil and water assessment tool: Historical development, applications, and future research directions', *Transactions of the Asabe*, 50(4), pp. 1211-1250.

Gburek, W.J. and Heald, W.R. (1970) 'Effects of direct runoff from agricultural land on the water quality of small streams', *Second Cornell University Conference on Agricultural Waste Management*. Ithaca, N.Y.

Gburek, W.J. and Heald, W.R. (1974) 'Soluble phosphate output of an agricultural watershed in Pennsylvania', *Water Resources Research*, 10(1), pp. 113-118.

Gburek, W.J. and Urban, J.B. (1990) 'The Shallow Weathered Fracture Layer in the near-Stream Zone', *Ground Water*, 28(6), pp. 875-883.

Gburek, W.J. and Sharpley, A.N. (1998) 'Hydrologic controls on phosphorus loss from upland agricultural watersheds', *Journal of Environmental Quality*, 27(2), pp. 267-277.

Gelb, A. (1974) *Applied optimal estimation*. Cambridge, Mass: MIT Press.

Georgakakos, K.P., Rajaram, H. and Li, S.G. (1988) *On improved operational hydrologic forecasting of streamflows* (325). Department of civil and environmental engineering and Iowa institute of hydraulic research.

Greene, S., McElarney, Y.R. and Taylor, D. (2013) 'A predictive geospatial approach for modelling phosphorus concentrations in rivers at the landscape scale', *Journal of hydrology*, 504, pp. 216 - 225.

Gupta, V.K., Rodriguez-Iturbe, I. and Wood, E.F. (1986) *Scale problems in hydrology*.

Halliday, S.J., Skeffington, R.A., Wade, A.J., Neal, C., Reynolds, B., Norris, D. and Kirchner, J.W. (2013) 'Upland streamwater nitrate dynamics across decadal to sub-daily timescales: a case study of Plynlimon, Wales', *Biogeosciences*, 10, pp. 8013 - 8038.

Halliday, S.J., Skeffington, R.A., Bowes, M.J., Gozzard, E., Newman, J.R., Loewenthal, M., Palmer-Felgate, E.J., Jarvie, H.P. and Wade, A.J. (2014) 'The water qulaity of the River Enborne, UK: Observations from high-frequency monitoring in a rural, lowland river system', *Water*, 6, pp 150 - 180.

Halliday, S.J., Skeffington, R.A., Wade, A.J., Bowes, M.J., Gozzard, E., Newman, J.R., Loewenthal, M., Palmer-Felgate, E.J. and Jarvie, H.P. (2015) 'High-frequency water quality monitoring in an urban catchment: hydrochemical dynamics, primary production and implications for the Water Framework Directive', *Hydrol. Process.*

Hayes, C.R. and Greene, L.A. (1984) 'The evaluation of eutrophication impact in public water supply reservoirs in east Anglia', *Water Pollut, Control* 83, pp. 45-51.

Haygarth, P.M. and Jarvis, S.C. (eds.) (1999) *Transfer of Phosphorus from Agricultural Soil*. Academic Press.

Haygarth, P.M., Condron, L.M., Heathwaite, A.L., Turner, B.L. and Harris, G.P. (2005a) 'The phosphorus transfer continuum: Linking source to impact with an interdisciplinary and multi-scaled approach', *Science of The Total Environment*, 344(1–3), pp. 5-14.

Haygarth, P.M., Wood, F.L., Heathwaite, A.L. and Butler, P.J. (2005b) 'Phosphorus dynamics observed through increasing scales in a nested headwater-to-river channel study', *Science of The Total Environment*, 344(1–3), pp. 83-106.

Heathwaite, A.L., Burt, T.P. and Trudgill, S.T. (1993) 'The Nitrate Issue: a Question of Scale', in *Nitrate: Processes, Patterns and Management*. Chichester, UK: John Wiley & Sons Ltd, pp. 3-22.

Heathwaite, A.L., and R.M. Dils. (2000) 'Characterising phosphorus loss in surface and subsurface hydrological pathways', *The Science of the Total Environment*, 251/252, pp. 523 - 538.

Heathwaite, A. L., Fraser, A.I., Johnes, P.J., Hutchins, M., Lord, E. and Butterfield, D. (2003) 'The phosphorus indicators tool: a simple model diffuse P loss from agriculture to water', *Soil Use and Management*, 19, pp. 1 - 11.

Hesketh, N. and Brookes, P.C. (2000) 'Development of an indicator for risk of phosphorus leaching.', *Journal of Environmental Quality*, 29, pp. 105 - 110.

Hesse, C., Krysanova, V., Pazolt, J. and Hattermann, F. F. (2008) 'Eco-hydrological modelling in a highly regulated lowland catchment to find measures for improving water quality ', *Ecological Modelling*, 218, pp. 135 - 148.

Hodge, A., Robinson, D. and Fitter, A. (2000) 'Are microorganisms more effective than plants at competing for nitrogen?', *Trends in Plant Sciences* 5, pp. 304-308.

