The phosphorus transfer continuum under climate change

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Declaration

Except where stated:

- Chapter 3 is published in Journal of Environmental Quality (Forber et al., 2017). UKCP09 Weather Generator analysis was provided by M.C. Ockenden.
- The HYPE results in chapter 4 and appendix 2 were provided by M.J. Hollaway (published in Nature Communications Ockenden et al., 2017).
- UKCP09 results and analysis in chapter 4 and appendix 2 were provided by M.C. Ockenden (published in Nature Communications Ockenden et al., 2017).
- Newby Beck DTC outlet data was provided by the Eden DTC team and accessed via an on-line sharing platform.

I declare that the contents of this thesis are my own work and have not previously been submitted, in part or in full, for the award of a higher degree elsewhere.

Kirsty Forber

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September 2017

I confirm that the above statement is correct.

M. C. Ockenden

P. M. Haygarth M.C. Ockenden

September 2017

“He shall be like a tree planted
by the rivers of water,

That brings forth its fruit in its
season,

Whose leaf also shall not
wither;

And whatever he does shall
prosper.”

Psalm 1:3 (NKJV)

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All the glory unto Him

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Abstract

Phosphorus (P) is a key nutrient in governing crop growth, and its fate and behaviour in the environment is critical to water quality. Climatic changes such as hotter, drier summers and warmer, wetter winters will cause changes to the movement of P across the land-water continuum yielding potentially detrimental impacts to water quality which underpin many ecosystem services. This thesis uses the ‘P transfer continuum’ as a framework to discuss and explore the possible impacts of climate change to P in the environment. I use the three National Demonstration Test Catchment (DTC) platforms (Eden, Cumbria; Wensum, Norfolk; and Avon, Hampshire) which are representative of typical catchment typologies and agricultural activities in the UK to frame this work. Potential changes to the P transfer continuum are essential to consider and react to if we are to improve water quality in order to preserve ecosystem services into an ever uncertain future.

Estimations of dry period characteristics (duration and temperature) under current and predicted climate (determined using data from the UK Climate Projections (UKCP09) Weather Generator tool) were used to design a laboratory experiment to examine whether changes in the future patterns of drying/re-wetting will affect the amount of soluble reactive phosphorus (SRP) solubilised from soil. This study is focused on the second tier of the P transfer continuum: mobilisation via solubilisation. For three UK soils critical breakpoints (6.9-14.5 d) of drying duration have been identified; before the breakpoint an increase in SRP loss with the number of dry days was observed; after this point the amount of SRP lost decreased or stayed fairly constant. It is likely that longer periods of dry days followed by rapid re-wetting events will not yield more SRP via solubilisation than at the breakpoint. However, because the frequency of longer dry periods will increase under climate change, the solubilisation of SRP from soil (-1 to +13%) will also change.

Using the Hydrological Predictions in the Environment (HYPE) model for three distinct UK DTC catchments, and Extended End-Member Mixing Analysis (E-EMMA), I explore how climate change (UKCP09 scenarios) might impinge on catchment total phosphorus (TP) retention and sensitivity, which is determined by catchment characteristics to P input pressures. This study encompasses the all tiers of the P transfer continuum: source, mobilisation, transfer (or delivery), and impact. Under a high emissions scenario (2080s), an increase of catchment TP retention was predicted in three UK catchments. I conclude that catchment sensitivity to climate change should be accounted for in determining appropriate water quality targets that can be effectively delivered via catchment stakeholders and government.

I use the Newby Beck (Eden DTC) sub-catchment as a critical example of how anthropogenic point sources of P can alter the retention of P even at the headwater scale where agricultural diffuse sources dominate. I use bi-weekly sampling of P, chloride (Cl^-) and flow (Q), load apportionment modelling (LAM) and mass balance, alongside sediment sampling to investigate retention at the headwater scale. I found that although diffuse sources contributed to more of the TP load, point sources dominate more frequently and are therefore proportionally perhaps more important in terms of continuous downstream water quality. Under climate change the transfer of

diffuse sources is likely to increase, therefore it might be hypothesised that climate change will yield extremes between nutrient quality in summer (high concentrations, low flows) and winter (high loads, high flows). This calls for policy and regulation to reflect the urgency of the impacts of climate change on the riparian health in rural headwater communities.

I conclude by discussing the implications of climate change on the P transfer continuum. I highlight the possible risks of climate change exacerbating, rather than changing, the processes described in the P transfer continuum for the Newby Beck catchment. My findings, in addition to those from the NUTCAT team, call for climate change to be taken seriously in forming new effective policies which preserve the health of UK water bodies, the sustainability and profitability of UK agriculture, the enjoyment and amenity value of our water courses, and avoid large financial costs into the future. I therefore provide a new framework which can be used to aid the challenges which surround the preservation of water quality into the future.

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Abbreviations

Al	Aluminium
API	Antecedent Precipitation Index
BFI	Baseflow Index
C	Carbon
Cl^-	Chloride
CO_2	Carbon Dioxide
d	Days
DO	Dissolved Oxygen
DRW	Drying and re-wetting
DTC	Demonstration Test Catchments
E-EMMA	Extended End-Member Mixing Analysis
EPC_0	Equilibrium Phosphorus Concentration
Fe	Iron
FYM	Farm Yard Manure
GEP	Good Ecological Potential
GES	Good Ecological Status
GLUE	Generalised Likelihood Uncertainty Estimation
h	Hours
HYPE	Hydrological Predictions in the Environment
IPCC	Intergovernmental Panel on Climate Change
LAM	Load Apportionment Modelling
LOESS	A locally weighted scatterplot smoothing regression
Mn	Manganese
N	Nitrogen
N_2O	Nitrous Oxide
NSE	Nash Sutcliffe Efficiency
NUTCAT 2050	Estimating Nutrient Transport in Catchments to 2050 a NERC project
O_3	Ozone

P	Phosphorus
Q	Flow
SRES	Special Report on Emissions Scenario
SRP	Soluble Reactive Phosphorus
STP	Sediment Total Phosphorus
TP	Total Phosphorus
TRP	Total Reactive Phosphorus
UKCP09	UK Climate Projections 2009
VARE	Velocity-Area Rating Extension
WFD	Water Framework Directive
WWTWs	Waste Water Treatment Works

Publications

Below are the relevant publications arising from the 'estimating nutrient transport in catchments to 2050' research project and which link to this PhD thesis:

Determining the effect of drying time on phosphorus solubilisation from three agricultural soils under climate change scenarios.
Forber, K.J., Ockenden, M.C., Wearing, C.L., Hollaway, M.J., Falloon, P.D., Kahana, R., Villamizar, M.L., Zhou, J.G., Withers, P.J., Beven, K.J., Collins, A.L., Evans, R., Hiscock, K.M., Macleod, C.J. 22/08/2017 (2017) In: Journal of Environmental Quality 46(5):1131-1136

> In the above paper I led the experimental design, analysis, and write up. The weather generator work was completed by Ockenden M.C.

Major agricultural changes required to mitigate phosphorus losses under climate change.
Ockenden, M.C., Hollaway, M.J., Beven, K.J., Collins, A., Evans, R., Falloon, P., Forber, K.J., Hiscock, K., Kahana, R., Macleod, K., Tych, W., Villamizar, M., Wearing, C.L., Withers, P., Zhou, J., Barker, P.A., Burke, S., Freer, J., Johnes, P., Snell, M., Surridge, B.W.J., Haygarth, P.M. 31/07/2017 In: Nature Communications. 8, 8 p.

> In this paper I assisted with data collection from the stakeholder workshops.

Changing climate and nutrient transfers: evidence from high temporal resolution concentration-flow dynamics in headwater catchments.
Ockenden, M.C., Deasy, C.E., Benskin, C., Beven, K.J., Burke, S., Collins, A.L., Evans, R., Falloon, P.D., Forber, K.J., Hiscock, K.M., Hollaway, M.J., Kahana, R., Macleod, C.J.A., Reaney, S.M., Snell, M., Villamizar, M., Withers, P., Zhou, J., Haygarth, P.M. 1/04/2016 In: Science of the Total Environment. 548-549, p. 325-339. 15 p.

> In the spirit of collaboration all team members are included due to continued input during team meetings.

1 Introduction

1.1 The phosphorus transfer continuum and climate change

As climate change becomes more evident and the global population rises, the uncertainty of environmental response increases, as does the subsequent improvement or degradation to ecosystem and human health (McMichael et al., 2003). Water is regarded as the most essential natural resource, and therefore its quality and quantity is vital to both human and ecosystem health (Vörösmarty et al., 2010). Phosphorus (P) is first and foremost a key nutrient in the regulation of crop growth and food production, as well as water quality. Therefore the understanding of this element's journey across the land water continuum (i.e. through a catchment) is critical in ensuring that water supports "human well-being and ecosystem integrity" (WWAP (United Nations World Water Assessment Programme), 2015) into an uncertain, changing future environment.

Within a catchment (a hydrologically defined unit in which precipitation collects and drains from a common outlet, e.g. a river or stream) P can be described aided by a four tiered framework: the 'P transfer continuum' (Haygarth et al., 2005). It describes the journey of P from source, through mobilisation, transport (or delivery) to impact, accounting for the interconnected, dynamic nature of P in the environment (Haygarth et al., 2005). Three of these four tiers (mobilisation, transport and impact) are in part governed by hydrological interactions between soils and water bodies, varying in influence from one part of the catchment to another (e.g. headwaters to mouth). Phosphorus enters the water environment from both agricultural 'diffuse' sources, and industrial/domestic waste water 'point' sources. Although P is naturally sourced in the environment due to weathering of parent rock, diffuse transfer is dependent on a range of natural and anthropogenic factors that are highly variable in space and time. Point sources on the other hand, are often highly concentrated (soluble P), discharging continuously from discrete points in the environment, such as Waste Water Treatment Works (WWTWs) (Withers and Jarvie, 2008). In the UK, which is the primary focus of this study, under the Water Framework Directive (WFD) (Directive 2000/60/EC), the regulation of both point and diffuse sources of P is vital in order to obtain all water bodies achieving 'good status' by 2017. However, the impact of climate change and its influence on P across the catchment environment is essential to consider and therefore respond to, if we are to improve the quality of our water, and thus ensure future ecosystem service delivery of which many are underpinned directly and indirectly by water quality (Keeler et al., 2012).

The IPCC 5th Assessment report predicts with a 'high degree of confidence' that areas such as the UK will experience extremes of precipitation and heat (IPCC, 2013). UK Climate Projections 2009 (UKCP09) suggest that as a result of such extremes we will experience hotter, drier summers and warmer, wetter winters into the 2100s (Murphy et al., 2009). Certainly, such predictions suggest the intensification of extreme precipitation events on both daily (Trenberth et al., 2003) and sub-daily timescales (Kendon et al., 2014). No doubt the UK will experience divisions in response between the north and south due to the variability of the UK climate. In both the south and the north of England, high resolution models (1.5 km) suggest increases in hourly rainfall intensities in winter, but also an intensification of short-duration events in summer which exceed thresholds indicative of flash flooding (Kendon et al., 2014). This poses a significant variance of risk of P transfers between summer and winter months and thus presents a challenge to the policy maker in formulating effective adaptation and mitigation measures, in terms of pollution and flood management, to such climate extremes. These climate extremes will also have a significant impact on the dynamics of P across the catchment environment; the P transfer continuum is consequently a useful tool to explore these dynamics and impacts. It is therefore vital that our knowledge of each tier of the continuum improves at a range of scales, which is the premise of this study.

1.2 'Estimating Nutrient Transport in Catchments to 2050'

My work draws closely on the work carried out on the NERC funded 'Estimating Nutrient Transport in Catchments to 2050' (NUTCAT 2050) project, and the UK National Demonstration Test Catchments (DTC) (McGonigle et al., 2014): Eden (Cumbria), Wensum (Norfolk), and Avon (Hampshire). Within this a framework for predicting nutrients (namely P) under different land use and climate change scenarios, in order to improve understanding of nutrient movement and aid land management planning was developed by a large consortia. This included a team of fifteen researchers, which included myself, from nine different institutions from across the UK.

1.3 The need for research

Understanding the potential impacts of future climate change on the P transfer continuum is critical in order to inform and build effective mitigation and adaptive policies to P pollution in the water environment. However, there is a current lack of integrated empirical understanding and evidence of the potential impacts of climate change on the P transfer continuum. This work is also in order to critically assess, inform and improve processes based model predictions of the future potential of solubilisation of P under climate change. My overall aim is to gain a better understanding of the possible changes which will be caused by climate change, this includes both individual processes (e.g. mobilisation) and catchment scale processes which encompass the P transfer continuum, specifically in a rural headwater catchment (Newby Beck, Eden DTC). I will therefore be able to highlight the possible risks of climate change exacerbating, rather than changing, the processes described in the P transfer continuum for the Newby Beck catchment. This will contribute to a renewed future P transfer continuum that can be used by both policy and land managers alike to inform land management decision making.

1.4 Objectives

My overall aim is to gain a better understanding of the possible changes which will be caused by climate change; this includes both individual processes (e.g. mobilisation) and catchment scale processes which encompass the P transfer continuum, specifically in a rural headwater catchment. I hypothesise that the P transfer continuum will alter under climate change, as the rates of P mobilisation, transfer and efficiency of delivery will increase, specifically in the Newby Beck catchment, and that radical interventions will be required to slow processes at each tier and mitigate the impacts of eventual P pollution. Specific objectives are:

- To appraise the likely changes to the P transfer continuum under climate change in regions of the world which already have extensive P issues and challenges by exploring the current literature.
- To identify whether extreme summer conditions predicted in the UK will yield and increase of mobilisation of P via solubilisation from three DTC soils. I hypothesise that changes in future patterns of drying and re-wetting will affect the amount of soluble reactive phosphorus solubilised from three UK soils.
- To explore the impact of climate change on catchment P retention in the three DTC catchments as a function of: (a) hydrological regime and residence time,

(b) net biochemical retention, and (c) ecological response. I hypothesise that climate change will alter catchment P retention in these three contrasting UK catchments. I postulate that the degree of change experienced as a result of perturbation by climate change is determined by the sensitivity of a catchment to changes in hydrology, biogeochemistry and ecology which influence the retention of P in the land-water continuum.

- To improve understanding of in-stream retention of P and the influence of anthropogenic sources of P at the headwater scale. I hypothesise that anthropogenic point sources of P can alter the degree of retention of P even at the headwater scale where agricultural diffuse sources dominate.

1.5 Content

In my research I use the national DTC sites, Newby Beck (Eden, Cumbria), Blackwater (Wensum, Norfolk) and Wylye (Avon, Hampshire) as examples that represent typical UK catchment typology and agricultural activity. I pursue the following objectives to understand the potential changes to P transfer continuum under climate change:

Chapter 2: ‘The phosphorus transfer continuum under climate change’: Literature study

- I explore how the P transfer continuum may be altered by climate change predictions in countries which are known to have an extensive eutrophication issues and challenges.

Chapter 3: ‘Determining the effect of drying time on phosphorus solubilisation from agricultural soils under climate change’: Laboratory Study

- I aim to assess the impact of predicted (UKCP09) summer hot, dry periods followed by high intensity rainstorms on the mobilisation by solubilisation of P from three different soil types (two soils from Eden DTC and one from Wensum DTC) which represent three different land management practices.
- I hypothesise, using an amended small scale laboratory method by (Blackwell et al., 2009), that I hypothesise that changes in future patterns of drying and re-wetting will affect the amount of soluble reactive phosphorus solubilised from three UK soils.

Chapter 4: ‘The effect of climate change on phosphorus retention in three contrasting UK headwater catchments, does catchment sensitivity matter?’: Model based study

- I postulate that the sensitivity of a catchment to climate change will be determined by catchment characteristics (e.g. hydrological behaviours, biogeochemistry and ecology) which underpin the retention of P in the landscape.
- I hypothesise a) that climate change will alter catchment P retention in the three contrasting UK DTCs (Newby Beck (Eden), Blackwater (Wensum) and the Wylye (Avon)) and b) that the degree of change experienced because of perturbation by climate change will be determined by the ability of each catchment to retain P.
- I use the process-based catchment model HYPE (Hydrological Predictions in the Environment) outputs for baseline and climate change scenarios (Low, Medium and High, 2050s and 2080s) and apply extended end-member mixing analysis methodology to estimate catchment retention under these scenarios for the three contrasting UK catchments.

Chapter 5: ‘The retention of phosphorus in a small rural headwater stream and the effects of anthropogenic inputs’: Field based study

- I aim to improve understanding of in-stream retention of P and the influence of anthropogenic sources at the headwater scale in Newby Beck, Eden DTC.
- I hypothesise that anthropogenic point sources of P can alter the degree of retention of P even at the headwater scale where agricultural diffuse sources dominate. I use load apportionment modelling to show where point sources dominate.
- I explore how hydrological regime and residence time, using mass balance calculations, affect the buffering capacity of this catchment to P pollution.

- Continuous flow and P are measured alongside fortnightly spot-sampling of Cl^- and P to calculate "conservative" P, and compared to "non-conservative" P in each tributary to deduce where retention is occurring and what spatial and temporal factors are influencing retention processes.
- Bed sediment sampling work will be used to support the identification of these critical areas of retention.

Chapter 6: 'Conclusions'

> This chapter aims to synthesise the learning from the above chapters to identify the impacts or changes to the P transfer continuum under climate change, using the DTC Newby Beck as a critical example. I also address the hypothesis that the P transfer continuum will alter under climate change as the rates of P mobilisation, transfer and efficiency of delivery will increase, specifically in the Newby Beck catchment, and that radical interventions will be required to slow processes at each tier and mitigate the impacts of eventual P pollution.

This study is based on the three major components outlined above which incorporate laboratory and field-based study, alongside model acquisition and data analysis. These are essential in order to develop empirical evidence of the movement of P under climate change in both soils and water.

1.6 References

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2 The phosphorus transfer continuum under climate change

2.1 Abstract

Phosphorus (P) inputs and their fate in the environment contribute to poor water quality and the degradation of linked ecosystem services at great cost to society. Climate change is likely to alter the forms and timings of P fluxes and their ecological impact, but these effects are uncertain and need to be considered to inform future catchment management. Using the P transfer continuum framework (Haygarth et al., 2005), I appraised the potential changes in P transfer and associated eutrophication risk that may occur under future climate change to help inform future research priorities. My appraisal suggests predicted changes in temperature and patterns of precipitation will increase P export from agricultural land and increase eutrophication risk, and that regional and seasonal variation in this response will be greatly accentuated. There is therefore little evidence to suggest that the societal costs of eutrophication will decrease in the future and are more likely to increase. I therefore propose a new P transfer continuum framework that highlights the need for further research and stakeholder engagement to make the necessary land management adaptations to ensure future food and water security.

2.2 Introduction

The earth system is under pressure from a continually expanding and urbanising population, which is resulting in potentially catastrophic changes to the atmosphere, hydrosphere and pedosphere (Rockstrom et al., 2009). Agriculture underpins human society through the provision of food, yet it contributes to substantial alterations in our earth system and climate. The most recent Intergovernmental Panel on Climate

Change (IPCC) forecast changes in global precipitation and temperature that will, in turn, have a profound effect on agricultural functioning, resilience and environmental impact. To expand agriculture and meet the demand for food, vast amounts of reactive nitrogen (N) manufactured from the atmosphere (two-fold increase since mid-1900s), and reactive phosphorus (P) mined and purified from phosphate rock (PR) (quadrupled since mid-1900s), have been applied to fields (Galloway et al., 2003; Smil, 2000). These inputs have entered a largely one-way flow from farms to cities to streams, lakes, rivers and oceans, resulting in dramatic impairment to freshwater and marine ecosystems (Elser and Bennett, 2011). Even without the perturbations of climate change, significant effort is needed and already being made to curb the detrimental impacts of agriculture on the environment (Sharpley et al., 2015; Tilman et al., 2002). However, with the uncertainties of climate change, the environmental benefits of these efforts may become increasingly difficult to see or inadequate (Ockenden et al., 2017), especially at the catchment scale where hydrology drives nutrient loss from agriculture land into water bodies.