Holford, I.C.R., Chater, M. and Mattingly, G.E.G. (1990) 'Effects of decalcification on the phosphates sorption characteristics of eight calcerous soils', *Australian Journal of Soil Resources*, 28(6), pp. 919-928.

Holloway, J.M., Dahlgren, R.A., Hansen, B. and Casey, W.H. (1998) 'Contribution of bedrock nitrogen to high nitrate concentrations in stream water', *Nature*, pp. 395-788.

Hornung, M. and Sutton, M.A. (1995) 'Impacts of Nitrogen Deposition in Terrestrial Ecosystems', *Atmospheric Environment*, 29(22), pp. 3395-3396.

Howden, N.J.K. and Burt, T.P. (2008) 'Temporal and spatial analysis of nitrate concentrations from the Frome and Piddle catchments in Dorset (UK) for water years 1978 to 2007: Evidence for nitrate breakthrough?', *Science of the Total Environment*, 407, pp. 507-526.

Howden, N.J.K., Bowes, M.J., Clarke, A.D.J., Humphreys, N. and Neals, C. (2009) 'Water quality, nutrients and the European Union’s water framework directive in a lowland, agricultural region: Suffolk, south-east England', *Science of the Total Environment*, 407, pp. 2966-2979.

Howden, N.J.K., Burt, T.P., Worrall, F., Whelan, M.J. and Bieroza, M. (2010) 'Nitrate concentrations and fluxes in the River Thames over 140 years (1868-2008): are increases irreversible?', *Hydrological Processes*, 24, pp. 2657 - 2662.

Imeson, A.C. and Cammeraat, L.H. (1999) 'Scaling up from field measurements to large areas using the desertification Response unit and indicator approaches in rangeland desertification', in Arnalds, O. and Archer, S. (eds.) *Advances in Vegetation Science* Dordrecht: Kluwer Academic Publishers, pp. 99-114.

Jackson, B.M., Wheater, H.S., Wade, A.J., Butterfield, D., Mattias, S.A., Ireson, A.M., Butler, A.P., Mclantyre, N.R. and Whitehead, P.G. (2006) 'A simple model of variable residence time flow and nutrient transport in the Chalk', *Journal of Hydrology* 330, pp. 221-234.

Jackson, B.M., Wheater, H.S., Wade, A.J., Butterfield, D., Mathias, S.A., Ireson, A.M., Butler, A.P., McIntyre, N.R. and Whitehead, P.G. (2007) 'Catchment-scale modelling of flow and nutrient transport in the Chalk unsaturated zone', *Ecological Modelling*, 209(1), pp. 41-52.

Jackson, B.M., Browne, C.A., Butler, A.P., Peach, D., Wade, A.J. and Wheater, H.S. (2008) 'Nitrate transport in Chalk catchments: monitoring, modelling and policy implications', *Environmental Science & Policy*, 11(2), pp. 125-135.

Jackson-Blake, L.A., Dunn, S.M., Helliwell, R.C., Skeffington, R.A., Stutter, M.I. and Wade, A.J. (2015) 'How well can we model stream phosphorus concentrations in agricultural catchments?', *Environmental Modelling & Software*, 64, pp. 31 - 46.

Jain, S. K., and Sudheer, K. (2008) 'Fitting of hydrologic models: a close look at the Nash-Sutcliffe index', *J. Hydrol. Eng.*, 13: 981 - 986.

Jang, J.S.R., Sun, C.T. and Mizutani, E. (eds.). (1993) *ANFIS archtecture* (Prentice Hall: New Jersey).

Jarvie, H.P., Whitton, B.A. and Neal, C. (1998) 'Nitrogen and phosphorus in east coast British rivers: speciation, sources and biological significance', *Science of The Total Environment*, 210/211, pp. 79-109.

Jarvie, H.P., Wade, A.J., Butterfield, D., Whitehead, P.G., Tindall, C.I., Virture, W.A., Dryburgh, W. and McGraw, A. (2002) 'Modelling nitrogen dynamics and distributions in the River Tweed, Scotland: an application of the INCA model', *Hydrology and Earth System Sciences*, 6(3), pp. 433-453.

Jarvie, H.P., Neal, C., Withers, P.J.A., Robinson, A. and Salter, N. (2003) 'Nutrient water quality of the Wye catchment, UK: exploring patterns and fluxes using the Environment Agency data Achives', *Hydrology and Earth System Sciences*, 7(5), pp. 722-743.

Jarvie, H.P., Neal, C. and Withers, P.J.A. (2006) 'Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus?', *Science of The Total Environment*, 360(1–3), pp. 246-253.

Jarvie, H.P., Withers, P.J.A., Hodgkinson, R., Bates, A., Neal, M., Wickham, H.D., Harman, S.A. and Armstrong, L. (2008) 'Influence of rural land use on streamwater nutrients and their ecological significance', *Journal of Hydrology*, 350(3–4), pp. 166-186.

Jarvie, H.P., Withers, P.J.A., Bowes, M.J., Palmer-Felgate, E.J., Harper, D., Wasiak, K., Wasiak, P., Hodgkinson, R.A., Bates, A., Stoate, C., Neal M., Whickam, H.D., Harman, S.A. and Armstrong, L.K. (2010) 'Streamwater phosphorus and nitrogen across a gradient in rural-agricultural land use intensity.', *Agriculture, Ecosystems & Environment*, 135, pp. 238 - 252.

Jarvis, N. (1994) 'The MACRO model-Technical description and sample simulations.' In, 51. Uppsala: Swedish University of Agricultural Sciences.

Johnes, P. J. (1996) 'Evaluation and management of the impact of land use on the nitrogen and phosphorus load delivers to surface waters: the export coefficient modelling approach', *J. Hydrol.*, 183, pp. 323 - 340.

Johnes, P.J., Whitehead, P.G., Snook, D., Davies, S., Wade, A., Butterfield, D. and Hoare, D. (2003) ''Effectiveness of eutrophication control by phosphorus reduction '' In, edited by Environment Agency, 135 p.

Johnes, P.J. (2007) 'Uncertainties in annual riverine phosphorus load estimation: Impact of load estimation methodology, sampling frequency, baseflow index and catchment population frequency', *Journal of hydrology*, 332, pp. 241 - 258.

Johnson, A.H., Bouldin, D.R., Goyette, E.A. and Hedges, A.M. (1976) 'Phosporus loss by stream transport from a rural watershed: Quantities, processes and sources', *J. Environ. Qual.*, 5(2), pp. 148-157.

Jordan-Meille, L., Dorioz, J.M. and Wang, D. (1998) 'Analysis of the export of diffuse phosphorus from a small rural watershed', *Agronomie*, 18(1), pp. 5-26.

Jordan, C., McGuckin, S.O. and Smith, R.V. (2000) 'Increased predicted losses of phosphorus to surface waters from soils with high Olsen-P concentrations.', *Soil Use and Management*, 16, pp. 27 - 35.

Jordan, P., Menary, W., Daly, K., Kiely, G., Morgan, G., Byrne, P. and Moles, R. (2005a) 'Patterns and processes of phosphorus transfer from Irish grassland soils to rivers—integration of laboratory and catchment studies', *Journal of Hydrology*, 304(1–4), pp. 20-34.

Jordan, C., and Smith, R.V. (2005b) 'Methods to predict the agricultural contribution to catchment nitrate loads: designation of nitrate vulnerable zones in Nothern Ireland', *J. Hydrol.*, 304, p. 316

Jordan, P., Arnscheidt, J., McGrogan, H.J. and McCormick, S. (2007) 'Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser', *Hydrology and Earth Systems Science*, 11, pp. 372 - 381.

Julien, P.Y. (1998) *Erosion and sedimentation*. Cambridge, UK: Cambridge University Press.

Kirchner, J.W., Feng, X.H., Neal, C. and Robson, A.J. (2004) 'The fine structure of water-quality dynamics: the (high-frequency) wave of the future', *Hydrol. Process.*, 18, pp. 1353 - 1359.

Kleeberg, H.-B. (1992) *Regionalisierung in der Hydrologie.* Weinheim.

Komor, S.C. and Magner, J.A. (1996) 'Nitrate in groundwater and water sources used by riparian trees in an agricultural watershed: a chemical and isotopic investigation in southern Minnesota', *Water Resources Research* 32, pp. 1039-1050.

Krysanova, V., Wechsung, F., Arnold, J., Srinivasan, R. and Williams, J. (2000) "SWIM (Soil and Water Integrated Model): User Manual." In. Potsdam.

Laflen, J.M., Lane, L.J. and Foster, G.R. (1991) 'Wepp - a New Generation of Erosion Prediction Technology', *Journal of Soil and Water Conservation*, 46(1), pp. 34-38.

Lane, S.N., Brookes, C.J., Heathwaite, A.L. and Reaney, S. (2006) 'Surveillant science: Challenges for the management of rural environments emerging from the new generation diffuse pollution models', *Journal of Agricultural Economics*, 57(2), pp. 239-257.

Lazar, A.N., Butterfield, D., Futter, M.N., Rankinen, K., Thouvenot-Korppoo, M., N. Jarrit, N., Lawrence, D.S.L., Wade, A.J. and Whitehead P.G. (2010) 'An assessment of the fine sediment dynamecs on an upland river system: INCA-Sed modifications and implications for fisheries', *Sci. Total Environ*, 408, pp. 2555 - 2566.

Lazarotto, P., Stamn, C., Prasuhn, V. and Fluhler, H. (2006) 'A parsimonious soil-type based rainfall-runoff model simultaneously tested in four small agricultural catchments', *Journal of Hydrology*, 321, pp. 21-38.

Logan, T.J. (ed.) (1995) *Water quality*. Boca Raton, FL, USA: CRC Lewis Publishers.