To help unravel the complexities of the transfer of P to water in rural landscapes (Scholefield et al., 2013), the P transfer continuum was developed as a conceptual framework for the movement of diffuse sources of P from land to water, and for evaluating options for mitigation (Haygarth et al., 2005; Withers and Haygarth, 2007). It adopts a simple four-tiered model of source- mobilisation- transport (or otherwise called delivery)-impact to emphasise the range of scales and complexities of P transfer, and is similar to the classic source-pathway-receptor model (Haygarth et al., 2005; Withers and Haygarth, 2007). In this model I include the addition of point sources, which often enter between the tiers transport and impacts (Figure 2.1), a vital source of particularly soluble P to river reaches from headwaters to seas. Here I use the P transfer continuum as a framework to consider the potential changes that may occur under climate change, to better understand the impact of future drivers on water quality and to prioritise where research is needed to quantify and mitigate the risks to ensure food and water security for future generations. I focus on developed nations where eutrophication issues are prominent whilst highlighting the wider global and regional differences that may occur.

2.3 Climate change predictions

The IPCC predicts with a ‘high degree of confidence’ that global temperatures will increase by 1.5ºC by 2100 (IPCC, 2014). Even if emissions are curbed and global temperatures do not increase significantly above this level (yet it is likely that, if business continues as usual, warming could reach 4.8ºC) the response of ecosystems to change will last centuries (IPCC, 2014). The degree of change and impact will vary greatly across spatial (global and local) and temporal (e.g. seasonal) scales (Table 2.1). In North America, predictions are that the warming signal will very likely exceed natural variability by 2046-2065 (RCP 4.5 medium emission scenario) in all seasons, leading to a 2 to 4 fold increase in heatwave frequency (Christensen et al., 2013). Patterns of precipitation will also change (Table 2.1); for example, extreme precipitation event frequency will increase in North America (Groisman et al., 2012; Ning et al., 2015; Schoof, 2015; Villarini et al., 2013), and Asia (Christensen et al., 2013). Extreme hot days (>35 ºC) in Australia are also predicted to substantially increase (Melbourne a 70-190% increase) (ACCSP, 2007). In addition, extreme precipitation events are also predicted especially during summer and autumn months in Australia, these extremes are more likely than increases in mean precipitation (ACCSP, 2007). In Europe, the IPCC predicts, with ‘high confidence’, continued warming, and increased frequency, length and intensity of warm spells (Christensen et al., 2013). Current high resolution climate models (1.5 km grid spacing), also indicate that hourly rainfall intensities will increase in both summer and winter months in the south (Kendon et al., 2014) and in the north of England, for example. Across the globe different climatic changes will occur, but extremes of climate, e.g. precipitation or temperature events, are probably the most frequently predicted under IPCC climate change scenarios and thus are prominent concerns. These highly variable annual shifts in temperature and precipitation will affect the P transfer continuum and extremes could cause major fluxes of P from land to water, and are therefore critical to consider.

Table 2.1 Summary of IPCC 5th Assessment global climate predictions of annual temperature change (°C) and precipitation change (%) for RCP 4.5 (medium emissions) to 2065 for Asia, Australasia, Europe and North America (amended from IPCC (2013)).

Global region	**Scenario**	**Surface annual temperature change (°C)**		**Precipitation change (%)**	
	RCP 4.5				
	2065	mean	likely range	mean	likely range
Global		+1.4	+0.9 to +2.0		
Asia	East	+1.9	+0.9 to +3.0	+6	-1 to +18
	Central	+2.2	+0.7 to +3.6	+2	-13 to +16
	South	+1.6	+0.8 to +2.5	+7	-2 to +26
Australasia	North	+1.6	+0.7 to +2.6	-2	-21 to +11
	South	+1.3	+0.6 to +1.7	-1	-18 to +10
Europe	North	+2.0	-0.5 to +3.8	+5	-5 to +17
	Central	+1.9	+0.4 to +3.2	+3	-6 to +9
	South	+1.7	+0.7 to +3.1	-5	-14 to +3
North America	West	+2.0	+0.9 to +3.4	+3	-3 to +11
	Central	+2.0	+1.0 to +3.4	+3	-7 to +14
	East	+2.1	+1.0 to +3.5	+5	-1 to +14

2.4 The phosphorus transfer continuum under climate change

Since the P transfer continuum attempts to account for the interconnected, dynamic nature of P in the landscape (Haygarth et al., 2005), then every component of this continuum will likely be impacted by climate change (Figure 2.1), leading to variable P export and ecological impacts in different regions and catchments. The sensitivity of individual catchments to climate change is inherently dependent on catchment typology and the P pressure imposed by human activities, i.e. no two catchments will respond the same (Arnell et al., 2015). For instance, headwater catchments may directly experience greater sensitivity to changes in source, mobilisation and transport as precipitation patterns increase in frequency and intensity. Conversely, lowland catchments may indirectly show greater sensitivity to sources and impacts as the cumulative effects of catchment P inputs cascade towards the coastal zone (McDonald et al., 2016).

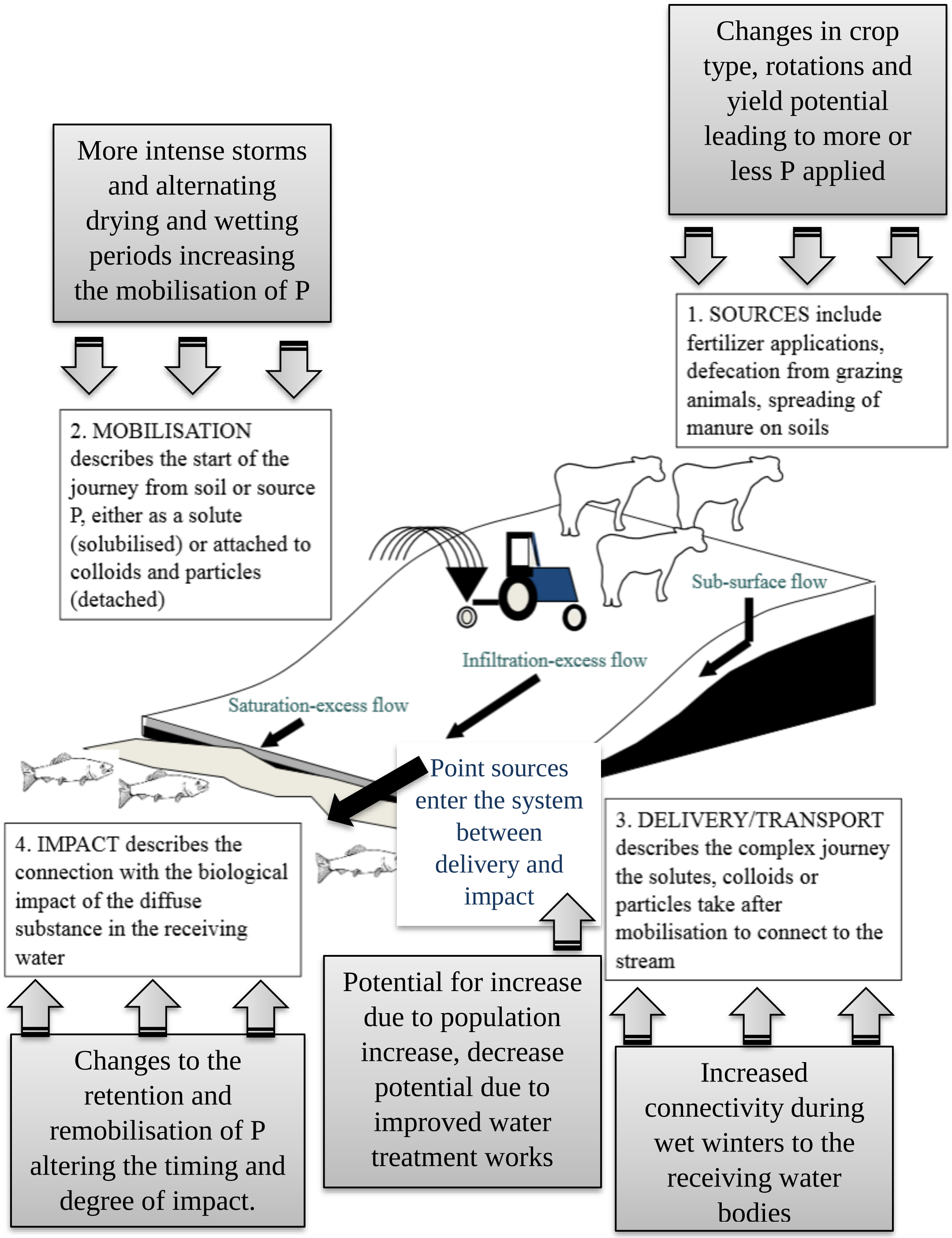


Figure 2.1 The phosphorus transfer continuum under climate change, describing the potential changes to 1) sources of P, including the addition of point sources; 2) mobilisation of P; 3) transport of P and 4) the impact of P in receiving waterbodies. Amended from Withers and Haygarth (2007).

2.4.1 Tier one: sources

"Sources" of P include direct inputs of P to the agricultural system, such as fertilisers, imported animal feed stuffs and the application of "new" manure (imported to the farm) and recycled bio-resources to soil, and crop residues (Haygarth et al., 2005). Inputs critically differ in amount, form and timing between current and past land use and land management (Foley et al., 2005; Hale et al., 2015), and influence the amount of total P exported in the following tiers of the continuum through effects on P bioavailability and accessibility to rainfall-dependent runoff pathways (Chen et al., 2015; Han et al., 2011; Hong et al., 2012). In addition, point sources entering the system (Figure 2.1) can critically regulate the amount of soluble P entering the system, and often agricultural sources can be falsely apportioned if point sources are not adequately accounted for (Jarvie et al., 2012).

Importantly, climatic changes (increasing carbon dioxide (CO_2), elevated tropospheric ozone (O_3), rising temperature trends and changes to precipitation) will alter the ability of global regions to grow specific crop types for both human and animal consumption, and is consequently a threat to sustaining global productivity and meeting food demands (Lobell and Gourdji, 2012). For example, climate variability can explain >60% of yield variability in areas such as the Midwest U.S. and the Chinese Corn Belt for maize, and Western Europe and Australia for wheat (Ray et al., 2015). Increased frequency of extreme temperatures in some U.S. states is likely to cause substantial declines (63-82% highest emissions scenario) in yields of corn and soybeans in the long term (Schlenker and Roberts, 2009). Changing crop patterns and yield potential will consequently alter decisions on P inputs because these are currently intrinsically linked to crop P offtake in current fertiliser recommendations systems (Defra, 2010; Jordan-Meille et al., 2012; Syers et al., 2008). Whilst, increased temperatures in boreal and some temperate regions will extend or shift growing seasons (Lobell and Gourdji, 2012), even allowing for double-cropping. For example, elevated temperatures in Europe are likely to intensify agricultural production in the north whilst reducing intensity in the south where precipitation is limiting, in addition to early sowing to avoid the hotter, drier summers predicted (Olesen et al., 2011). Enhanced favourable conditions in some regions, such as the north of Europe, could thus increase nutrient inputs as either crop or animal outputs intensify, consequently altering the pattern of future P inputs. Global trade and market demands will accordingly shift to reflect these changes in inputs, some countries increasing their requirements whilst others reducing imports. These trade patterns will therefore alter both national and regional P budgets (MacDonald et al., 2015; Nesme et al., 2016), and impact on the amounts of legacy P accumulating in soils (Powers et al., 2016). Coupled with the increasing demand for P-rich diets, this will also augment P migration into urban areas and subsequently enhance effluent P loss downstream.

Additionally, animal husbandry contributes to climate change adding to CO_2, N_2O and CH_4 emissions, as well as large sources of P to the environment through direct defecation and application of manures. By 2050 meat production for human consumption is predicted to double from ~56 billion (animals reared) (Koneswaran and Nierenberg, 2008), consequently more P will be sourced to the environment. In regions such as Asia the intensification and industrialisation of animal rearing yields P fertiliser for croplands, which are likely to be applied to nearby fields concentrating soil P sources and localising risks of P pollution hotspots (Thorne, 2007).

Therefore, high inputs of nutrient fertilisers will likely remain as efforts to increase yields continues unless innovation technologies can uncouple the link between crop production and nutrient requirements (Sylvester-Bradley and Withers, 2011). Mueller et al. (2012) suggest that to close global yield gaps, whilst eliminating over-use, P inputs could be reduced by 2% worldwide, yet if inefficiencies are not addressed a 16% increase could occur. Whilst Sattari et al. (2012) suggest that global P application rates per hectare will increase, despite including residual soil (legacy) P, therefore yielding global P input to croplands at 1,200 million tons P for 2008-2050. Yet, Cordell et al., (2009) suggest that global phosphate production will peak in 2030, and therefore call for P sustainability to come higher on the food security agenda. There is therefore scope to not only improve inefficiencies in P use, but to minimise crop P requirements by reducing crop tissue P, which will have benefits to growth and nutrition along the food chain whilst reducing P sources (Withers et al., 2014).

Sources of P are consequently likely to increase globally, but advances in P stewardship to reduce P inputs, recycle and re-use P and improve efficiency (Withers et al., 2015) can help minimise the environmental impacts (Figure 2.2). For example, under wetter soil conditions in winter, timing of P inputs will become more critical and may require the introduction of closed periods for spreading of fertilisers and manures.

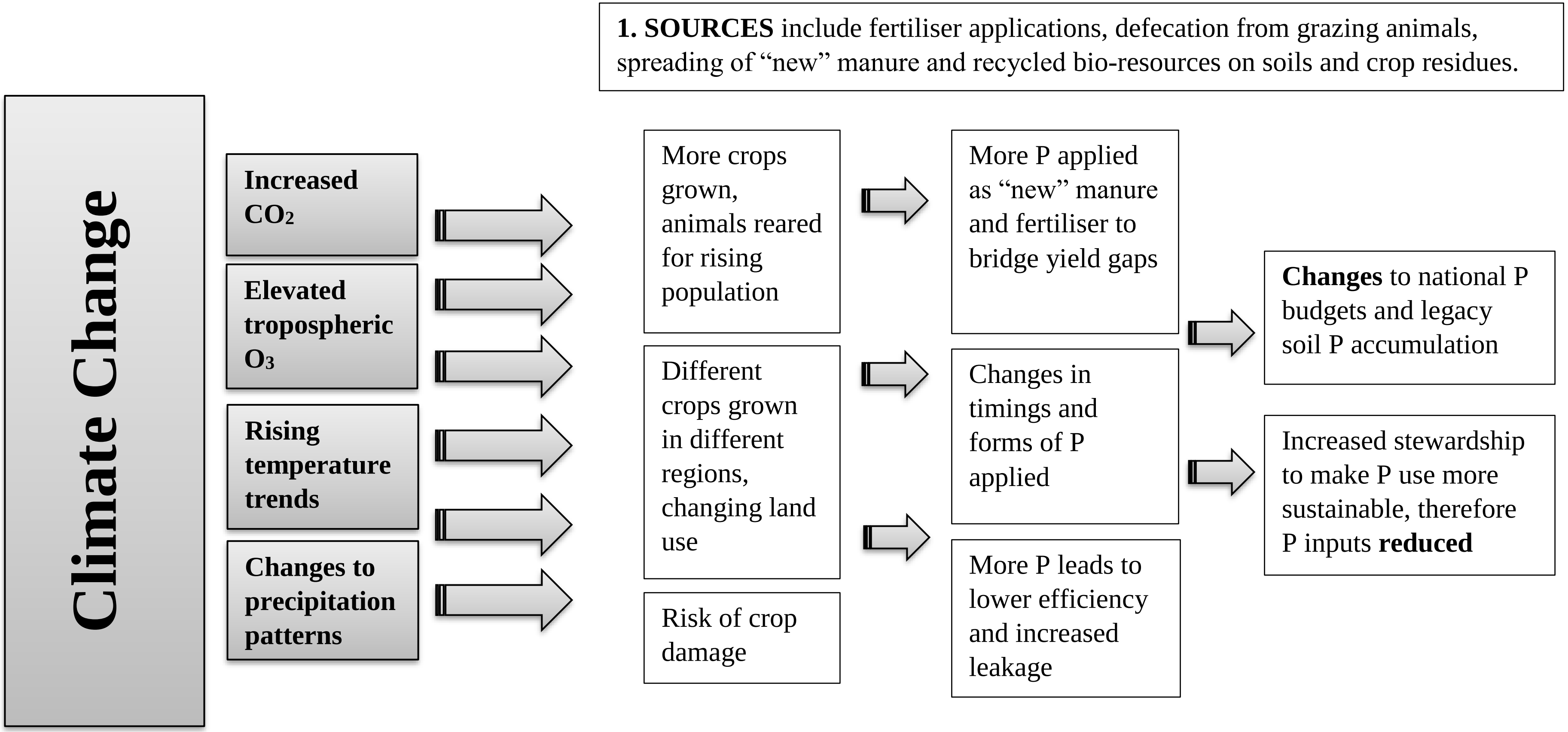


Figure 2.2 The likely changes to sources of phosphorus (P) as a result of climate change, which include increased carbon dioxide (CO_2); elevated tropospheric ozone (O_3); rising temperature trends; and changes to precipitation patterns.

2.4.2 Tier two: mobilisation

The mobilisation of P has been described as the “start of the journey” (Macleod et al., 2012), including both the solubilisation and detachment of P in land runoff (Haygarth et al., 2005), of which rainfall and temperature are critical regulators. Solubilisation includes biological (Gordon et al., 2008; Turner and Haygarth, 2001) and chemical (Blake et al., 2002) processes that release soluble P into runoff water or leachate, whilst detachment is the physical dispersion of soil particles and colloids to which P is attached (particulate P) (Macleod et al., 2012; Quinton et al., 2001). Significant changes to both the solubilisation and detachment of P can therefore be anticipated as soil physical, chemical and biological processes are altered by climate change (Figure 2.3).

2.4.2.1 Soil physical processes affecting phosphorus mobilisation via detachment

Under hotter, drier conditions, soil carbon (C) will oxidise causing a reduction in soil structural integrity due to poor aggregate stability and formation (Lal and Shukla, 2004), and the disruption of organic matter coatings on clay and mineral particle surfaces (Bartlett and James, 1980). This will alter both abiotic and biotic soil properties, affecting P dynamics (Blackwell et al., 2009; Xu et al., 2011) and increase both the mineralisation of organic P (Condron et al., 2005) and the risk of detachment of soil particles, and therefore particulate P, by rain splash and overland flow (Macleod et al., 2012) (Figure 2.3). For example, slaking of unstable soils caused by rain splash increases soil particle dispersion and exposes particle surface sites for P desorption (Bünemann et al., 2013; Chepkwony et al., 2001). The intensity of rainfall storms also influences the amount and size of particles detached; smaller storms primarily detach a greater proportion of finer clay particles which have a greater enrichment of P than larger storms (Quinton et al., 2001). Large, intense storms can however account for a significant proportion of annual total P transfer (Chow et al., 2017; Fraser et al., 1999; Ockenden et al., 2016; Sharpley et al., 2008), but the risk of detachment is highly dependent on soil type susceptibility to particle dispersion, the amount of bare soil present, and is therefore controlled ultimately by land use, and land management (Macleod et al., 2012). Yet, increased intensity storms (which may be more frequent) will detach more soil particles from surfaces due to greater hydrological energies, irrespective of land use, especially if following extended dry spells. Pulsed precipitation bursts have also shown to give rise to increased runoff and sediment transportation (de Lima et al., 2013), perhaps due to the formation of micro-cracks which can occur even in wet soil (Grant and Dexter, 1989), thus in this case we might expect an increase in the risk of *mobilisation* and *transport* of P (Figure 2.3).