Lunn, R.J., Adams, R. and Dunn, S.M. (1996) 'Development and application of a nitrogen modelling system for large catchments', *J. Hydrol.*, 174, pp. 285 - 304.

Lyons, J., Trimble, S.W. and Paine, L.K. (2000) 'Grass versus trees: managing riparian areas to benefit streams of central North America', *Journal of the American Water Resources Association* 36, pp. 919-930.

Mannix, A. (2005) *The source and fate of nitrates in the upper Eden catchments.* . Unpublished MSc thesis.

Mathias, S.A., Butler, A.P., Jackson, B.M. and Wheater, H.S. (2006) 'Transient simulations of flow and transport in the Chalk unsaturated zone', *J. Hydrol.* , 330, pp. 10-28.

McComb, A.J., Qiu, S., Lukatelich, R.J. and McAuliffe, T.F. (1998) 'Spatial and temporal herogeneity of sediment phosphorus in the Peel-Harvey', *Estuarine Coastal and Shelf Science* 47, pp. 561-577.

McGechan, M.B., Lewis, D.R. and Hooda, P.S. (2005) 'Modelling thro-soil transport of phosphorus to surface waters from livestock agriculture at the field and catchment scale', *Science of The Total Environment*, 344, pp. 185 - 199.

McGuckin, S.O., Jordan, C. and Smith, R.V. (1999) 'Deriving phosphorus export coefficients for corine land cover types', *Water Science and Technology*, 39(12), pp. 47-53.

Menzel, R.G. (ed.) (1980) *Enrichment ratios for water quality modelling*. USDA Conservation Research Report: USDA-ARS.

Met Office (2012) *Summer 2012 was the wettest in 100 years*. Available at: http://www.metoffice.gov.uk/news/releases/archive/2012/second-wettest-summer (Accessed: 4 September 2012).

Milledge, D.G., Lane, S.N., Heathwaite, A.L. and Reaney, S.M. (2012) 'A Monte Calro approach to the inverse problem of diffuse pollution risk in agricultural catchments', *Science of The Total Environment*, 433, pp. 434 - 449.

Mills, C.F., Bathhurst, J.C. and Quinn, P.F. (2008) *Proceedings of Sediment Dynamics in Changing Environments*. Christchurch, New Zealand, December, 2008. IAHS Publ.

Mills, C. (2009) *Spatial variability and scale dependency of sediment yield in a rural river system – The River Eden, Cumbria, UK*. Unpublished PhD thesis. Newcastle University.

Mills, C. F., and Bathurst, J.C. (2015) 'Spatial variability of suspended sediment yield in a gravel-bed river across four orders of magnitude of catchment area ', *Catena*, 133, pp. 14 - 24.

Murphy, J. and Riley, J.P. (1962) 'A modified single solution method for the determination of phosphate in natural waters', *Anal. Chim. Acta* 27, pp. 31-36.

Nash, J.E. and Sutcliffe, J.V. (1970) 'River flow forecasting through conceptual models 1: A discussion of principles', *Journal of hydrology*, 10, pp. 282 - 290.

Nasr, A., and Bruen, M. (2013) 'Derivation of a Fuzzy national phosphorus export mofel using 84 Irish catchments', *Science of The Total Environment*, 443, pp. 539 - 548.

Neal, C., H. P. Jarvie, A. J. Wade, M. Neal, R. Wyatt, H. Wickam, L. Hill, and N. Hewitt. (2004) 'The water quality of the LOCAR Pang and Lambourn catchments', *Hydrology and Earth System Sciences*, 8: 614 - 635.

Neal, C. and Jarvie, H.P. (2005) 'Agriculture, community, river eutrophication and the Water Framework Directive', *Hydrological Processes*, 19, pp. 1895-1901.

Neitsch, S.L., Arnold, J.G., Kiniry, J.R. and Williams, J.R. (2005) *Soil and Water Assessment Tool Theoretical Documentation* [Online]. Available at: www.brc.tamus.edu/swat/doc.html (Accessed: 10 July 2011).

O'Connell, P.E., Quinn, P.F., Beven, K.J., Burt, T.P., Kirkby, M.J., Pickering, A., Robinson, M., Soulsby, C., Werritty, A. and Wilcock, D. (2002) *Prediction in Ungauged Basins: PUB Kick-off*. Brasilia. IAHS Publication.

Ockenden, M.C., Chappell, N.A. and Neal C. (2014) 'Quantifying the differential contributions of deep groundwater to streamflow in nested basins, using both water quality characteristics and water balance', *Hydrology Research*, 45.2, pp. 200-212

Office, M. (2009) *UK climate averages* [Online]. Available at: http://www.metoffice.gov.uk/climate/uk/averages/19712000/sites/netwon_rigr.html (Accessed: 04/04/2009).

Olarewaju, O.E., Adetunji, M.T., Adeofun, C.O. and Adekunle, I.M. (2009) 'Nitrate and phophorus loss from agricultural land: implications for nonpoint pollution', *Nutrient Cycle Agrosystem*, 85, pp. 79-85.

Olsen, S.R. and Sommers, L.E. (1982) 'Phosphorus', in Page, A.L., Miller, R.H. and Keeney, D.R. (eds.) *Methods of Soil Analysis*. Madison, WI: SoilScience Society of America, Inc., pp. 403-430.

Osborne, S. and Cook, H.F. (1997) 'Nitrate vulnerable zones and nitrate sensitive areas: a policy and technical analysis of groundwater source protection in England and Wales', *J. Environ. Plan. Manag.*, 40, pp. 217-233.

Owens, P.N., Walling, D.E., Carton, J., Meharg, A.A., Wright, J. and Leeks, G.J.L. (2001) 'Downstream changes in the transport and storage of sediment-associated contaminants (P, Cr and PCBs) in agricultural and industrialized drainage basins', *Science of the Total Environment*, 266, pp. 177-186.

Owens, P.N. and Walling, D.E. (2002) 'The phosphorus content of fluvial sediment in rural and industrialized river basins', *Water Research* 36, pp. 685-701.

Owens, P.N., Batalla, R.J., Collins, A.J., Gomez, B., Hicks, D.M., Horowitz, A.J., Kondolf, G.M., Marden, M., Page, M.J., Peacock, D.H., Petticrew, E.L., Salomons, W. and Trustrum, N.A. (2005) 'Fine-grained sediment in river systems: Environmental significance and management issues', *River Research and Applications*, 21(7), pp. 693-717.

Pacini, N. and Gachter, R. (1999) 'Speciation of riverine particulate phosphorus during rain events', *Biogeochemistry* 47, pp. 87-109.

Page, A.L., Miller, R.H. and Keeney, D.R. (eds.) (1982) *Method of soil analysis Part 2*. Second Edition edn.

Palmer-Felgate, E.J., Mortimer, R.J.G., Krom, M.D. and Jarvie, H.P. (2010) 'Impact of pont-source pollution on phosphorus and nitrogen cycling in strewm-bed sediments', *Environmental Science and Technology*, 44, pp. 908 - 914.

Peterjohn, W.T. and Correll, D.L. (1986) 'The effect of riparian forest on volume and chemical composition of base flow in an agricultural watershed', in *Watershed Research Perspectives*. Smithsonian Institute Press, pp. 244-262.

Phillips, J.M., Webb, B.W., Walling, D.E. and Leeks, J.G.L. (1999) 'Estimating the suspended sediment loads of rivers in the LOIS study area using infrequent samples', *Hydrol. Process.*, 13, pp. 1035 - 1050.

Pinay, G., Ruffinoni, C., Wonderzell, S. and Gazelle, F. (1998) 'Change in groundwater nitrate concentration in a large river foodplain: denitrification uptake, or mixing?', *Journal of the North American Benthological Society* 17, pp. 179-189.

Pionke, H.B., Hoover, J.R., Schnabel, R.R., Gburek, W.J., Urban, J.B. and Rogowski, A.S. (1988) 'Chemical-Hydrologic Interactions in the near-Stream Zone', *Water Resources Research*, 24(7), pp. 1101-1110.

Pionke, H.B. and Kunishi, H.M. (1992) 'Phosphorus Status and Content of Suspended Sediment in a Pennsylvania Watershed', *Soil Science*, 153(6), pp. 452-462.

Pionke, H.B., Gburek, W.J., Sharpley, A.N. and Schnabel, R.R. (1996) 'Flow and nutrient export patterns for an agricultural hill-land watershed', *Water Resources Research* 32(6), pp. 1795-1804.

Pohlert, T., Huisman, J.A., Breuer, L. and Freude, H.G. (2007) 'Integration of a detailed biogeochemical model into SWAT for improved nitrogen predictions: Model development, sensitivity, and GLUE analysis', *Ecol. Model*, 203 ((3 ‐ 4)), pp. 215 ‐ 228.

Preedy, N., McTiernan, K., Matthews, R., Heathwaite, L. and Haygarth, P. (2001) 'Rapid incidental phosphorus transfers from grassland', *J. Environ. Qual.*, 30, pp. 2105 - 2112

Quinn, P.F. and Beven, K.J. (1993) 'Spatial and temporal dynamics of the soil moisture dynamics, runoff, variable source areas and evapotranspiration for Plynlimon, Mid-Wales,' *Hydrological Processes*, 7, pp. 425 - 448.

Quinn, P.F., Anthony, S. and Lord, E.I. (eds.) (1999) *Basin scale nitrate modelling using a minimum information requirement approach.* Chichester: Wiley.

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(3–4), pp. 197-217.

Quinn, P.F., Hewett, C.J.M. and Dayawansa, N.D.K. (2007) 'TOPCAT-NP: a minimum information requirement model for simulation of flow and nutrient transport from agricultural systems', *Hydrological Processes*.

Reaney, S.M., Lane, S.N., Heathwaite, A.L. and Dugdale, L.J. (2011) 'Risk-based modelling of diffuse land use impacts from rural landscapes upon salmonid fry abundance', *Ecol. Model*, 222, pp. 1016 - 1029.