2.4.2.2 Soil chemical processes affecting phosphorus mobilisation via solubilisation

Climate predictions suggest longer periods of wet weather, especially in temperate regions such as the UK (Murphy et al., 2009). Hence, we might expect soils to remain moister, and experience longer periods of waterlogging. If soil conditions consequently become anaerobic, even in small zones and for limited periods (Tiedje et al., 1984), Fe-oxides change their oxidation states and release P (Obour et al., 2011; Scalenghe et al., 2010). Phosphorus is then either retained in the soil or is liable to leaching (Scalenghe et al., 2010; Scalenghe et al., 2014). Pulsed cycles of wet-dry regimes cause more P to be rapidly solubilised into solution (via reduction and oxidation of Mn and Fe-oxides releasing occluded or absorbed P), before reaching a peak and being re-adsorbed (Scalenghe et al., 2012), as Fe-oxides can retain some of their sorption capacity in the reduction process (Mello et al., 1998). Temperature is also a critical control on the rates of P diffusion from soil to solution and is likely to increase as soils warm and remain warmer for longer, especially when the soil is moist (Dijkstra et al., 2012). It is likely that soils which remain wetter for longer under climate change will be more vulnerable to release of soluble P, especially those with high soil P fertility which maintain higher concentrations of P in solution; the implications of this have not been tested.

Increased temperatures may in some regions yield drier soils; dry soils compared to wet soils yield more P upon re-wetting of which a significant portion can be attributed to non-microbial organic and inorganic P (Blackwell et al., 2009; Bünemann et al., 2013; Butterly et al., 2009; Butterly et al., 2011). The oxidation of soil organic carbon $^{-}$Fe and $^{-}$Al associations can be induced by drying (Bartlett and James, 1980; Haynes and Swift, 1985; Schlichting and Leinweber, 2002), resulting in the release of organic P and the subsequent mineralization of inorganic P (Styles and Coxon, 2006). However, there is some evidence to suggest that low moisture contents can buffer against P loss even if P has been applied to the soil (Styles and Coxon, 2007), probably due to accelerated fixation and isotopic exchange reactions (Sheppard and Racz, 1984). The impact of temperature on the bioavailability and cycling of P will therefore differ between soil types and plant communities (Vincent et al., 2014), and subsequently may have a positive or negative impact on mobilisation.

2.4.2.3 Soil biological processes affecting phosphorus mobilisation via solubilisation

Soil microbial biomass also has an influential role to play in the cycling of P (Achat et al., 2012; Bünemann et al., 2013; Turner and Haygarth, 2001), and is likely to be influenced by climate change (Figure 2.3). After a drying and re-wetting (DRW) event the cell lysis of microbes can kill between 17 and 58% of the community (Kieft et al., 1987; Salema et al., 1982), resulting in an increase in soluble P (mobilisation via solubilisation). This response by the microbial community to stress is influenced by the historic moisture regime of the soil, for if the disturbance is within the historical range of variability the community may be, for a time, resistant to the imposed stress (Chowdhury et al., 2011; Evans and Wallenstein, 2011). Microbial community structure and resilience can therefore determine the solubilisation of P. Yet, the contribution of P from the microbial biomass may become less important in future climate scenarios (e.g. as hotter, drier summers become more frequent), because communities that are regularly exposed to moisture stresses can adapt (Pailler et al., 2014), resulting in a lack of a response after DRW (Butterly et al., 2011; Fierer et al., 2002; Wang et al., 2013). However, in the near term it is likely that in regions where community resilience is not currently present, extreme heat followed by intense rainfall will yield greater risks to microbial P mobilisation via solubilisation.

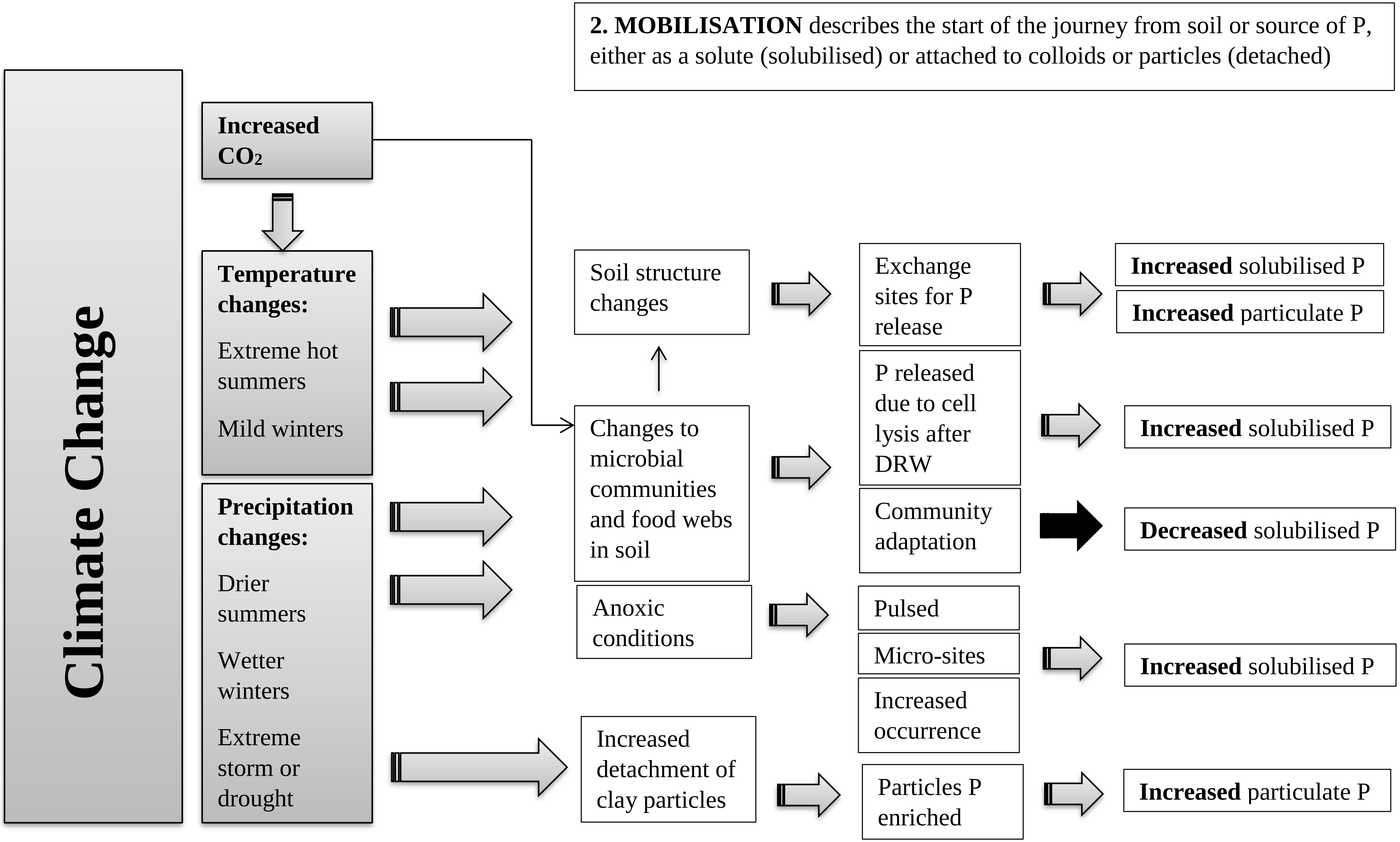


Figure 2.3 The key processes which may be influenced under climate change in tier two of the phosphorus (P) transfer continuum: mobilisation. DRW = drying and re-wetting.

2.4.3 Tier three: transport/delivery

Transport, sometimes called delivery (Beven et al., 2005), includes the pathways of P transfer (Schoumans et al., 2014), that occur via overland flow (via infiltration excess or saturation excess surface runoff), or sub-surface drainage. The form of P mobilised influences the transport route and cycling of P along the land-water continuum. As climate change will influence the form of P mobilised it will therefore also alter pathway dominance and the speed of water routing (Figure 2.4). This will be driven by hydrology and landscape topography, soil characteristics, and vegetation cover (Haygarth et al., 2005), for example, export rates will likely be reduced in catchments with dense crop cover protecting the soil from the formation of transport pathways (especially in winter). Whilst the opposite will be achieved if vegetation cover is poor, especially in terms of particulate P transport, consequently impacting on the following parts of the P transfer continuum.

As climate change alters the degree of intensity and duration of extreme precipitation events, the rate and extent of transport of soil particles (particulate P) by overland flow will increase (Martınez-Casasnovas et al., 2002). Such extremes may lead to an increase in gully and rill erosion (Mullan, 2013; Nearing et al., 2004), especially on hillslopes; potentially resulting in increases to annual erosion rates across many parts of the world (Favis-Mortlock and Boardman, 1995; Favis-Mortlock and Guerra, 1999; Nearing et al., 2004), and increased particulate P transport. Response to extreme events and the form of transported P, however is highly dependent on soil properties, e.g. hydraulic conductivity (McDowell et al., 2004; O'Neal et al., 2005), and indirectly on land use and management (Mullan, 2013; Mullan et al., 2012; O'Neal et al., 2005).

Regions which become drier may lose particulate P transport potential via erosion as it ceases or declines (Mullan et al., 2012). Yet, if soils are subject to extensive cracking, soluble P can undergo significant downward movement through the soil profile (Beauchemin et al., 1998; Pierzynski et al., 2005; Simard et al., 2000), which is especially important if heavy storms occur. However, dry soils can produce more particulate P in comparison to wet soil due to the effects of slaking and dispersion of particles, when overland flow suddenly occurs (McDowell et al., 2004). Dry soils are also particularly vulnerable to aeolian erosion, and can critically reduce the bioavailable P content of soil that is bound to the smallest soil particles (Katra et al., 2016). Prolonged dry spells also increase the hydrophobicity of soil surfaces consequently increasing the routing flow in favour of surface runoff (Shakesby et al., 2000), therefore potentially contributing to significant loads of particulate P to receiving water bodies (Sharpley et al., 2013).

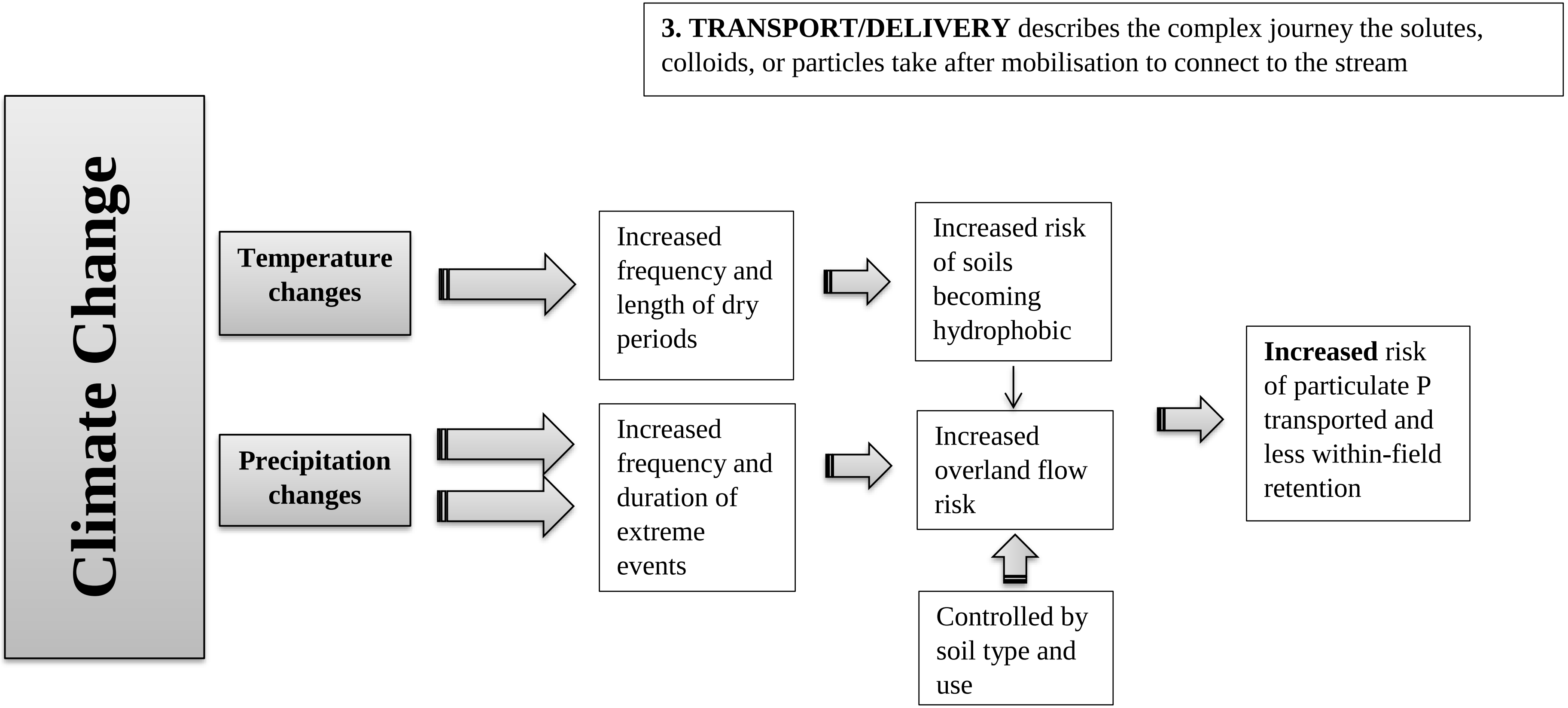


Figure 2.4 The potential impacts of climate change (namely temperature and precipitation changes) on tier three of the phosphorus transfer continuum: transport/delivery.

2.4.4 Tier four: impact

‘Impact’ encompasses the ecological response to P export from point and diffuse sources. This is regulated by the biological, chemical or physical processes that govern in-stream retention (deposition of particulate P, uptake of soluble P by aquatic biota) and remobilisation of these biotic and abiotic P stores (the net effects of which are generally poorly understood (Jarvie et al., 2013; Sharpley et al., 2009)). The result is varying scales of impact across the catchment environment from headwaters to seas (Jarvie et al., 2011; Kemp et al., 2009). In general UK headwater streams are less impaired than downstream rivers, and impairment varies across catchment typology, lowland-high-alkalinity catchments, for example, are considered the most impaired (Jarvie et al., 2018). This variation of impact with scale will likely alter under climate change (Figure 2.5), resulting in the need for tailored management strategies to decrease or adapt to the changes caused by climate change.

Under climate change, periods of low flow or complete cessation of flow, and increased stream temperatures are likely during summer/autumn months; at these times the riparian environment will be at most ecological risk (Scavia et al., 2014; Withers and Jarvie, 2008). Reduced capacity for dilution and increased temperatures will accelerate nutrient cycling and biomass growth, consequently lowering dissolved oxygen concentrations, reducing the self-cleansing capacity of waterbodies and leading to increased eutrophication risk (Kundzewicz and Krysanova, 2010; Whitehead et al., 2009). The proliferation of algae may increase as streams stay warmer for longer, potentially affecting macrophyte biomass, invertebrate and fish population health (Wade et al., 2002), and biodiversity as more tolerant species survive (Whitehead et al., 2009).

During winter, increased precipitation will increase flows, and this might be expected to increase the capacity for dilution by water from less intensive upland areas, reducing the impact of P in the water environment in terms of exceeding P status restrictions. However, >80% of total P load can be transported out of headwater catchments during high flow events (Bowes et al., 2003; Jordan et al., 2007; Ockenden et al., 2016), resulting in high concentrations of P (Jarvie et al., 2002) and poor water quality at these times (Ockenden et al., 2016). Ockenden et al., 2017 show that under climate change scenarios increased winter rainfall in three UK headwater catchments will result in an increase of TP load (up to 31%). These high flow events will also move vast amounts of sediments downstream, moving P-enriched sediments to coastal areas, and increasing the risk of impact during summer months. Jarvie et al., 2018 concluded that the degree of nutrient enrichment in UK catchments increases with scale due to the cumulative effect of anthropogenic nutrient enrichment. Consequently, if high flows increase in frequency across winter months this cumulative impact of P with scale will likely increase.