Refsgaard, J.C. and Knudsen, J. (1996) 'Operational validation and intercomparison of different types of hydrological models', *Water Resources Research*, 32(7), pp. 2189-2202.

Refsgaard, J.C., Thorsen, M., Jensen, J.B., Kleeschulte, S. and Hansen, S. (1999) 'Large scale modelling of groundwater contamination from nitrate leaching', *J. Hydrol.*, 221, pp. 117 - 140.

Reynolds, B., and Edwards, A. (1995) 'Factors influencing dissolved nitrogen conentrations and loadings in upland streams of the UK', *Agri. Water Manage.*, 27, pp. 181 - 202.

Rueth, H.M. and Baron, J.S. (2002) 'Differences in Englemann spruce forest biogeochemistry east and west of the Continental Divide in Colorado, USA', *Ecosystems*, 5(1), pp. 45-57.

Rueth, H.M., Baron, J.S. and Allstott, E.J. (2003) 'Responses of Engelmann spruce forests to nitrogen fertilization in the Colorado Rocky Mountains', *Ecological Applications*, 13(3), pp. 664-673.

Rozemeijer, J.C., and Broers, H.P. (2007) 'The groundwater contribution to surface water contamination in a region with intensive agricultural land use (Nord-Brabant, The Netherlands)', *Environmental Pollution*, 148, pp. 695 - 706.

Rozemeijer, J.C., van der Velde, Y., Van Geer, F.C., Bierkens, M.F.P. and Broers, H.P. (2010) 'Direct measurements of the tile drain and groundwater flow route conrributions to surface water contamination: from field-scale concentration patterns in groundwater to catchment-scale surface water quality', *Environmental Pollution*, 158, pp. 3571 - 3579.

Rubæk, G.H., Kristensen, K., Olesen, S.E., Østergaard, H.S. and Heckrath, G. (2013) 'Phosophorus accumulation and spatial distribution in agricultural soils in Denmark ', *Geoderma*, 209 - 210, pp. 241 - 250.

Russell, M.A., Walling, D.E., Webb, B.W. and Bearne, R. (1998) 'The composition of nutrient fluxes from contrasting UK river basins', *Hydrological Processes* 12, pp. 1461-1482.

Scandor, J., Kiss, I. and Ember, I. (2001) 'Association between gastric cancer mortality and nitrate content of drinking water: ecological study on small area inequalities', *Eur, J. Epidem*, 17, pp. 443-447.

Schaefli, B., and Gupta, H.V. (2007) 'Do Nash values have value?', *Hydrol. Process.*, 21, pp. 2075 - 2080.

Scher, H., Margolin, G., Metzler, R., Klafter, J. and Berkowitz, B. (2002) 'The dynamical foundation of fractal stream chemistry: the origin of extremely long retention times', *Geophys. Res. Lett.*, 29, p. 1061.

Schnabel, R.R., Urban, J.B. and Gburek, W.J. (1993) 'Hydrologic controls on nitrate, sulfate, and chloride concentrations', *J. Environ. Qaul.*, 22(3), pp. 589-596.

Schumm, S.A. (1977) *The Fluvial System*. London: John Wiley and Sons.

Sharpley, A. and Tunney, H. (2000) 'Phosphorus research strategies to meet agricultural and environmental challenges of the 21st century', *Journal of Environmental Quality*, 29, pp. 176-181.

Sharpley, A.N. and Menzel, R.G. (1987) 'The Impact of Soil and Fertilizer Phosphorus on the Environment', in Brady, N.C. (ed.) *Advances in Agronomy*. Academic Press, pp. 297-324.

Sharpley, A.N. and Smith, S.J. (1992) 'Prediction of bioavailable phosphorus in agricultural runoff', *Journal of Environmental Quality* 22, pp. 32-37.

Shaw, E.M., Beven, K.J., Chappell, N.A. and Lamb, R. (2011) *Hydrology in practice*. UK: Spon Press.

Shepherd, A.N., Leith, I.D., Crossley, A., van Dijk, N., Fowler, D., Sutton, M.A. and Woods, C. (2008) 'Stress responses of Calluna vulgaris to reduced and oxidised N applied under ‘real world conditions', *Environmental Pollution* 154, pp. 404-413.

Silgram, M., Anthony, S.G., Fawcett, L. and Stormqvist, J. (2008) 'Evaluating catchment-scale models for diffuse pollution policy support: some results from EUROHARP project', *Environmental Science & Policy*, 11, pp. 153 - 162.

Sonnenborg, T.O., Butts, M.B. and Jensen, K.H. (1994) 'Application of stochastic unsaturated flow theory', *proceedings of the Nordic hydrological conference*. Thorshavn.

Soulsby, C., Tetzlaff, D., Dunn, S.M. and Waldron, S. (2006) 'Scaling up and out in runoff process understanding: insights from nested experimental catchment studies', *Hydrological processes*, 20, pp. 2461-2465.