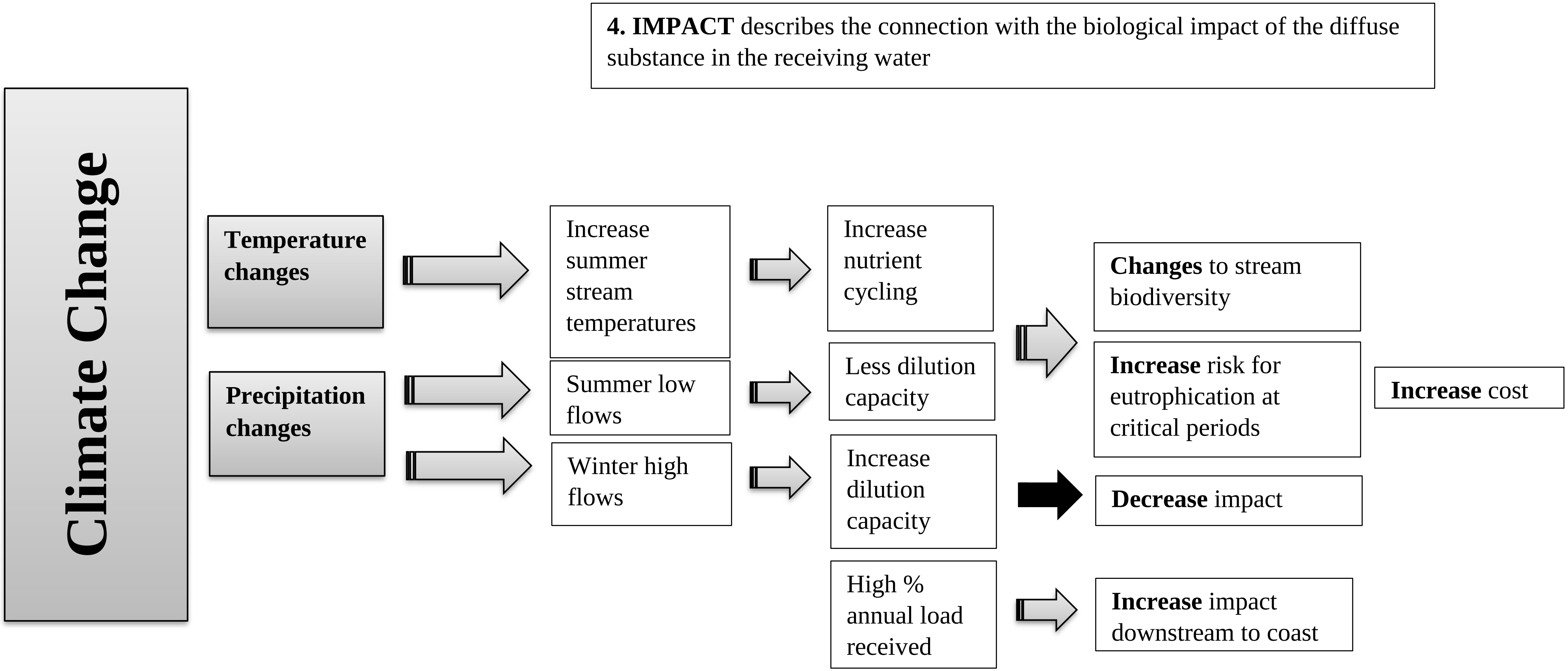


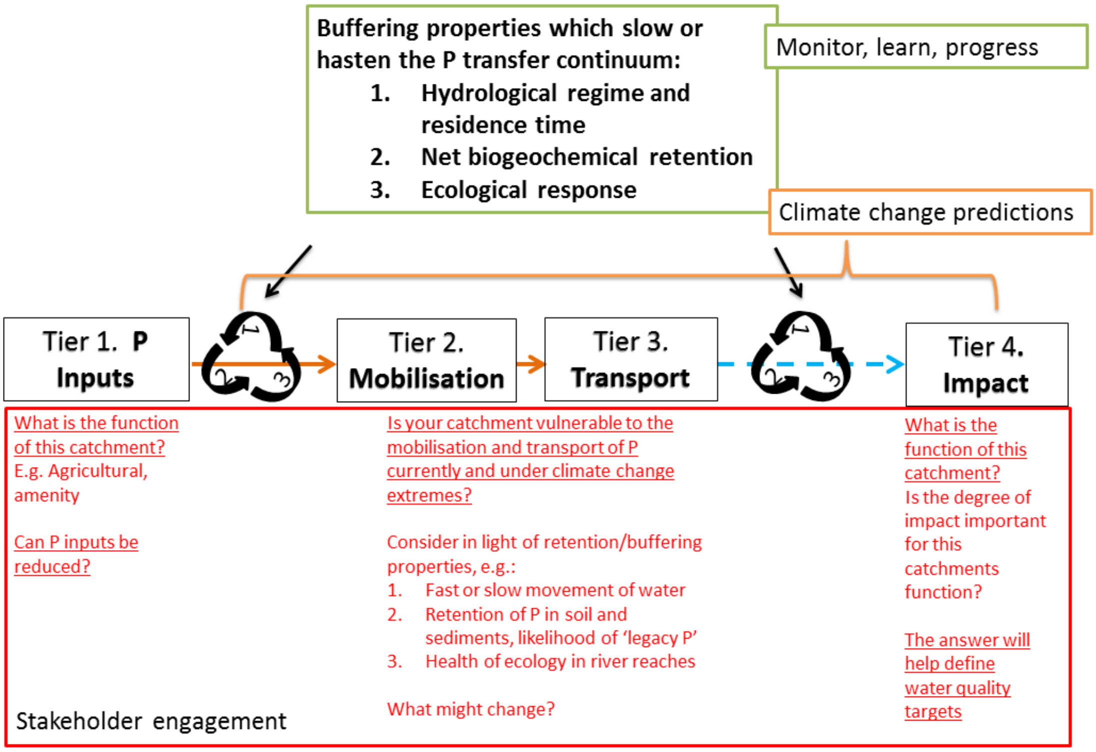
Figure 2.5 The final tier of the phosphorus transfer continuum: impact, and the possible changes under climate change (namely temperature and precipitation changes).

2.5 Implications for policy and decision makers

Under current activities climate change will alter the P transfer continuum and likely lead to the increased degradation of water quality both upstream and downstream (Figure 2.1 – 2.5). Consequently, it calls for climate change to be taken seriously in forming new effective policies which preserve the health of UK water bodies, the sustainability and profitability of UK agriculture, the enjoyment and amenity value of our water courses, and avoid astronomical financial costs into the future. The UK currently stands perfectly poised to create new policies which implement a climate resilient Catchment-Based Approach (CaBA) at the management (or stakeholder) level and at the policy level. This means that although the Catchment Sensitive Farming scheme has successfully engaged farmers and improved awareness of the use of best practices, the predicted 5-10% improvements in nutrient loads is unlikely to do the job (Kleinman et al., 2015). We perhaps require a much more potent plan of action that doesn’t require seeing how best practice activities and gentle coercion via cross-compliance pans out (Kleinman et al., 2015; McGonigle et al., 2012). The difficulty lies in the inherent uncertainty in catchment response to remediation efforts, as each has different internal sensitivities and buffering components which determine its recovery trajectory (Jarvie et al., 2013). Doody et al. (2014) provide a framework which can assist in the prioritisation of catchments for water quality or agricultural intensification, suggesting where compliance gaps are small recovery is possible but where large compliance gaps exist recovery may be unfeasible. The problem with climate change is that we may find ourselves deeming all catchment recovery unfeasible or ineffective in the years to come. The degree of mitigation and adaptation needed to curb the flow of P through the environment requires imaginative, collaborative, critical thinking from all stakeholder groups and policy makers in order that the CaBA approach can be effective at both levels. So, although complex, an effective strategy may be to design and implement regulation at the catchment scale, as well as having general state level regulation. For this to be successful it must be acknowledged that we live in a consumer, market driven society, for if society doesn't care, we would simply be implementing legislation farmers cannot afford to take on as the consumer is not paying for "an environmentally friendly product". So, to achieve such a challenge lies, I propose, in three core areas which require continued focus:

1. **Stakeholder engagement**. This goes beyond water companies and farmers, but into the core of a community, to engage society with their water and with those that provide their food and tend their rural environment.
2. **Climate change predictions.** Continued development in model predictions of climate change effects at local scales can help implement prioritisations for action (as Doody et al. (2014) propose), uncertain information is better than none at all.
3. **Monitor, learn, progress.** This requires continued monitoring of critical established research sites (e.g. DTCs) to continually provide new information which can improve and bolster the two above points.

I also propose a renewed P transfer continuum that can be used to frame these three core ideas, visualised in Figure 2.6. I suggest that for CaBA policies and management strategies to be successful and resilient to change all the above must be continually developed and incorporated to inform decision making.



What is the function of this catchment?
E.g. Agricultural, amenity

Can P inputs be reduced?

Is your catchment vulnerable to the mobilisation and transport of P currently and under climate change extremes?

Consider in light of retention/buffering properties, e.g.:

1. Fast or slow movement of water
2. Retention of P in soil and sediments, likelihood of 'legacy P'
3. Health of ecology in river reaches

What might change?

What is the function of this catchment?
Is the degree of impact important for this catchments function?

The answer will help define water quality targets

Figure 2.6 The renewed phosphorus (P) transfer continuum which can be used to frame the key areas of research requiring attention: Stakeholder engagement; climate change predictions; and monitor, learn, progress.

2.6 Conclusions

Phosphorus transfer through landscapes is complex and the routing through catchments generates time lags that are poorly understood in terms of their ecological impacts and management response. Climate change adds to this complexity not only because of the uncertainties in climate predictions for different regions of the world, but also because of the many different ways in which temperature and precipitation affect P mobility, retention in the landscape and ultimately ecological response. As global temperatures rise, and the frequency and intensity of extreme temperature and precipitation events increase, each tier of the P transfer continuum will be affected and both regional and seasonal differences in P transfer and eutrophication impacts are likely to become more accentuated (Figure 2.1).

Future inputs of P will be strongly influenced by changing patterns of land use and management decisions under climate change, further driven by economics and global market demands. Importantly, climate change will alter the ability of regions to grow specific crops and the length of the growing season. Mobilisation and transport of P under climate change will likely increase due to increase solubilisation and detachment, and there is little evidence to suggest, therefore, that the societal costs of eutrophication will decrease in the future and are more likely to increase. Progress towards adaptation and mitigation of potential climate change impacts on water quality and biodiversity can be made by further research, framed around the renewed P transfer continuum (Figure 2.6), into the likely changes to the P transfer continuum under different climate change scenarios.

In the following chapter I will explore the second tier of the P transfer continuum. By using a laboratory based method I address whether predicted changes in drying and re-wetting patterns will affect the mobilisation (via solubilisation) of P from three contrasting UK soils.

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3 Determining the effect of drying time on phosphorus solubilisation from three agricultural soils under climate change scenarios

In the previous chapter the implications of climate change on the entire P transfer continuum were discussed. Here, the second tier of the P transfer continuum is investigated. I use a small scale laboratory experiment to determine the implications of climate change to the mobilisation (via solubilisation) of P in three different UK soils. It should be noted that the analysis and graphical presentation of UKCP09 data was not carried out by me but another member of NUTCAT team. This work has been published in the Journal of Environmental Quality (Forber, K.J., Ockenden, M.C., Wearing, C.L., Hollaway, M.J., Falloon, P.D., Kahana, R., Villamizar, M.L., Zhou, J.G., Withers, P.J., Beven, K.J., Collins, A.L., Evans, R., Hiscock, K.M., Macleod, C.J. 22/08/2017 (2017), 46(5):1131-1136).

3.1 Abstract

Climate projections for the future indicate that the UK will experience hotter, drier summers and warmer, wetter winters, bringing longer dry periods followed by re-wetting. This will result in changes in phosphorus (P) mobilisation patterns that will influence the transfer of P from land to water. This chapter tested the hypothesis that changes in the future patterns of drying/re-wetting will affect the amount of soluble reactive phosphorus (SRP) solubilised from soil. Estimations of dry period characteristics (duration and temperature) under current and predicted climate were determined using data from the UK Climate Projections (UKCP09) Weather

Generator tool. Three soils (sieved <2 mm), collected from two regions of the UK with different soils and farm systems, were dried at 25°C for periods of 0, 2, 4, 5, 6, 8, 10, 15, 20, 25, 30, 60, and 90 d, then subsequently re-wetted (50 mL over 2h). The solubilised leachate was collected and analysed for SRP. In the 2050s warm period temperature extremes > 25°C are predicted in some places and dry periods of 30-90 d extremes are predicted. Combining the frequency of projected dry periods with the SRP concentration in leachate suggests that, overall, this may result in increased mobilisation of P; however, critical breakpoints of 6.9-14.5 d dry occur whereby up to 28% more SRP can be solubilised following a rapid re-wetting event. The precise cause of this increase could not be identified and warrants further investigation as the process is not currently included in P transfer models.

3.2 Introduction

Agricultural diffuse pollution from soil causes significant pressure on water quality (European Commission, 2012). The challenges of mitigating agricultural phosphorus (P) pollution are complex (Kleinman et al., 2015), and despite significant efforts to reduce diffuse P pollution, evidence suggests success is rare and poor water quality proliferates (Jarvie et al., 2013). Such challenges will become more prevalent as pressures driven by climate change increase.

In large parts of Europe it is likely that the frequency of warm days (i.e. heat waves) has increased (IPCC, 2014). Globally, the probability of heat waves occurring has more than doubled in some locations (IPCC, 2014). The UK Climate Projections (UKCP09) provides probabilistic estimates for temperature change and other climatic variables (which do not include event duration e.g. dry spells) in the UK. Under a medium emissions scenario, the mean annual temperature in England is projected to increase between 0.9ºC and 4.0ºC by the 2050s when compared to the 1961-1990 climate mean, with a central estimate of 3.6ºC warming. Summer temperatures are projected to rise even more, (1.0 to 4.6ºC) with a central estimate of 4.1ºC, with higher increases in the South East of England (1.3 to 4.6ºC) than the North West of England (1.2 to 4.1ºC). Summer rainfall is also likely to decrease in both the North West (-36 to +1%) and South East (-41 to +7%) of England. Current high resolution climate models (1.5 km grid spacing), indicate that hourly rainfall intensities will increase in both summer and winter months (Kendon et al., 2014). Hence, dry periods of increased duration followed by intense re-wetting are likely to become more prevalent. For catchments where the main source of P is agricultural, most annual total P loads are transferred during high discharge events (Ockenden et al., 2016), of which a significant portion is bioavailable dissolved P (Joosse and Baker, 2011). Therefore, increased frequency of extreme meteorological/hydrological events in the future is likely to increase the transfer of P to water bodies (Ockenden et al., 2016) increasing the risk of eutrophication. It seems likely that climate change will alter the degree, rate and frequency of drying and re-wetting (DRW) events, so altering the nutrient cycling of P within soils as it undergoes both abiotic and biotic stress. Such changes may alter the amount and form of P mobilised via solubilisation and detachment, consequently increasing the amount of P that can undergo transport and impact watercourses, as described by the P transfer continuum (Haygarth et al., 2005). This is especially important to consider into the future as although net P inputs to land may decline, accumulated P stores will continue to be mobilised, posing continual and long term risks to watercourses (Powers et al., 2016).

There is evidence to suggest that DRW events do cause an increase in soil nutrient availability in leachate (Blackwell et al., 2009; Blackwell et al., 2012; Bünemann et al., 2013; Butterly et al., 2011; Nguyen and Marschner, 2005; Soinne et al., 2010; Xu et al., 2011). Drying soils to a gravimetric water content (GWC) of <10% significantly increases P mobilisation at re-wetting, especially at <2.5% (Bünemann et al. (2013) and 2-4% (Dinh et al., 2017). This increase in P availability in dried soil upon re-wetting has been attributed to microbial cell lysis (Turner and Haygarth, 2001), yet it is likely that a significant proportion is of non-microbial origin organic P or inorganic P (Blackwell et al., 2009; Bünemann et al., 2013; Butterly et al., 2009; Butterly et al., 2011). For example, high organic carbon soils can result in significantly more available P after drying and re-wetting (Nguyen and Marschner, 2005; Styles and Coxon, 2006). Chen et al. (2016) also found that frequent DRW cycles can cause greater, more long lasting impacts on soil biomass P dynamics than carbon dynamics. In addition, soils with high microbial biomasses yield more P upon re-wetting (Styles and Coxon, 2006) especially if the community is not resilient to DRW cycles (Butterly et al., 2011; Fierer et al., 2002; Pailler et al., 2014; Wang et al., 2013). Drying can induce the oxidation of soil organic carbon Fe and Al associations (Bartlett and James, 1980; Haynes and Swift, 1985; Schlichting and Leinweber, 2002), and thus directly release organic P, and indirectly release inorganic P via mineralisation that is subsequently stimulated (Styles and Coxon, 2006). Slaking has also been identified as one the most important mechanisms to disrupt soil aggregate structure and integrity, exposing specific surface areas to desorb both inorganic and organic P (from non-living organic matter) from dried soil as it is re-wetted (Bünemann et al., 2013; Chepkwony et al., 2001). Upon drying without re-wetting however, some (peat) soils can further adsorb more P associated with these organic matter complexes (which are also more extractable if re-wetted) (Schlichting and Leinweber, 2002). This has been observed in the field in western Ireland, where during summer, lower moisture contents and higher P sorption capacities can buffer against P loss even following P application (Styles and Coxon, 2007).

Despite this, as far as we are aware there is no literature on the effect of the duration of drying period of the soil on the solubilisation of P after a rapid re-wetting event. This needs to be known if we are to consider the impacts of predicted climatic change. In addition, such information may help inform land managers of optimum P application timings during the growing season. The experiment was designed to inform a multi-model exercise that explores model performance/prediction of transport of nutrients in the Defra (Department for the Environment and Rural Affairs)-funded UK Demonstration Test Catchments (DTC) (McGonigle et al., 2014) under climate change. In this study three sub-catchments were chosen to represent two of the DTCs. These sub-catchments are included in extensive catchment-scale research platforms which explore the effects of diffuse agricultural pollution on stream ecosystems (Ockenden et al., 2016; Outram et al., 2016; Outram et al., 2014; Snell et al., 2014; Wade et al., 2012). In this study, we test the hypothesis that changes in the future patterns of DRW will affect the amount of soluble reactive phosphorus (SRP) solubilised. The specific objectives were:

- To determine how the duration and frequency of dry periods would change from present day to the future (2050) at the local scale for three UK catchments.
- To use laboratory experiments on soils from three catchments in the UK to determine how the duration of drying period before an intense rewetting event affects the amount of SRP solubilised and measured in leachate.

- To combine the frequency and duration of future dry periods with the results of laboratory experiments to estimate how total SRP solubilised after drying/rewetting events may change.

3.2.1 Materials and methods

3.2.1.1 Estimation of dry period characteristics

UKCP09 Weather Generator was used to determine characteristics of temperature (25°C for extreme dry periods) and dry period duration in the future (up to 90 d) which were used to inform the DRW event in our experiment. Further details are given in Appendix 1.

3.2.1.2 Choice of sampling location

Soils were chosen to represent the different land uses and soils within the Eden and Wensum DTCs. Newby Beck (12.5 km^2, 54.59ºN 2.62ºW) and Pow Beck (10.5 km^2, 54.84ºN, 2.96ºW) are two rural headwater sub-catchments within the Eden DTC, Cumbria, UK. The Newby Beck sub-catchment is predominantly improved grassland (76%); soil was collected from a field which is grazed on rotation by sheep and dairy cattle (P application rate 28.76 kg P ha^{-1} for 2014). Pow Beck is also predominantly improved grassland (46%) and is more intensively farmed than Newby Beck. Soil was collected from a field in which beef cattle are grazed (no recorded P applied for 2014). Limited fertiliser and slurry application data are available for these two catchments (see Appendix 1). The Blackwater (19.7 km^2, 52.78ºN, 1.15ºE) is a sub-catchment within the Wensum DTC, Norfolk, UK. Soil was also collected from an arable (winter wheat) field within the Blackwater (2013-2014 spring bean rotation with an inorganic and organic P application rate of 1-49 kg P ha^{-1} (Outram et al., 2016)). Detailed farm business data for the Blackwater are published in Outram et al. (2016), and further information can be found in Appendix 1.

3.2.1.3 Soil type, collection and preparation

Soils from the Newby, Pow and Blackwater catchments were collected from the top 25 cm of soil at one point in a single field between September and October 2014. Small sampling pits were dug and a bulk sample was removed inclusive of plant material present. Soil samples were sieved wet to 2 mm, removing visible plant and root material, and kept in sealed bags at 4˚C until use. Soils from the Newby and Pow catchments are similar (Typic Haplaquept Inceptisols, or Chromic Eutric Albic Luvic Stagnosols (Cranfield University, 2017; IUSS Working Group WRB, 2015)), the Newby soil being of fine loamy texture, and the Pow soil fine and coarse loamy. The Blackwater soil (Aquic Dystrochept Inceptisol or Endostagnic Luvisols (Cranfield University, 2017; IUSS Working Group WRB, 2015)), a loamy and clayey soil (NSRI, 2014), characterised by a subsurface accumulation of clays. For Olsen's P analysis soil was air dried to a constant weight and sieved to 2 mm. For further chemical analysis prepared soil was ground using a pestle and mortar for carbon (C), nitrogen (N) and total soil P (TP) analysis. Soil pH was measured in a deionised water suspension using a Jenway 3510 according to Rowell (1994). Soil C% and N% were measured using a Vario El Elemental Analyser and C:N was calculated. Total soil P was determined by wet oxidation digestion (Rowland and Grimshaw, 1985), Olsen's P was determined by the method of Olsen and Sommers (1982) and both were measured according to Murphy and Riley (1962) (Seal Analytical AQ2+).

3.2.1.4 Soil drying and re-wetting

Soils were prepared according to the method from Blackwell et al, (2009). Soils were pre-incubated in sealed bags at 25˚C for 24 h prior to being dried. Soil samples of approximately 300 g were then air-dried undisturbed in a temperature controlled room fixed at 25ºC in 2 L rectangular tubs for each drying increment. The temperature (25ºC) and maximum duration of dry period (90 d) were justified from UKCP09 as indicative of the most extreme dry periods in the future for these sites. Newby and Pow soils were dried for 0, 2, 4, 5, 6, 8, 10, 15, 20, 25, 30, 60, 90 d. The Blackwater soil was dried for 0, 5, 10, 15, 20, 25, 30, 60, 90 d as a limited amount of soil was available. Matric potential was measured using a Decagon WP4-C Dewpoint Potentiometer in 3 sub-samples for each drying period. Five sub-samples (21g Dry Weight Equivalent) of soil for each drying period were removed and placed into 50 mL plastic conical funnels each plugged with 0.3 g of non-absorbent glass wool. The soil was loosely packed in the funnel by gently tapping and placed in a centrifuge tube. All soil was then rewetted over 2 h (50 mL, pipetting 5 mL aliquots evenly spaced over 2 h); 0.45µm Whatman filter paper was placed on the soil surface to aid even distribution of water; leachate was collected in the centrifuge tube. A re-wetting rate of 25 mL over 2 h was used in Blackwell et al, (2009) and resulted in the most significant leaching of dissolved P in those experiments, and was therefore doubled here to increase the intensity of re-wetting event. Filtered (using 0.45 µm syringe filters) leachate samples were used to measure SRP according to Murphy and Riley (1962) using a Thermo Scientific Multiskan GO Plate Reader. Information regarding statistical analysis can be found in Appendix 1.

3.3 Results and discussion

3.3.1 Change in dry period characteristics: duration and temperature of dry period

The 95th percentile (mean average over 100 runs) duration of dry periods increased in both catchments between the present day and the future scenario period; dry periods increased by up to 40% for the Blackwater and 25% for Newby Beck (Appendix 1 Table 2). There was a 17, 23, and 7% increase in the frequency periods of 11-15 d dry in the Newby, Pow and Blackwater catchments in the scenario period (Appendix 1 Figure 1 and 2). The frequency of dry periods of >16 d increased in the scenario period in all catchments, however dry periods between 1-5 d either increased by <1.5% (Newby and Pow) or decreased in frequency (Blackwater) under climate change (Appendix 1 Figure 3). The 90th percentile of mean average temperature during dry periods (Appendix 1 Figure 2) increased by ~3°C in each catchment. Under climate change longer periods of dry weather (extremes 90 d) at higher temperatures (extremes 25ºC) may be experienced. These results were used to inform the laboratory experimental design to ensure the probabilistic range indicated by the weather generator was covered.

3.3.2 Difference between soils in different catchments

The C and N% for the Newby (4.18, 0.47) and Pow (6.43, 0.62) soils was greater than the Blackwater soil (1.47, 0.17) (Appendix 1 Table 3). Carbon to nitrogen ratio was calculated as 8.89, 10.37 and 8.65 for Newby, Pow and Blackwater respectively, with soil pH determined for the Newby, Pow and Blackwater as 5.84, 5.56, and 5.78. The Blackwater soil had a lower initial TP content (780 mg kg^{-1}) than Newby (1600 mg kg^{-1}) and Pow (1200 mg kg^{-1}) soils. Available P (Olsen’s P) was the same in the Blackwater and Newby soils (3.4 mg kg^{-1}); Pow had the highest content (12.8 mg kg^{-1}). Moisture content for Newby, Pow and Blackwater soils was 32.93, 34.97, and 14.65% respectively (Appendix 1 Table 3). The matric potential at 0 d dry was similar between soils, measured as -0 (0), -0.24 (0.11), and -0.46 (0.095) for Newby, Pow and Blackwater. Bulk density was not determined *a priori* in this experiment, but was estimated for each soil type in this location as 1.22, 1.2, and 1.4 g cm^{-3} for Newby, Pow and Blackwater, respectively (NSRI, 2014).

Figure 3.1 shows the concentration of SRP (µg L^{-1}) in leachate subsequent to re-wetting for each replicate at the individual drying increments. In the Pow and Newby soil SRP concentrations were outside the detectable limit in leachate samples from soils dried between 0 and 2 d, these are therefore reported as 0. At 90 d the SRP concentration in leachate was higher than that reported at 0 d for all soils (Appendix 1 Table 4). However, the highest concentration of SRP was measured in leachate from soil dried for the duration of 15 (129.7 ± 7.7 µg L^{-1}), 10 (68.1 ± 23.2 µg L^{-1}), and 20 (305.9 ± 67.8 µg L^{-1}) d for Newby, Pow and Blackwater soil respectively. There was no significant difference between the volume of leachate collected at each drying increment, the mean average volume collected for Newby, Pow and Blackwater was 35.9 (± 3.4), 38.7 (± 3.4), and 40.3 (± 2.1) mL respectively. Therefore, the relationship between time dried and load of SRP (µg P) was similar to the relationship between time dried and concentration of SRP (µg L^{-1}), as confidence intervals for the breakpoints overlap (Appendix 1 Figure 4, Figure 1).

Table 3.1 Results of segmented linear regression for Newby Beck, Pow Beck and Blackwater soils (standard error) for matric potential and Soluble Reactive Phosphorus (SRP), and the increased frequency and potentially leachable SRP under UKCP09 medium emissions climate change.

Soil	Breakpoint (d) SRP	Segmented regression R^2 SRP	Potentially leachable SRP (μgP L^{-1}) at breakpoint (segmented model)	Potentially leachable SRP (μgP L^{-1}) at breakpoint (collected data)	Increased frequency of breakpoint occurring under climate change (%)	Increased potentially leachable SRP under climate change (%)	Increased frequency of 7-15 dry days occurring under climate change (%)
Newby	14.5 (1.8)	0.705	108	129 (8)	28	13	6
Pow	10.0 (1.4)	0.559	318	68 (23)	13	11	8
Blackwater	6.9 (2.3)	0.311	336		-13	-1	-4

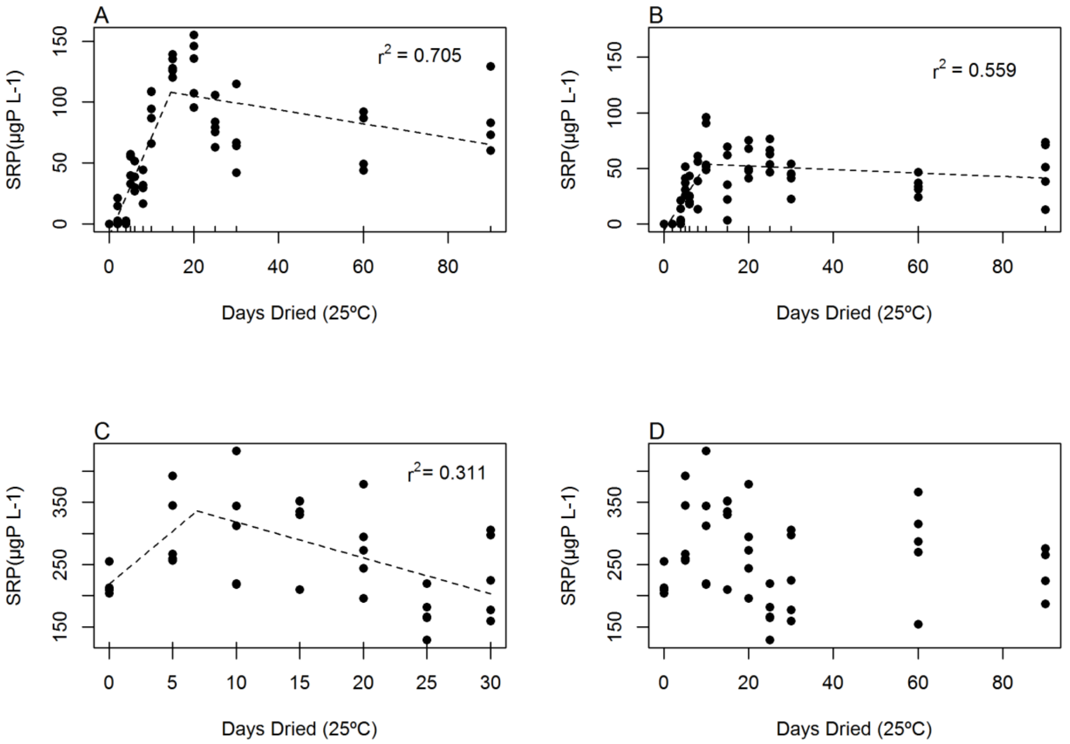

Figure 3.1 Soluble reactive phosphorus (SRP) (µgP L^{-1}) plotted against the duration of time dried (at 25ºC) in days for the Newby (a), Pow (b), and Blackwater (c, 0-30 d data, and d complete dataset). The segmented model prediction (dashed line) suggests that the significant breakpoint in the data is at 14.5 (r^2= 0.705), 10.0 (r^2= 0.559), 6.9 (r^2= 0.311) d, for Newby, Pow and Blackwater respectively, where the relationship between the length of time (days) dried and SRP solubilisation changes.

Analysis has identified breakpoints at 14.5 ± 1.8 (r^2= 0.705), 10.0 ± 1.4 (r^2= 0.559) and 6.9 ± 2.3d (r^2= 0.311) for Newby, Pow and Blackwater soil respectively (Figure 3.1, Table 3.1). Segmented linear regression identified a breakpoint in the data (performed in R using the Segmented package (Muggeo, 2003, 2008)). Before the breakpoint the model identified an increase in SRP loss with the number of dry days, but after this point the amount of SRP solubilised was reduced or stayed fairly constant. The Newby soil identifies well with the model (r^2= 0.705), yet contrastingly the Blackwater soil does not (r^2= 0.311). Greater C% does not yield greater concentrations of SRP in leachate, but it may account for the more pronounced breakpoint response from the Newby and Pow soils (Nguyen and Marschner, 2005). There was not, however, a clear decrease of mean average SRP concentration in leachate between each drying increment subsequent to the breakpoint (Appendix 1 Table 4). At these breakpoints none the less, up to 28% more SRP in leachate was yielded (solubilised) than in lesser and longer drying periods.

Matric potential in all soils rapidly increased (value gets more negative) between 0 and 5 d of drying time (Appendix 1 Table 4). Breakpoints were identified for all soils at 5.3 ± 0.2 d (r^2= 0.943) (mean average reported). After this breakpoint matric potential did not change significantly, meaning that the ability of water to move through the soils remains similar. Soil preparation (sieving to 2 mm), alongside the experimental conditions the soils were dried in (temperature controlled room at 25ºC), could have significantly exacerbated the drying process resulting in the shorter matric potential breakpoint compared to the SRP breakpoint. As the breakpoint drying times have been identified in a laboratory environment they are likely to differ in the field where it would take longer to attain the same degree of dryness (matric potential). However, the frequency of longer drying events increases under climate change so the effect may still be true in the field, and, indeed be more pronouced as drying will predominantly occur at the suface (where P is more concentrated) gradually spreading down the soil profile to for example, the depth sampled here. Soil preparation likely removed some of the natural drying features that would occur to soil in the field upon drying, as sieving can remove preferential flow characteristics (Koestel et al., 2012) that can enhance P loss to waterbodies (Sharpley et al., 2013), and root removal which can modify soil structure and affect water retention (Daly et al., 2015). None the less, some artificial pathways would have been created as the dry soil was repacked, in addition to the micro-cracks potentially formed upon re-wetting (Grant and Dexter, 1989), affecting the rate of water flow with differing kinetic energies (Blackwell et al., 2009) and possibly contributing to the variation between repetitions of SRP concentration in leachate. Increased cracking and preferential pathways, together with increased hydrophobicity of the soil may be accountable for the diminished SRP concentration after the breakpoint and warrants further investigation as to whether this process was responsible for the observed breakpoint. With this dataset however, no relationship could be found between matric potential and SRP concentration in leachate.

Increased frequency of dry periods between 6 and 55 d under climate change could yield a total change in mobilised SRP via solubilisation of +13, +11, and -1% for Newby, Pow and Blackwater soils respectively (Table 3.1). Increased frequency of dry periods of 11-55 d under climate change could yield a total change in SRP solubilised of +31, +38, and +21% for Newby, Pow and Blackwater soils respectively. Increased frequency of estimated breakpoints at 7-15 d under climate change, will likley increase SRP solubilisation for the Newby and Pow soils (+6 and +8% respectively) but decrease in the Blackwater soil (-4%) (Table 3.1). However, air-drying soil changes the solubility of P and may not reflect true solubility in the field (Soinne et al., 2010), so translation of these laboratory results to field scale should be treated cautiously, yet the identification of a breakpoint in SRP solubilisation from soil is novel and important. The increased frequency of shorter dry days (11-15 d) may therefore be more important to consider as greater concentrations of SRP in leachate were found. Scalenghe et al. (2002) similarly found that under reducing conditions (albiet under flooding) the maximum rate of solubilisation occurred within 1-3 weeks. It would be useful, therefore, to investigate this further with a greater variety of soils.

3.4 Conclusion

Under climate change projections the duration and frequency of dry periods will increase compared with present day conditions in three contrasting UK catchments. For three soils critical breakpoints (6.9-14.5 d) of drying duration have been identified; before the breakpoint an increase in SRP loss with the number of dry days was observed; after this point the amount of SRP lost decreased or stayed fairly constant. The frequency of these breakpoints occurring under climate change was predicted to increase and therefore yield an increase in SRP solubilisation in only two of the studied soils (Table 3.1). It is likely that longer periods of dry days followed by rapid re-wetting events will not yield more SRP via solubilisation than at the breakpoint. However, because the frequency of longer dry periods will increase under climate change, the solubilisation of SRP from soil (-1 to +13%) will also change. Therefore, we can accept our original hypothesis that changes in the future patterns of DRW affect the amount of SRP solubilised.

In the next chapter the scale of investigation is enlarged from small scale laboratory to large scale catchments. I examine how different catchment characteristics determine the retention of P both under present day and climate change conditions. This analysis encompasses all tiers of the P transfer continuum and how the flow of P is slowed or hastened depending on specific catchment properties and activities.

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4 The effect of climate change on phosphorus retention in three contrasting UK headwater catchments

In the previous chapter I explored how possible climate changes may affect the second tier of the P transfer continuum. In this chapter I focus on catchment retention under climate change which encompasses all tiers of the P transfer continuum. It should be noted that the set-up and running of the Hydrological Predictions in the Environment model used in this chapter to gain flow and TP flux data for each studied catchment was not completed by me but by another member of the NUTCAT team. I used the output data from the model for my analysis; however, an explanation of model set-up is included in this chapter for completeness.

4.1 Abstract

Phosphorus (P) impairment of surface waters is a continual and evolving threat to aquatic biodiversity and human health, and may worsen under a changing climate. A major difficulty in mitigating this impairment lies in identifying and linking catchment sources directly with water quality and ecological impacts, both now and in the future. Climate change will add further complexity by altering catchment sensitivity to P input pressures through its effects on: (a) hydrological regime and residence time, (b) net biogeochemical retention, and (c) ecological response. Using the Hydrological Predictions in the Environment (HYPE) model for three distinct UK catchments, and Extended End-Member Mixing Analysis (E-EMMA), I show how climate change (UKCP09 scenarios) might impinge on such sensitivity. Under a high emissions scenario (2080s), an increase in total phosphorus (TP) flux and net TP retention was predicted in all three catchments but to differing degrees. I conclude

that catchment sensitivity to climate change should be accounted for in determining appropriate water quality targets that can be effectively delivered via catchment stakeholders and government.

4.2 Introduction

Freshwaters are vulnerable to a range of anthropogenic stressors including diffuse pollution, and their health, biodiversity and the ecosystem services they provide have been compromised over the last 50 years due to large increases in global agricultural productivity (Steffen et al., 2015). Pressures to maximise productivity have resulted in past over-application of fertiliser, such as phosphorus (P), which, in combination with fragmented management practices, have degraded the resilience of the landscape to retain the leakage of such nutrients from land to water. These nutrient pressures, which vary in extent and degree, and change as food production systems have become increasingly specialised and disconnected, have caused significant water quality degradation across multiple scales (Sharpley et al., 2015). As a result significant progress has been made in identifying the causes of nitrogen and P enrichment to both adjacent water and downstream water bodies, and in implementing catchment-centric measures to mitigate their costly societal impacts (Dodds et al., 2008; McDowell et al., 2015). Yet, more than half of all European water bodies will likely continue to fail to reach Good Ecological Status (GES) or Good Ecological Potential (GEP) by 2027 set out under the Water Framework Directive (WFD) (Directive 2000/60/EC) (European Environment, 2012). For example in the UK, it is reported that 68% and 45% of UK water bodies are significantly affected by diffuse and point source pollution, respectively (European Commission, 2012). Catchment-based approaches to diffuse pollution mitigation based on stakeholder collaboration may not deliver the required change in practices and desired improvements in water quality, as they do not take account of the complex and catchment specific response to nutrient pressures (Watson, 2015). In other words, we are trying to achieve broad non-catchment specific water quality targets, using a catchment specific management strategy.

Two key issues that are at least partly responsible for a slow response to the implementation of measures to reduce diffuse pollution relative to point source pollution are: 1) the continual loss of P from “legacy” P stores, namely in soils, sediments (fluvial) and groundwater bodies, causing distinctive lags in water quality response to mitigation efforts (Sharpley et al., 2013); 2) the large intra and inter-annual variability of flows and P loads caused by diversity in catchment typologies, as well as shifting human and social change, making the detection of long-term trends difficult (Hale et al., 2015; Wilby and Harris, 2006). For example, Newcomer Johnson et al. (2016) reviewed retention studies and found that newly restored riparian sites have the highest rate of nutrient retention which then fell over time, calling for retention to be evaluated over time. It is this distinctive non-conservative behaviour of P (i.e. its variable retention and remobilisation across catchments), that can constrain the impacts of contemporary mitigation measures. Therefore, the pressure-impact relationship between land use and aquatic ecosystems in different catchments needs to be better understood and managed to help prioritise the need for land use change (Doody et al., 2015). It calls into question whether today’s eutrophication problems are due to current agricultural practices, those of the past several decades, or if the impact of agriculture is unduly overestimated in some catchments (Neal et al., 2012; Withers et al., 2014).

The difference in the sensitivity of catchments to diffuse P pollution depends on three underlying catchment properties that interact in both space and time to retain P; a) hydrological regime and residence time, b) net biogeochemical retention and c) ecological response (Doody et al., 2015) (Figure 4.1). Hydrological retention reflects the residence time of P as it moves in drainage waters through the catchment (flow, source pathways, land use and management). Biogeochemical retention occurs through P biotic and abiotic immobilisation (e.g. sorption and deposition) in soils and sediments (parent material, stream morphology), whilst ecological response (i.e. uptake) depends on for example, temperature, shading and food web dynamics. All three of these catchment properties can be influenced differently by external drivers such as climate (namely temperature and precipitation). Understanding the sensitivity of these properties to change (i.e. increasing nutrient pressure due to agricultural intensification and climate change) within an individual catchment will be crucial in determining whether water quality targets are attainable with appropriate, cost effective measures in place.

With this is mind, I question whether current policy is over-simplifying eutrophication control strategies because they do not take adequate account of the variation in catchment buffering capacity. I use the process-based catchment model HYPE outputs for baseline and climate change scenarios (UKCP09 Low, Medium and High, 2050s and 2080s) and apply extended end-member mixing analysis (Jarvie et al., 2011) to estimate catchment TP retention under these scenarios, for three contrasting UK catchments. I hypothesise a) that climate change will alter catchment TP retention in these catchments, and b) that the degree or sensitivity of change experienced will be determined by individual catchment characteristics (e.g. hydrological behaviours, biogeochemistry and ecology) and pressures which underpin the retention of P in the landscape.