Stoddard, J.L. (1994) 'Long-Term Changes in Watershed Retention of Nitrogen - Its Causes and Aquatic Consequences', *Environmental Chemistry of Lakes and Reservoirs*, 237, pp. 223-284.

Stromqvist, J., and Collins, A.L. (2008) 'PSYCHIC - A process-based model of phosphorus and sediment transfers within agricultural catchments. Part 2. A reliminary evaluation', *Journal of hydrology*, 350: 303 - 316.

Styczen, M., and Storm, B. (1993) 'Modelling of nitrogen movements on a catchment scale. A tool for analysis and decision making. (1) Model description.', *Fert. Res.*, 36, pp. 1 - 6.

Terry, J.A., Benskin, C.M., Eastoe, E.F. and Haygarth, P.M. (2014) 'Temporal dynamics between cattle in-stream presence and suspended solids in a headwater catchments', *Environmental Science, Processes and Impacts*, 16, pp. 1570-1577.

Tesoriero, A.J., Duff, J.H., Saad, D.A., Spahr, N.E. and Wolock, D.M. (2013) 'Vulnerability of streams to legacy nitrate sources', *Envronment, Science and Technology*, 47, pp. 3623-3629.

Tetzlaff, D. and Soulsby, C. (2008) 'Sources of baseflow in larger catchments – using tracers to develop a holistic understanding of runoff generation', *Journal of Hydrology* 359, pp. 287-302.

Thomson, E.M., Avis, E.L., Harrop, S.E., Skeggs, M.S., Talbot, S. and Williamson, M.J. (1983) *Soils of England and Wales sheet 1 Nothern England*, 1:250 000. Rothamsted Experimental Station, Harpenden, Hertfordshire: Ordnance Survey for the Soil Survey of England and Wales.

Tripkovic, V. (2013) 'Quantifying and upscaling surface and subsurface runoff and nutrient flows under climate vaiability', Unpublished PhD thesis, Newcastle University.

Ulén, B., Bechmann, M., Folster, J., Jarvie, H.P. and Tunney, H. (2007) 'Agriculture as a Phosphorus Source for Eutrophication in the north-west European Countries’ Norway, Sweden, United Kingdom and Ireland: A Review', *British Society of Soil Science*, 22(1), pp. 5-15.

UNESCO (2003) *Water for people, water for life*. [Online]. Available at: www.unesco.org (Accessed: 15/12/2014).

Vadas, P.A., Bolster, C.H. and Good, L.W. (2013) 'Critical evaluation of models used to study agricultural phosphorus and water quality ', *Soil Use Manag.*, 29, pp. 36 - 44.

Vitousek, J.P.W., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H. and Tilman, D.G. (1997) 'Human alteration of the global nitrogen cycle: sources and consequences', *Ecol. appl.*, 7, pp. 737-750.

Wade, A., Durand, P., Beaujouan, V., Wessel, W., Raat, K., Whitehead, P., Butterfield, D., Rankinen, K., and Lepisto, A. (2002) 'A nitrogen model for European catchments: INCA, new model structure and equations', *Hydrol. Earth Syst. Sci.*, 6, pp. 559 - 582.

Wade, A.J., Butterfield, D., Griffiths, T. and Whitehead, P.G. (2007a) 'Eutrophication control in river-systems: an application of INC-P to the River Lugg', *Hydrology and Earth System Sciences*, 11(1), pp. 584 - 600.

Wade, A.J., Butterfield, D., Lawrence, D.S.L., Barlund, I., Ekholm, P., Lepisto, A., Yli-Halla, M., Rankinen, K., Granlund, K., Durand, P., Kaste, Ø., and Halliday, S. (2007b) ''The Integrated Catchment Model of Phosphorus (INCA-P), a new structure to simulate particulate and soluble phosphorus transport in European catchments '' In.: UCl, London.

Wade, A. J., Palmer-Felgate, E.J., Halliday, S.J., Skeffington, R.A., Loewenthal, M., Jarvie, H.P., Bowes, M.J., Greenway, G.M., Haswell, S.J., Bell, I.M., Joly, E., Fallatah, A., Neal, C., Williams, R.J., Gozzard, E. and Newman, J.R. (2012) 'Hydrochemical processes in lowland rivers: insights from in situ, high resolution monitoring', *Hydrol. Earth Syst. Sci.*, 16, pp. 4323 - 4342.

Walling, D.E. and Webb, B.W. (1987) *Water for the Future: Hydrology in Persective*. Rome. IAHS

Walling, D.E., Webb, B.W. and Russell, M.A. (1997) 'Sediment-associated nutrient transport in UK rivers', in Webb, B. (ed.) *Freshwater Contamination*. IAHS Publication, pp. 69-81.

Walling, D.E., Owens, P.N. and Leeks, G.J.L. (1999) 'Fingerprinting suspended sediment sources in the catchment of the River Ouse, Yorkshire, UK', *Hydrological Processes*, 13(7), pp. 955-975.