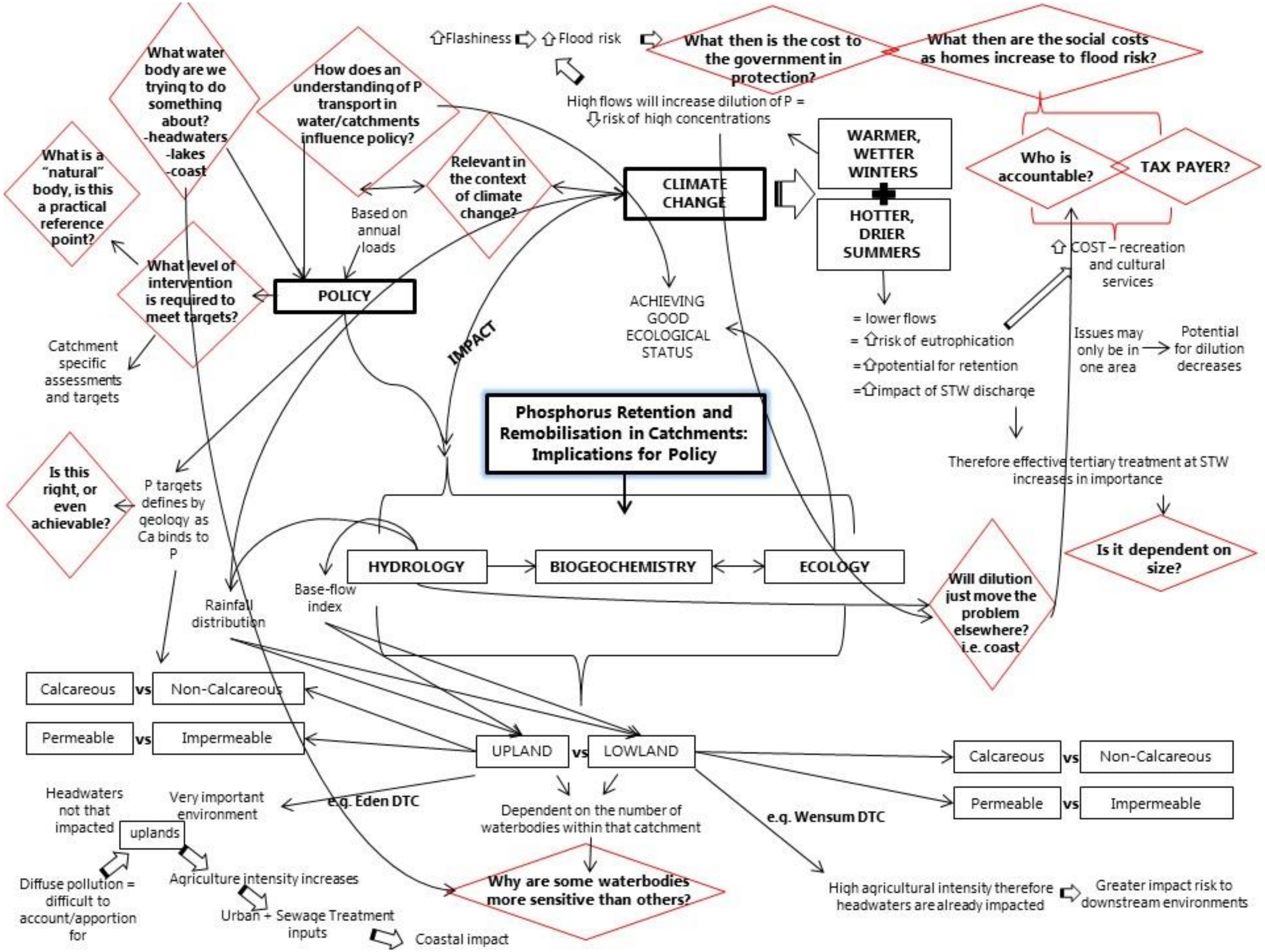

Figure 4.1 A conceptual diagram of the difficulty in developing policies for P mitigation: behaviour of P in catchments due to hydrology, biogeochemistry and ecology, drivers of change e.g. climate change. Small arrows show the interconnections between issues. Large arrows with black bottoms describe causation. Large arrows represent increase or decrease in processes. Red diamonds display questions to consider.

4.3 Methods

4.3.1 Site description

High resolution flow and water quality data were generated for three different catchments in England as part of the national Demonstration Test Catchments (DTC) programme (McGonigle et al., 2014) and catchment details are summarised in Table 4.1.

Newby Beck (12.5 km^2) is a typical grassland rural headwater in the Eden river catchment (Cumbria, UK) (Figure 4.2). The bedrock of the larger Eden catchment valley bottom is Permian and Triassic sandstones, which overly rocks of the Carboniferous limestone and limestone/mudstone on the valley sides (Ockenden et al., 2016). Allen et al. (2010) suggest that localised aquifers may exist across the catchment, but the degree of hydraulic interconnection is not known. It is primarily grazed by sheep and cattle (dairy and beef), with minimal areas of arable production (6%). Generally, application rates of P fertiliser to grasslands are ~17 kg P ha^{-1} yr^{-1}; however the UK mean average reported for 2015 was 9 kg P ha^{-1} yr^{-1} (Table 4.1) (Defra, 2016). Most P applications in Newby Beck are applied to improved grassland areas either used for grazing or silage, rather than arable areas (29 kg P ha^{-1} yr^{-1}, UK mean average 2015 (Defra, 2016)). Arable crop rotations include stubble turnips, spring wheat/barley and winter wheat/barley. The wet and cool climate in the Eden yields few optimum days for cultivation, often resulting in significant sediment and associated P loss in runoff due to poor seed establishment and resulting ground cover (Outram et al., 2014).

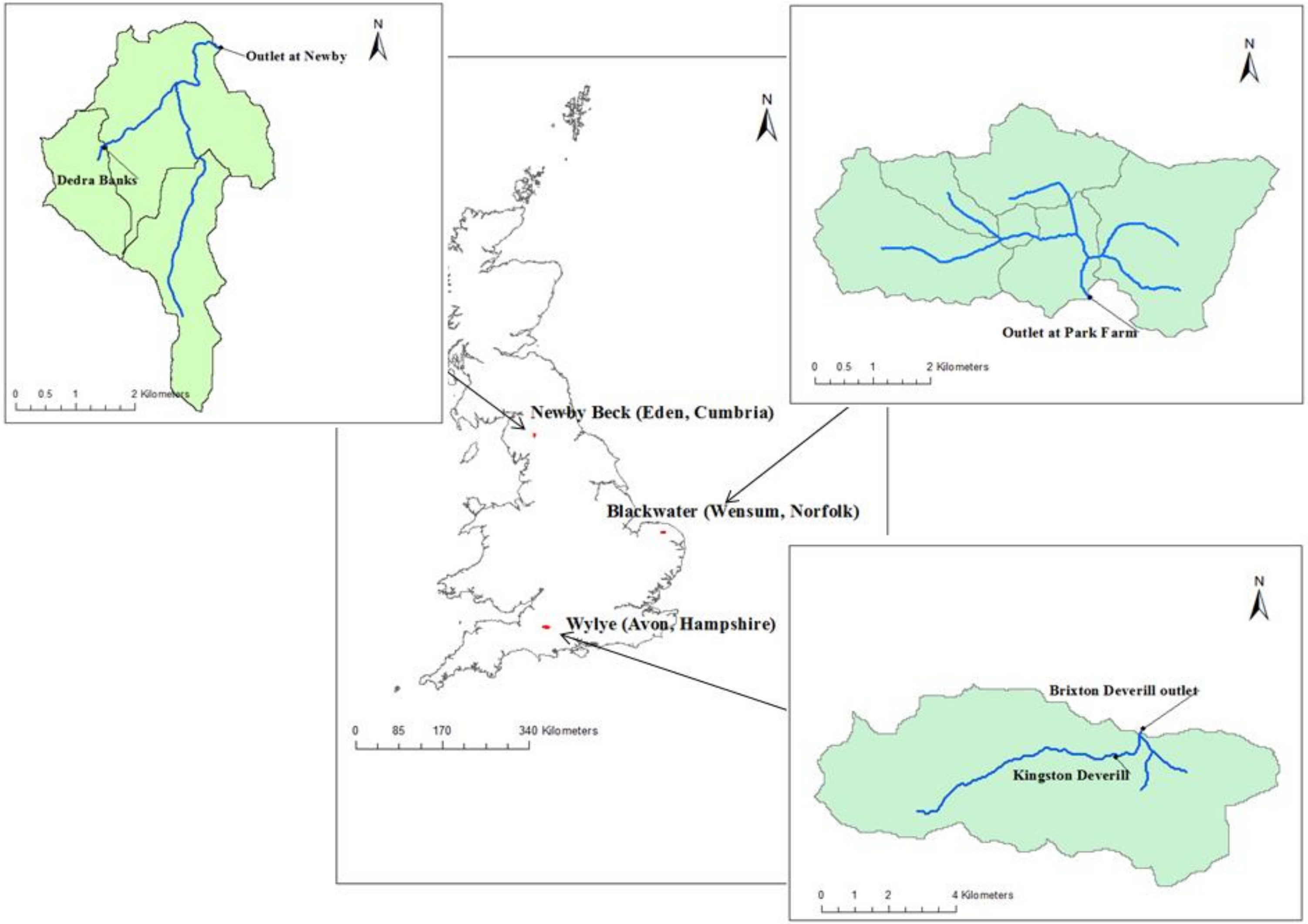

Figure 4.2 The Demonstration Test Catchment locations within the UK. Newby Beck (Eden, Cumbria), Blackwater (Wensum, Norfolk), Wylye (Avon, Hampshire).

Table 4.1 A summary of characteristics of the three UK DTCs Newby Beck (Eden, Cumbria), Blackwater (Wensum, Norfolk), Wylye (Avon, Hampshire).

		Eden, Cumbria	**Wensum, Norfolk**	**Avon, Hampshire**
Sub-catchment		Newby Beck	Blackwater	Wylye
Catchment size (km^2)		12.5	19.7	50.2
Sampling Location		HY 600 213	TG 125 246	ST 868 401
Average slope (%)		6-8	<2	6-8
Aspect (^{o} from north)		28	144	106
Land Use (%)	Arable	6 [a]	74 [b]	9 [c]
	Improved pasture	76 [a]	12 [b]	65 [c]
	Rough grazing	14 [a]	-	7 [c]
	Woodland	2 [a]	11 [b]	14 [c]
	Urban	0.7 [a]	<3 [b]	5 [c]
Fertiliser (kg P ha^{-1} yr^{-1})		9-29 [d]	4-55 [b]	As required
FYM (kg P ha^{-1})		0.64-0.91	-	19.2-80
Soil P sorption capacity		-	23.90 (± 6.71)	-
Olsen's P (mg kg^{-1})		8-46	16-247	32-56
Soils		Clay loam and sandy clay loam soils of the Brickfield, Waltham and Clifton series	Chalky boulder clay and sandy loam soils of the Burlingham 1, Beccles 1 and Wick 2 and 3 series	Sandy loam and silty clay loam soils of the Ardington, Blewbury, Coombe and Icknield series
Geology		Glacial till over Carboniferous limestone	Quaternary glacial till, sands and gravels over Pleistocene Crag and Cretaceous Chalk	Cretaceous Chalk and Upper Greensand
Annual average rainfall		1167	655	886-909
Baseflow Index (BFI)		0.39	0.80	0.93
Stream length (km)		8.6	12.6	11.9
Percentiles of flow (m^3 s^{-1}) [e]	Q_{10}	0.033	0.025	0.082
	Q_{50}	0.108	0.062	0.184
	Q_{90}	0.510	0.236	0.784
WFD status [f]	Overall	Poor	Moderate	Poor
	Ecological	Poor	Moderate	Poor
	Chemical	Good	Good	Good

[a] **From CEH (2007); Ockenden et al. (2016)**

[b] **The year 2014, from Outram et al. (2016)**

[c] **From DTC Phase 1 report- ADAS land use database for reference year 2010**

[d] **Defra (2016) UK 2015 Fertiliser Statistics**

[e] As calculated from observed data 1 October 2011- 30 September 2013

[f] WFD status from 2015 cycle 2 (Environment Agency, 2016)

The Blackwater (19.7 km^2) at Park Farm (Figure 4.2) is an intensive arable sub-catchment within the Wensum catchment (Norfolk, UK). In contrast to the Eden, very gentle slopes and well drained sandy soils favour subsurface leaching rather than overland flow pathways over much of the catchment (Cooper et al., 2017). A Chalk aquifer underlies the Wensum with overlying sands and gravels in the east of the catchment (well-drained sandy loam soils) and glacial till in the West of the catchment (seasonally waterlogged clay-rich soils) (Outram et al., 2014). The river channels draining the catchment are no longer connected to its flood plains due to extensive deepening and straightening to reduce water residence times (Cooper et al., 2017). Land use is predominantly arable (74%) in the Blackwater catchment, with 14 different recorded crops grown, of which sugar beet, spring beans, spring and winter barley, winter oil seed rape, and winter barley comprise the largest area (1184 ha in 2014) (Outram et al., 2016). Winter oil seed rape and spring beans contribute most to the annual percent of P fertiliser applied, at 27 and 26% respectively (2014). In 2014, 4-55 kg P ha^{-1} yr^{-1} was applied as phosphorus fertiliser in the Blackwater, in addition 69% of riverine TP load was event driven that year (Outram et al., 2016).

The river Wylye (50.2 km^2) at Brixton Deverill (Figure 4.2) is a sub-catchment of the Hampshire Avon with intensive mixed arable and livestock production. The Avon is underlain by the Cretaceous Chalk aquifer which dominates the hydrogeology of the tributaries, and consequently throughflow is the dominant flow pathway (Yates and Johnes, 2013). The shallow silty chalk-land soils are well drained but surface runoff on the more steeply sloping land can occur when the soil surface becomes compacted (Withers et al., 2007). In the west of the sub-catchment, Upper Greensand lithology with very fine, highly permeable sandy soils predominates and the underlying impermeable Gault Clay causes overlying shallow aquifers to be very productive (Allen et al., 2014). Above the Kingston Deverill outlet 3 septic tank systems are known, pumped recharge occurs from the underlying aquifer, and non-consented discharge from a small sewage treatment works also has a perennial head at this location (Yates and Johnes, 2013). Improved pasture is the dominant land use class (65%) in the Wylye, only 9% is cultivated land (Table 4.1); general grassland P applications are hence ~17 kg P ha^{-1} yr^{-1}, with variable slurry and manure applications to arable land. Initial DTC baseline surveys suggest that FYM has been applied in some cases daily; 32 – 80 kg P ha^{-1} was applied to much of the arable land, whilst ~19.2 – 25.6 kg P ha^{-1} yr^{-1}was applied to grassland.

4.3.2 Net catchment retention of TP

Net TP retention in each catchment for measured flow and TP flux, and for baseline and climate change scenario predictions of flow and TP flux using the HYPE model were calculated by applying the E-EMMA approach outlined in Jarvie et al. (2011). In this approach, TP flux (or any other pollutant flux) is plotted against river discharge (Q) for a two-component mixing series. It assumes that there are two dominant, different sources of water contributing to the flux of P at the outlet: (i) a baseflow end-member source, and (ii) a stormwater end-member source. By comparing a theoretical linear conservative mixing line plotted between the baseflow and stormflow end-member TP fluxes, to the observed nonlinear (a locally weighted scatterplot smoothing regression: LOESS) relationship between TP flux and Q, net TP retention can be quantified. An example of the approach is given in Appendix 2 Figure 1. The baseflow end-member for each catchment was defined as the lowest observed TP flux and the stormflow end-member was defined as the predicted TP flux on the LOESS curve at 99th percentile of the river flow. E-EMMA was applied to observed data (1st October 2011 to 30th September 2013) for each catchment. For observed data series, missing data (17, 36 and 49% missing for Newby Beck, Blackwater and Wylye respectively) was accounted for by applying a correction factor for the amount of data missing (retention was multiplied by the amount of data points there should be, i.e. two hydrological years, divided by the actual observed number of data points).

4.3.3 Effects of climate change: Hydrological Predictions for the Environment (HYPE) model

UK Climate Projections (UKCP09) suggest that by the 2080s under medium emissions, the whole of the UK will warm, with greater increases in summer mean temperatures (South East of England (1.3 ºC to 4.6 ºC) North West of England (1.2 ºC to 4.1 ºC)) (UKCP, 2009). In addition, the distribution of precipitation between summer and winter months will change significantly. Increases of up to +33% (+9 to +70%) in winter precipitation, are predicted along the west of the UK, whereas summer precipitation decreases by about -40% (-65 to -6%) in the far south of England (UKCP, 2009). This variance in predicted change across the UK poses a significant challenge to water quality. As the UK Government is committed to "building resilience in agriculture through effective water management" (HM Government, 2013), and achieving GES and GEP across all water bodies, the effect of climate change and its impact on water quality is critical to explore. Here, the UKCP09 Weather Generator (Jones et al., 2010) was used to generate future daily time series data for each study catchment from IPCC Special Report Emission Scenarios: b1 (Low); a1b (Medium); a1fi (High). It should be noted that the Weather Generator is a statistical model based on empirical relationships between and within observed climate data, and therefore is reliant on the quality of observed data it is driven with. It provides multiple plausible daily time series which are statistically consistent with baseline and UKCP09 projections.

The HYPE model was used to generate flow and TP flux predictions for the three catchments. The HYPE model (Lindström et al., 2010) is a semi-distributed water quality model, which was calibrated for all three DTC catchments using available flow, nutrient and meteorological data (hourly resolution), as reported in Ockenden et al. (2017). Daily flows and TP loads were calculated from the sub-daily data available. HYPE was calibrated on the period 1 October 2011- 30 September 2013, and validated on the period 1 October 2013- 30 September 2014. The model was driven with future climatic data from the Weather Generator. For each scenario (low, medium and high emissions for both 2050s and 2080s) 100 runs of 28 years (first four years used for model spin-up) were generated for baseline and scenario conditions. Parameters for HYPE were chosen using the Generalised Likelihood Uncertainty Estimation (GLUE) methodology (Beven and Binley, 1992), this samples the multi-dimensional parameter space to find parameter groups which produce acceptable models that satisfy the evaluation criteria. Models were then evaluated using the Nash Sutcliffe Efficiency (NSE) (Nash and Sutcliffe, 1970) for TP and Q. Thresholds were set to give the best 10-15 parameter sets, for Newby Beck these were: NSE ≥ 0.6 for Q and NSE ≥ 0.5 for TP; for Blackwater these were NSE ≥ 0.55 for Q and NSE ≥ 0.53 for TP; for Wylye these were NSE ≥ 0.6 for Q and NSE ≥ 0.6 for TP. Detailed parameter sets are available in Ockenden et al. (2017). It should be noted that the version of HYPE used does not directly model groundwater flow but a groundwater parameter is included. E-EMMA was applied to the 100 runs of 28 (hydrological) years dataset for each climate change scenario and each catchment, and retention of

TP was calculated. For each 28 year dataset, averages over all behavioural runs are presented.

In using E-EMMA we can account for the TP which is associated with water and undergoing transport within the catchment. The amount of retention is therefore determined by the catchment characteristics (namely hydrological regime and biogeochemical retention) which prevent TP from being exported at the outlet. HYPE models soil, water and nutrient processes which are calculated at individual soil layers. Although HYPE does account for the biogeochemical cycling of P, Ockenden et al., (2017) show that the increase in TP export under climate change can be predominantly explained by changes in seasonal rainfall in all three catchments, rather than temperature changes. This means that the delivery of TP is primarily based on water flow pathways both in present day and climate change simulations. Here, TP is reported and therefore changes to particulate P or soluble P under climate change cannot be directly quantified. HYPE is an appropriate model to use do to the dominance of hydrological regime governing P delivery in the Eden and Avon catchments.

4.4 Results and discussion

In all three catchments the annual TP flux is delivered by agriculture with little contribution of TP from wastewater point sources. E-EMMA provides a means of exploring the non-conservative behaviour of TP under baseline (actual measured and modelled) and climate change modelled scenarios for three widely contrasting catchments. In all three catchments and scenarios, the relationships between TP flux and flow were nonlinear, and the degree of non-linearity can be used a metric for net TP retention due to the combined hydrological, biogeochemical and ecological processes that occur after TP is mobilised by rainfall (Figure 4.3). Under climate change these three properties are likely to respond differently to external climatic drivers such as precipitation and temperature, consequently causing annual TP retention to increase to differing degrees in each catchment and therefore defining its sensitivity to change. This means that the mobilisation, delivery and impact tiers of the P transfer continuum in each catchment will also alter to differing degrees as different hydrological, biogeochemical and ecological behaviours influence these three tiers.

4.4.1 E-EMMA analysis of measured data, difference in net TP retention between catchments and the P pressure applied

For the period of observed data for all catchments, 1st October 2011 to 30th September 2013, retention was calculated as 0.062, 0.001 and 0.011 kg TP ha^{-1} yr^{-1} for Newby Beck, Blackwater and Wylye respectively (Figure 4.3). For this time period the respective TP export was calculated as 1.351, 0.166 and 0.202 kg TP ha^{-1} yr^{-1}. Therefore TP retention was 4.6, 0.6 and 5.4% of TP export per hectare per year for Newby Beck, Blackwater and Wylye subsequently.

Newby Beck had the highest total amount of retention (kg TP ha^{-1} yr^{-1}), perhaps due to the fact TP load was more variable with regards to flow. Newby Beck has a low BFI, high average rainfall, steep slopes, and a large range in flow (Q_{10} 0.033 – Q_{90} 0.510 m^3 s^{-1}) (Table 4.1), which would enable P to be transferred quickly through the system when precipitation occurs (LOESS regression moves toward the linear conservative mixing series). More TP is therefore retained at lower flows as only at low flows is residence time sufficiently high enough to allow retention to occur. This is supported by analysis at Newby Beck, which suggests that >90% TP load is transferred during highest flows (Ockenden et al., 2016). This difference between low (retention) and high (remobilisation) flows is visible by the shape of the graph in

Figure 4.3 as it is distinctly different from the other two catchments. Newby Beck also is the smallest in terms of catchment size and stream length, this means there is a greater surface-to-volume ratio which could cause rapid P uptake and processing, as variables that demonstrate size (e.g. catchment size, discharge, velocity) have been found to be positively related to uptake lengths (Newcomer Johnson et al., 2016).

The Blackwater has the smallest range in flows (Q_{10} 0.025 - Q_{90} 0.236) and TP fluxes in comparison to the other two catchments. This is due to lower rainfall, high BFI, combined with generally flat, well-drained soils. Consequently yielding a more curve-linear relationship between TP load and flow, which implies more TP is retained at medium flows (Figure 4.3).

In comparison the Wylye has intermediate flows and TP fluxes, due to medium rainfall rates and steeper slopes than the Blackwater, but similarly has well-drained soils and high BFI. Therefore, most retention occurs at high flows when greater amounts of TP are mobilised by rainfall and runoff as the P pressure is high (due to high soil P levels) compared to the Newby and Blackwater. The Wylye total retention (kg TP ha^{-1} yr^{-1}) is low compared to Newby Beck, but retention percent is greater. This is likely due to the non-flashy nature of the Wylye which has groundwater contributions, and/or P sources which increase equally with flow, similarly to the Blackwater (Figure 4.3).

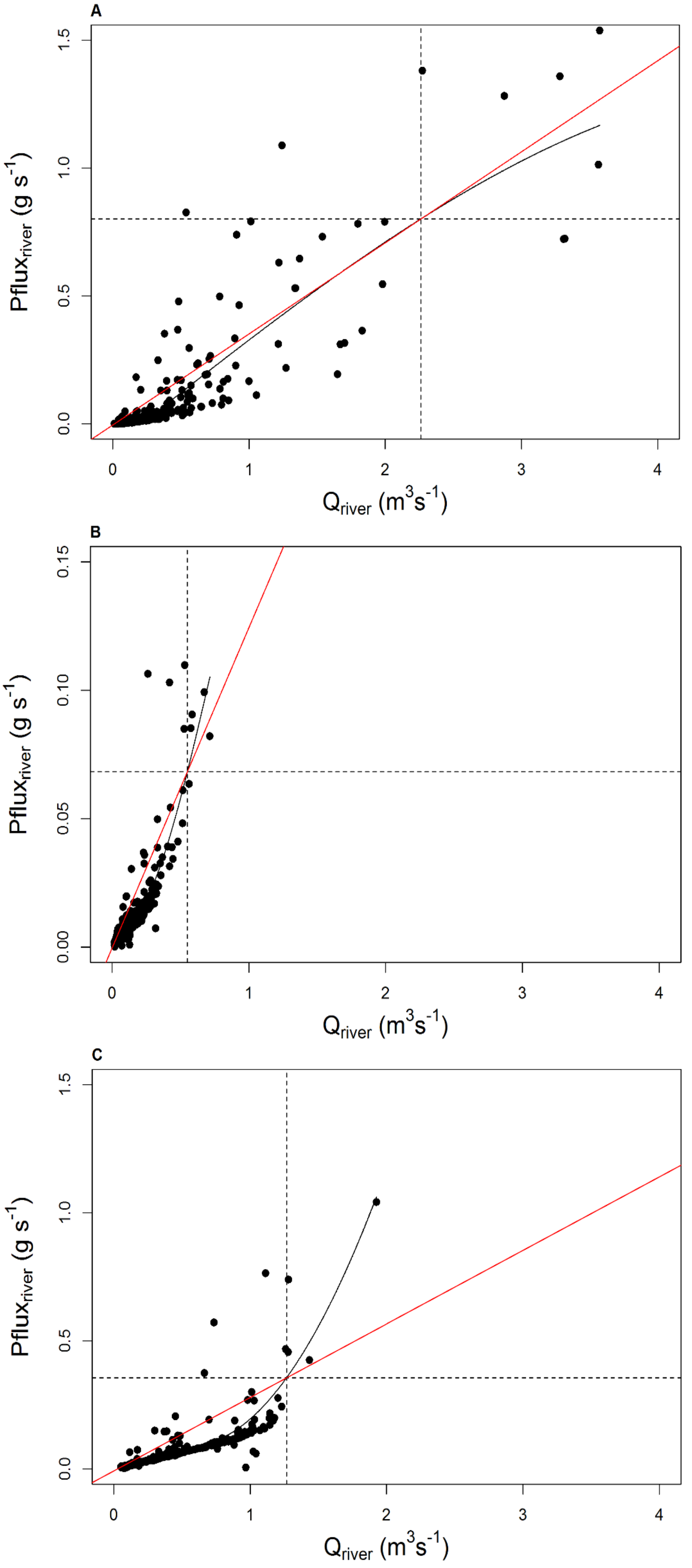

Figure 4.3 Extended End Member Mixing Analysis using high frequency observed data (1st October 2011 to 30th September 2013) of river total phosphorus flux (TPflux river g s^{-1}) and discharge (Qriver m^3 s^{-1}) from the three Demonstration Test Catchments, A) Newby Beck (Eden) B) Blackwater (Wensum), C) Wylye (Avon). The red line depicts the conservative mixing series and the black the LOESS regression. The dashed lines indicate the 99th percentile of Qriver.

4.4.2 Net TP retention predictions under climate change (HYPE model output)

Under baseline conditions regression analysis of the HYPE model output suggested that retention versus export of TP for the three catchments combined was positively related (r^2 =0.99) (Figure 4.4). Therefore, the more TP is exported and therefore mobilised (tier two of P transfer continuum), catchment retention consequently increases. Under all climate change scenarios, catchment retention of TP was increased in all the catchments, (Figure 4.5). The sensitivity of catchment buffering to climate change can be measured by the gradient of change in net TP retention (Figure 4.6), or how much the relationship has deviated from the original described in Figure 4.4. The potential causes to the change of retention under climate change are discussed in the following section.

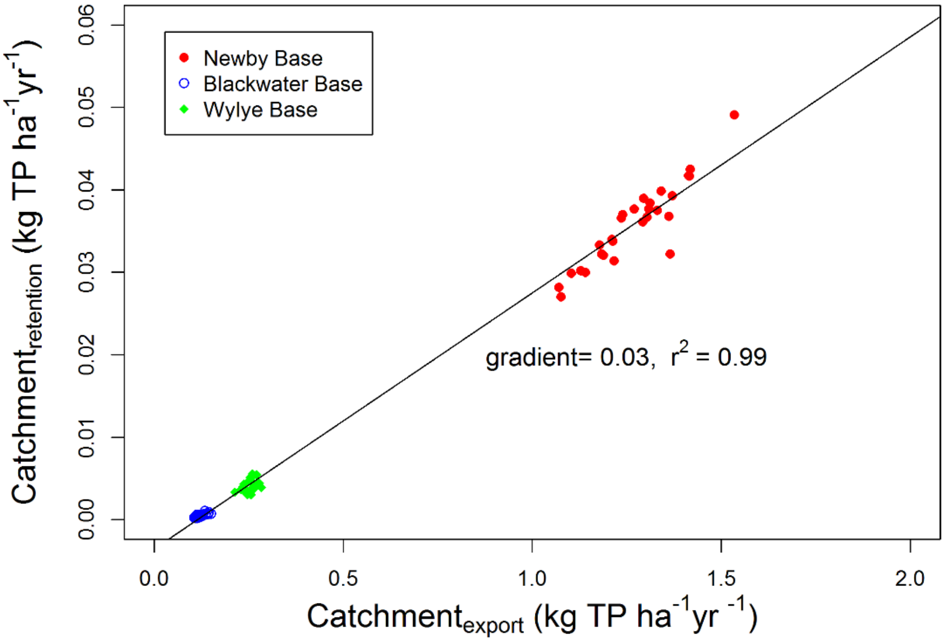

Figure 4.4 Catchment retention (kg TP ha^{-1} yr^{-1}) versus export of TP (kg TP ha^{-1} yr^{-1}) for HYPE baseline periods for the Newby Beck (Eden), Blackwater (Wensum), Wylye (Avon). The black line = linear regression analysis between all three catchments, reporting gradient = 0.03, r^2 = 0.99.

Hydrological residence time is directly influenced by precipitation as it results in changes to flow pathways and discharge rates that determine the opportunity for TP to be retained biogeochemically or ecologically. Thus, influencing the rate and time of delivery (tier three) as well as the degree and timing of impact (tier four). Increased winter precipitation, alongside the likelihood of greater storm intensities (Kendon et al., 2014) will result in increased discharge (+3 to +11%) and TP load (+18 to +31%) in all three DTCs (Appendix 2 Table 1). Ockenden et al. (2016) report that annual rainfall explains 91, 65 and 69% of TP load in the Newby Beck, Blackwater and Wylye catchments respectively (2050s high emissions scenarios). This implies that increased mobilisation and delivery of P, due to changes in precipitation, could account for a large proportion of the increased retention predicted under climate scenarios.

Table 4.2 The average and standard deviation (std.d) of total phosphorus (TP) retention expressed as a percentage of TP exported from each catchment outlet, Newby Beck (Eden), Blackwater (Wensum), and Wylye (Avon). The average is the calculated across the 28 year simulations, which is itself an average of the 100 realisations.

TP retention as percentage of TP export						
	Newby Beck		Blackwater		Wylye	
	Average	Std.d	Average	Std.d	Average	Std.d
Baseline	2.81	0.18	0.37	0.14	1.64	0.25
Low 2050s	3.11	0.15	0.52	0.19	2.56	0.38
Low 2080s	3.11	0.12	0.57	0.21	2.99	0.45
Medium 2050s	3.06	0.16	0.52	0.16	2.78	0.49
Medium 2080s	3.14	0.17	0.60	0.18	3.29	0.41
High 2050s	3.17	0.14	0.59	0.17	2.82	0.38
High 2080s	3.34	0.16	0.61	0.20	3.91	0.43

Under all scenarios Newby Beck retained the most TP in terms of amount kg P ha^{-1} yr^{-1} (Figure 4.5), and on average the most amount of TP in terms of export percent (2.81-3.34 %) (Table 4.2). It has the highest percent of TP export explained by rainfall (91%), it is likely at high flows that TP acts conservatively (linear with flow), whilst during low flows TP is retained. Discharge in summer months is predicted to decrease, and in winter increase, consequently changing slightly annually (-2 to +2%) (Appendix 2 Table 1). The changes during the summer months are likely to give way to more TP being retained across the catchment system, especially within the river reach, but this will be highly dependent on high enough magnitude summer storms which can mobilise TP to be retained. Increased retention of TP within the river reach will govern the degree of impact (tier four), a decrease in flow combined with increased temperatures may yield low DO concentrations and poor water quality status.

Although ~65% of TP load is explained by rainfall in the Blackwater, <0.001 kg TP yr^{-1} (<0.37% of exported TP, Table 4.2) is retained under the baseline scenario (Figure 4.5), and undergoes little change between the individual climate change scenarios despite a large increase between baseline conditions and climate change scenarios (Figure 4.5).

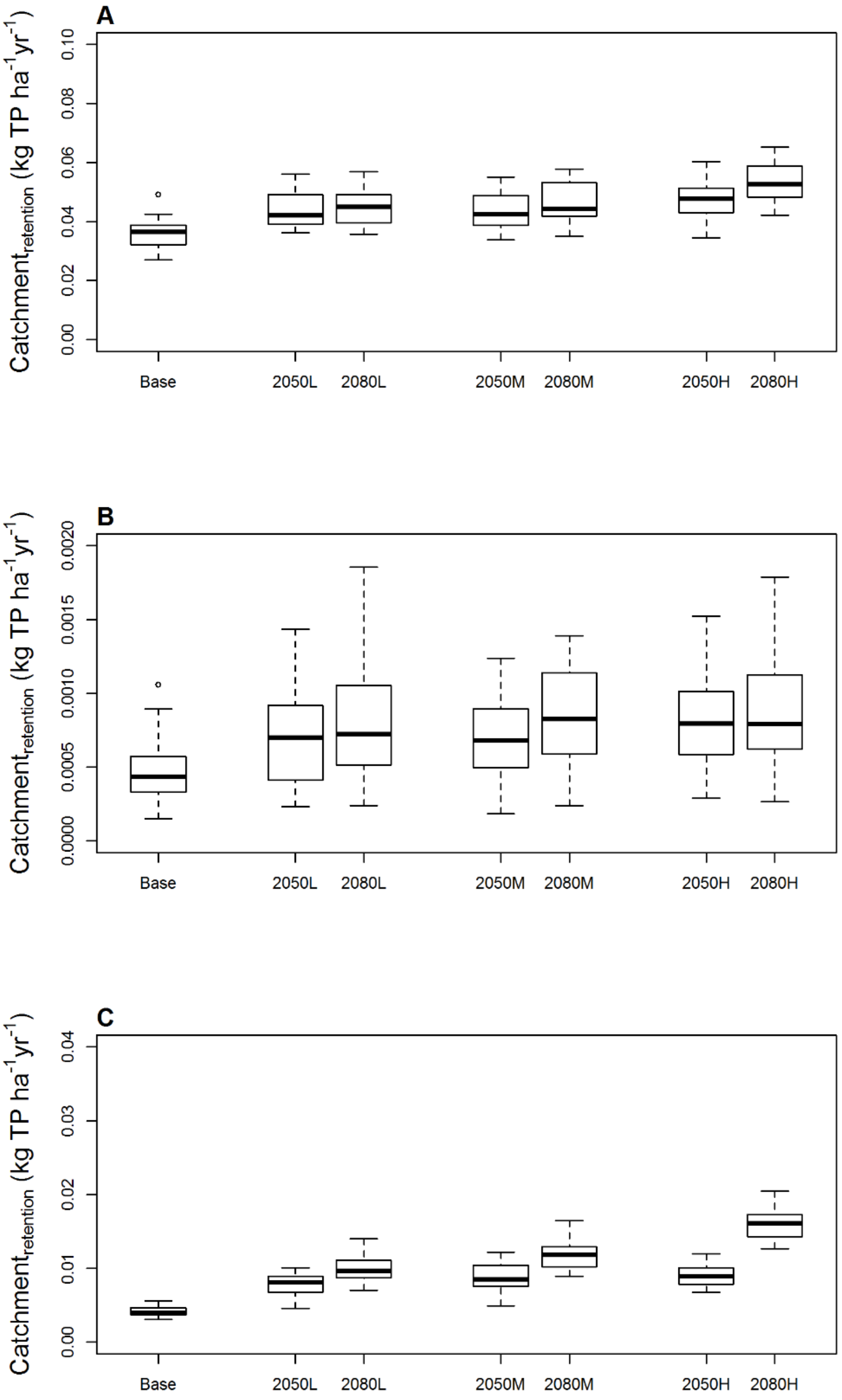

Figure 4.5 Retention of total phosphorus (kg TP ha^{-1} yr^{-1}) for A) Newby Beck (Eden), B) Blackwater (Wensum), C) Wylye (Avon) for baseline, UKCP09 low, medium and high scenarios. The middle black line represents the median, the end of the box shows the upper and lower quartiles, and the extreme lines show the highest and lowest values excluding outliers which are shown as empty dots.