Walling, D.E., Russell, M.A. and Webb, B.W. (2001) 'Controls on the nutrient content of suspended sediment transported by British rivers', *Science of the Total Environment*, 266(1-3), pp. 113-123.

Walsh, C.L. (2004) *Simulation and analysis of river flow regimes: implications for sustainable management of Atlantic salmon (Salmo Salar) under climate change*. Unpublished PhD thesis. Newcastle University.

Webb, B.W., Phillips, J.M., Walling, D.E., Littlewood, I.G., Watts, C.D. and Leeks, J.G.L. (1997) 'Load estimation methodology for British rivers and their relevance to the LOIS RACS(R) programme', *The Science of the Total Environment*, 194/195, pp. 379 - 389.

Whitehead, P.G., Wilson, E.J., and Butterfield, D. (1998) 'A semi-distributed Integrated Nitrogen model for multiple source assessment in Catchment (INCA). Part I. Model structure and process equations', *Sci. Total Environ*, 210/211, pp. 547 - 558.

Whitehead, P.G., Jin, L., Baulch, H.M., Butterfield, D.A., Oni, S.K., Dillon, P.J., Futter, M., Wade, A.J., North, R., O'Connor, E.M. and Jarvie, H.P. (2011) 'Modelling phosphorus dynamics in multi-branch river systems: a study of the Black River, Lake Simcoe, Ontario, Canada', *Sci. Total Environ*, 412 - 413, pp. 315 - 323.

Whitehead, P.G., Jin, L., Crossman, J., Comber, S., Johnes, P.J., Daldorph, P., Flynn, N., Collins, A.L., Butterfield, D., Mistry, R., Bardon, R., Pope, L. and Willows, R. (2014) 'Distributed and dynamic modelling of hydrology, phosphorus and ecology in the Hampshire Avon and Blashford Lakes: Evaluating alternative strategies to meet WFD standards', *Science of The Total Environment*, 481(0), pp. 157-166.

Wicks, J.M. and Bathurst, J.C. (1996) 'SHESED: A physically based, distributed erosion and sediment yield component for the SHE hydrological modelling system', *Journal of Hydrology*, 175(1-4), pp. 213-238.

Wilkinson, M.E. (2008) *A multiscale nested experiment for understanding and prediction of high rainfall and flood response spatial behaviour in the Eden catchment, Cumbria UK.* Unpublished PhD thesis. Newcastle University.

Williams, J.R., Dyke, P.T., Fuchs, W.W., Benson, V.W., Rice, O.W., Taylor, E.D., Sharpley, A.N. and Williams, J.R. (1990) *EPIC-Erosion/Productivity Impact Calculator: 2 User Manual*.

Withers, P.J.A. and Lord, E.I. (2002) 'Agricultural nutrient inputs to rivers and groundwaters in the UK: policy, environmental management and research needs', *Science of The Total Environment*, 282–283(0), pp. 9-24.

Withers, P.J.A., Jarvie, H.P. and Stoate, C. (2011) 'Quantifying the impact of septic tank systems on eutrophication risk in rural headwaters', *Environment International*, 37, pp. 644 - 653.

Withers, P.J.A., May, L., Jarvie, H.P., Jordan, P., Doody, D., Foy, R.H., Bechmann, M., Cooksley, S., Dils, R. and Deal, N. (2012) 'Nutrient emissions to water from septic tank systems in rural catchments: Uncertainties and implications for policy', *Environmental Science & Policy*, 24, pp. 71 - 82.

Wolf, J., Beusen, A.H.W., Groenendijk, P., Kroon, T., Rotter, R. and van Zeijts, H. (2003) 'The integrated modelling system STONE for calculating nutrient emissions from agriculture in the Netherlands', *Environmental Modelling & Software*, 18, pp. 597 - 617.

Wood, F.L., Heathwaite, A.L. and Haygarth, P.M. (2005) 'Evaluating diffuse and point phosphorus contributions to river transfers at different scales in the Taw catchment, Devon, UK', *Journal of Hydrology*, 304(1–4), pp. 118-138.

Wriedt, G., Spindler, J., Neef, T., Meissner, R. and Rode, M. (2007) 'Groundwater dynamics and channel activity as major controls of in-stream nitrate concentrations in a lowland catchment system?', *Journal of hydrology*, 343: 154 - 168.

Younger, P.L. and Milne, C.A. (1997) 'Hydrostratigraphy and hydrogeochemistry of the Vale of Eden, Cumbria, UK', *Proceedings of the Yorkshire Geological Society*, 51, pp. 349-366.

Zhang, Y., Collins, A.L. and Gooday, R.D. (2012) 'Application of the FARMSCOPER tool for assessing agricultural diffuse pollution mitigation methods across the Hampshire Avon Demonstration Test Catchment, UK', *Environmental Science & Policy*, 24(0), pp. 120-131.

Ziegler, A.C. (2002) *Issue related to the use of turbidity measurements as a surrogate for suspended sediment.* Turbidity and other surrogates workshop. Reno, NV.