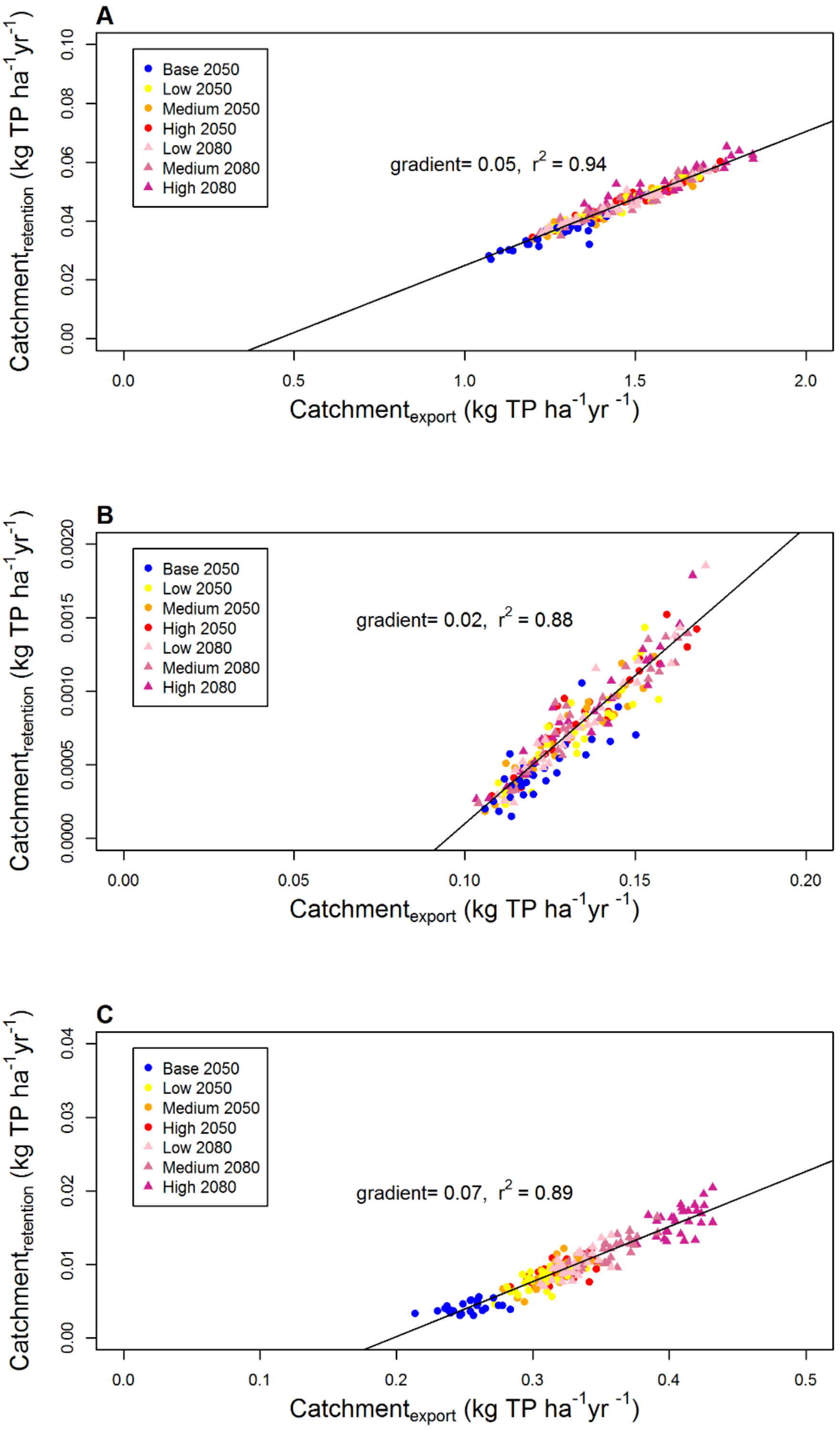

Figure 4.6 Catchment total phosphorus retention (kg TP ha^{-1} yr^{-1}) plotted against catchment TP export (kg TP ha^{-1} yr^{-1}) for each UK demonstration test catchment A) Newby Beck (Eden), B) Blackwater (Wensum), and C) Wylye (Avon) for baseline, UKCP09 low, medium and high scenarios.

This would imply that there is limited retention occurring within the Blackwater catchment, and it is the least sensitive of the three catchments to climate change (Figure 4.6). Notably, discharge in the Blackwater under climate change increases very little (+3% high emissions 2050s), therefore the hydrological regime of this catchment to change is not very sensitive due to low baseline rainfall, low slopes and well-drained soils. In addition, the variance of retention experienced under present day conditions is within the variance predicted under climate change scenarios (Figure 4.6). This may reflect its heavily impacted nature and low topography, resulting in little connection between the river and the floodplain, consequently yielding relatively low contributions from runoff as a pollutant delivery pathway (Cooper et al., 2017). Therefore, even though TP can be easily mobilised from arable fields and bank sediments (Cooper et al., 2013; Outram et al., 2014), the contribution is comparatively small or that under climate change a limited number of new connections between field and river are made, i.e. that the degree of transport (or delivery, tier three) does not change significantly. However, Cooper et al. (2015) found that within the Blackwater catchment that the source of suspended particulate matter and its buffering capacity for P from for example field drains, are potentially important in driving in-stream concentrations of SRP and these sources and buffering capacities can vary seasonally. This however, is not captured by HYPE and therefore this subtle input which is excluded may have significant implications for how TP is retained in this catchment. Nonetheless it is also possible that overland flow pathways, with the onset of increased temperatures, are also more susceptible to evaporation (Crossman et al., 2014), thus reducing the speed of transport pathways from soil to river by reducing connectivity. An evapotranspiration parameter is used for each land use class in HYPE (Appendix 2 Table 2), which is dependent on temperature, and could therefore this assumption could plausibly be accounted for in the model. Consequently, it is likely that TP retention in the Blackwater will remain largely limited or solely within the land system, instead of being mobilised from land to water and undergoing retentive processes within the watercourse (which are also captured by E-EMMA).

This is in contrast to the similarly permeable, but more steeply sloping, subsurface dominated catchment of the Wylye (common typologies throughout the UK (Outram et al., 2014)) which retains <0.01 kg TP ha^{-1} yr^{-1} (baseline) but comparatively retention increases more under high emissions 2080s (Figure 5.4, Table 4.2). The gradient of the relationship between catchment retention and export (Figure 4.6) for the Wylye suggests that it is more sensitive to climate change than both the Newby and Blackwater catchments. This means that variance in P retention under present day conditions is not within the variance of P retention under climate change (Figure 4.6). This implies that the catchment is the most sensitive of the three catchments to climate change. Observations of high-frequency data in the Wylye suggest that during storm events TP peaks were associated with a high antecedent precipitation index (API), suggesting that P-rich near surface sources were activated at these times, i.e. that diffuse P sources here are transport (tier three) limited (Outram et al., 2014). If increased rainfall therefore coincides with high API (rainfall explains 69% TP load, 2050s high emissions) otherwise disconnected depositional zones may be activated causing vast initial fluxes of P via overland flow, as well as increasing secondary fluxes by connected sub-surface pathways (Perks et al., 2015). Not only can antecedent wetness influence the amount of P released, but it can also impact the form of P (e.g. more particulate P) released especially under storm conditions (Halliday et al., 2014; Halliday et al., 2015; Macintosh et al., 2011; Macleod et al., 2012; Wade et al., 2012), of which the impact is much greater in smaller catchments (Seeger et al., 2004). In addition, the high soil P status of the sandy soils which dominate this catchment are highly liable to undergo mobilisation (tier two), especially under increased precipitation or extreme precipitation events (Withers et al., 2007). Therefore, this may account for the significant increase of TP retained under climate change compared to present day conditions (Figure 4.6). This would imply that specifically the overland hydrological regime in the Wylye is extremely sensitive to change, i.e. that the mobilisation (tier two) and transport (tier three) of P is highly sensitive to change in the context of the P transfer continuum.

It is possible that increased air temperatures have increased stream temperatures (El-Jabi et al., 2014; Kundzewicz and Krysanova, 2010; Langan et al., 2001; Murdoch et al., 2000; Schindler, 1997) under the climate change scenarios in all catchments. In-stream primary production and mineralization are controlled by two temperature functions within HYPE and may contribute to changes of retention between the catchments under climate change. Although this cannot be quantified, increased temperatures in combination with lower flows during summer months are most likely to cause the degree of biogeochemical retention and ecological response to change, resulting in alterations to the retentive capacity and health of the reach.

Behrendt and Opitz (1999) have calculated retention of TP within 100 different river systems in Europe. They found that in-stream retention of TP was critically dependent on the specific runoff of the catchment, i.e. mobilised P (tier two). They showed that a relationship exists between the ratio of the average annual TP load (named transport) to the sum of the TP inputs (diffuse and point sources, named emissions) and the mean specific runoff. By calculating the ratio between TP load and TP inputs (Appendix 2), the retention calculated by E-EMMA can be compared to this method

(Figure 4.7). All catchments were calculated to have a TPload:TPinput ~0.9 for all scenarios (Appendix 2 Table 5), but specific runoff values were much greater for Newby Beck causing it to fall within the 90% prediction limits of the Behrendt and Opitz (1999) retention model (Figure 4.7). This would suggest that retention processes in Newby Beck are likely to be occurring most strongly within the river reach, whilst in the Blackwater and Wylye retention is perhaps primarily occurring via terrestrial processes as they lie outside the predictions limits. This therefore supports the conclusions that Newby Beck has the potential to retain more TP within the reach at low flows, which may be exacerbated by increased temperatures. That the Blackwater's insensitivity to change is due to the low topography, allowing any mobilised TP to be primarily retained terrestrially. Whilst increased mobilisation in the Wylye may be due to sandy soils, yielding greater changes to retention capacity across the catchment system.

The E-EMMA method is not able to quantify the true total amount of TP retained in each catchment compartment described in Figure 4.1. Yet all P which has undergone mobilisation is quantified and therefore the total retentive capacity of an entire catchment system is captured. Although these results are only as good as the data HYPE provides, all representative end-members would have been covered as HYPE outputs daily water quality data. Therefore, this simple tool has therefore highlighted that each studied catchment does not respond with the same sensitivity to climate change, and coarsely attributes this to hydrological, biogeochemical or ecological process which govern the retention and release of P (i.e. buffering capacity). By showing that neither catchment responded the same to the same climate change scenarios highlights the need for water quality targets and catchment remedial strategies to reflect these differences.

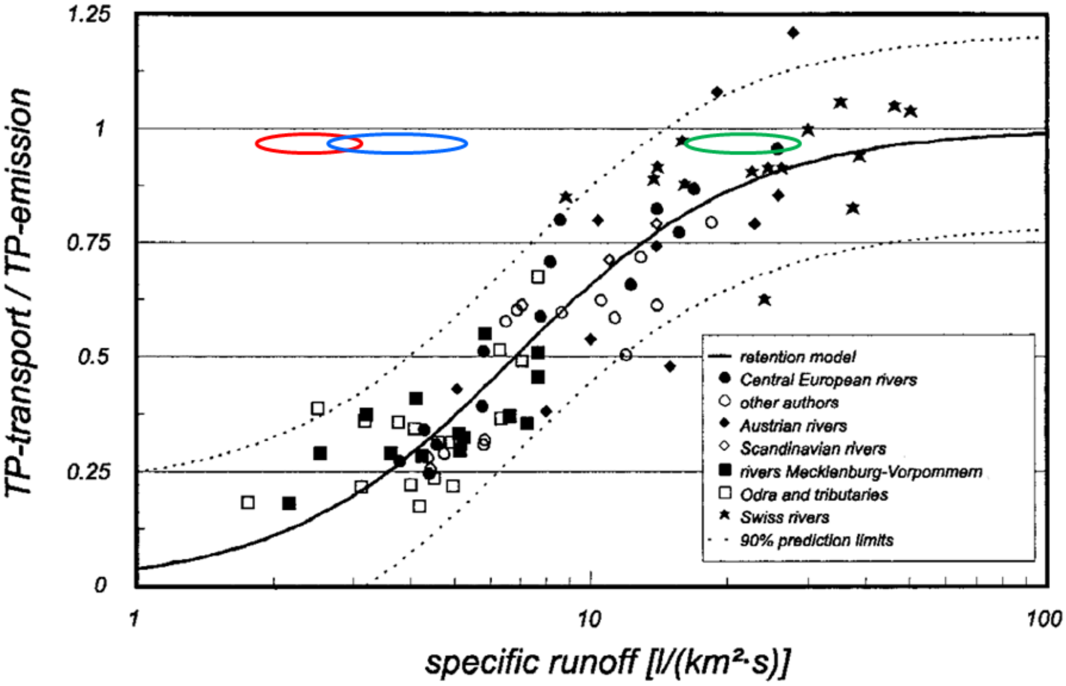

Figure 4.7 The dependency of the transport to emission ratio of total phosphorus (TP) on the specific runoff for the different river basins in Europe as in Behrendt and Opitz (1999). The green, red and blue rings indicate where the Newby Beck (Eden), Blackwater (Wesum), Wylye (Avon) respectively, approximately lie.

4.5 Conclusion

Understanding the characteristics and driving forces of TP retention in different catchments is crucial in order that we might establish whether water quality targets are attainable with appropriate, cost effective measures in place. These results suggest that three contrasting UK catchments retain different amounts of TP for both observed and baseline conditions. Under climate change scenarios (UKCP09) each catchment retains more TP, consequently the hypothesis a) that TP retention under climate change will alter can be accepted. The degree of retention was found to be a function of TP export, and influenced primarily by landscape characteristics that determined hydrological regime and residence time. Therefore the hypothesis b) the degree or sensitivity of change experienced will be determined by individual catchment characteristics (e.g. hydrological behaviours, biogeochemistry and ecology) and pressures which underpin the retention of TP in the landscape can be accepted. The Blackwater (Wensum) and Newby Beck (Eden) are comparatively, the least sensitive to change in net TP retention, whilst the Wylye (Avon) was the most sensitive to change. This response can be attributed to the sensitivity of the three catchments to increased P mobilisation, tier two of the P transfer continuum, which in turn influenced the degree of TP retention. It is also critical to consider that as more P is mobilised, transported and retained by each river under climate change, the likelihood to exceed water quality targets in both winter and summer month's increases (i.e. increasing the degree of impact: tier four). Hence, as each catchment response to nutrient loadings under climate change is different, its response to remediation will be highly specific in nature, and therefore calls for policy and regulation to reflect this. Additionally, as each catchment demonstrates a differing degree of sensitivity to change, so thus will the P transfer continuum be in each catchment, and raises the need for the renewed P transfer continuum (Figure 2.6) to be implemented in order to achieve effective remediation. Although uncertainties are associated with using model predictions, validity can be found in being able to estimate future retention of TP and therefore its impacts, in order that we might improve policies to adequately protect our water environment. A greater understanding and accreditation of catchment sensitivity to TP fluxes is required, especially considering climatic changes predicted in the UK (hotter drier summers, warmer wetter winters), and therefore a revision in how water quality is managed to reflect this.

This chapter has explored catchment TP retention under climate change in three contrasting catchments in the UK. In the following chapter I use the Newby Beck catchment as a critical example, using observed data, to improve understanding of the retention of TP in headwaters.

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5 The retention of phosphorus in a small rural headwater stream and the effects of anthropogenic activity

In the previous chapter I explored P retention at the catchment scale under climate change scenarios using data from a hydrological model. In this chapter I focus specifically to one catchment in order to gain further insight into retention at the headwater scale, enabling me to compare model results with real-world data acquisition and testing. It should be noted that Newby Beck outlet data was not collected by me but the Eden DTC team, I was able to access the dataset via an online sharing platform.

5.1 Abstract

Anthropogenic activity in rural landscapes has resulted in changes to the ability of headwater catchments to buffer phosphorus (P) inputs. Despite their dynamic nature, headwaters can critically regulate downstream water quality. Climate change will likely impinge on this buffering capacity, and it is therefore essential to gain a greater insight into P retention and release, and the influence of anthropogenic activity at the headwater scale. Using bi-weekly sampling of total phosphorus (TP), soluble reactive phosphorus (SRP), chloride (Cl^-), flow (Q), load apportionment modelling (LAM), mass balance, and sediment sampling I show that anthropogenic point sources of P can alter the degree of retention of P at the headwater scale where agricultural diffuse sources dominate in the headwater catchment of Newby Beck+ (17.8 km^2, extended Demonstration Test Catchment, Cumbria, UK). Load apportionment modelling, and total phosphorus (TP) and Cl^- load data suggest diffuse sources dominate in the

headwaters and contribute to more of the TP load downstream (65%). However, point sources dominate more frequently (64% of the time) and are therefore proportionally perhaps more important in terms of continuous downstream water quality. Mass balance suggests that interactions at the streambed level could critically contribute to the mass of P exported. Sediment equilibrium phosphorus concentration (EPC_0) data suggests that upstream sediments are potential sources of SRP to the water column, whilst sediments beyond the small village of Morland have the potential to interchange between sources and sinks. Therefore, demonstrating the effect of anthropogenic point sources changing the buffering capacity of a small headwater stream. Under climate change, it is perhaps unlikely that point sources will remain as significant in contributing more frequently to load, as higher loads in winter driven by diffuse source contributions will likely "outwash" the contribution from point sources such as water treatment works.

5.2 Introduction

Water quality is dependent on variable natural and anthropogenic factors that affect pollutant delivery within a catchment (Álvarez-Cabria et al., 2016). Consequently, water quality is highly dynamic across space and time reflecting not only the changes to inputs, but also the complex nature of the cycling of pollutants, such as phosphorus (P), across the land-water continuum. Headwater streams, despite often their flashy nature, can play a critical role in the retention and remobilisation of all forms of P, critically linking the catchment to downstream reaches (Reddy et al., 1999; Withers and Jarvie, 2008). The ability for headwaters to retain P, especially dissolved P, is thus considered essential to preserve good water quality, especially since recent agriculture intensification has contributed to impacted streams having greater uptake lengths than non-impacted streams (Hall et al., 2013; Weigelhofer, 2016). The sensitivity of headwaters to changes in human activity (Kristensen and Globevnik, 2014); nutrient and/or sediment inputs; water temperature (Reddy et al., 1999; Withers and Jarvie, 2008); and stream regulation (Ensign and Doyle, 2005) can result in reduced physical, biological and chemical retention capabilities. Thus, headwaters often simply transport P to downstream reaches (Dodds and Oakes, 2008).

Under climate change the role of headwaters in the retention and remobilisation of both diffuse and point P sources is likely to change. With the onset of hotter, drier summers in the UK (UKCP, 2009) stream temperatures are likely to increase alongside the frequency of drying and re-wetting of stream sediments, influencing P uptake and release patterns (Reddy et al., 1999; Withers and Jarvie, 2008). In addition, lower flows and associated high P concentrations are likely to become more frequent and longer lasting in summer months (Ockenden et al., 2016). Warmer, wetter winters (UKCP, 2009) have the potential to increase the frequency of high flow events, transporting high loads of TP from headwater systems especially (Ockenden et al., 2016). Increased frequency of storms will likely cause frequent changes in stream P concentration as the greatest changes, especially in particulate forms, occur after storm events (Evans and Johnes, 2004; Haygarth et al., 2005; McDowell and Sharpley, 2002; Stutter et al., 2008). Therefore, it is critical to gain a greater insight into the complex dynamics of the retention and remobilisation of P, in order to improve model predictions, in which it is considered a distinctive “black box” (Jarvie et al., 2012), especially at the headwater scale.

In this chapter I investigate the influence of anthropogenic inputs (both point and diffuse) on the retention of P at the headwater scale. I hypothesise that anthropogenic point sources of P can alter the degree of retention of P even at the headwater scale where agricultural diffuse sources dominate. Here I attempt to use chloride (Cl-) as a conservative tracer to determine the retention of (non-conservative) P using bi-weekly sampling data of Cl^-, P, and flow (Q). In addition I use catchment mass balance and source apportionment, aided by sediment sampling (sediment total phosphorus and equilibrium phosphorus concentration), to assess the sources and retention of P in the small headwater catchment of Newby Beck, Cumbria, UK.

5.3 Methods

5.3.1 Site description

The Newby Beck catchment (12.5 km^2, 54.59ºN 2.62ºW) is a rural headwater catchment located within the River Eden catchment in Cumbria, UK. This catchment is part of the National Demonstration Test Catchment (DTC) programme (McGonigle et al., 2014), but the catchment has been extended (17.8 km^2) as part of this study and hereafter named Newby Beck+. Six additional sites to the DTC outlets were chosen according to where a tributary joined the main beck. Sites 2 and 3 are on tributaries, the remaining sites were located on the main Newby Beck+ (Figure 5.1). The studied catchment ranges from 347m (southern region of catchment) to 110m (northern region) above sea level, with higher elevations generally steeper at 5º.

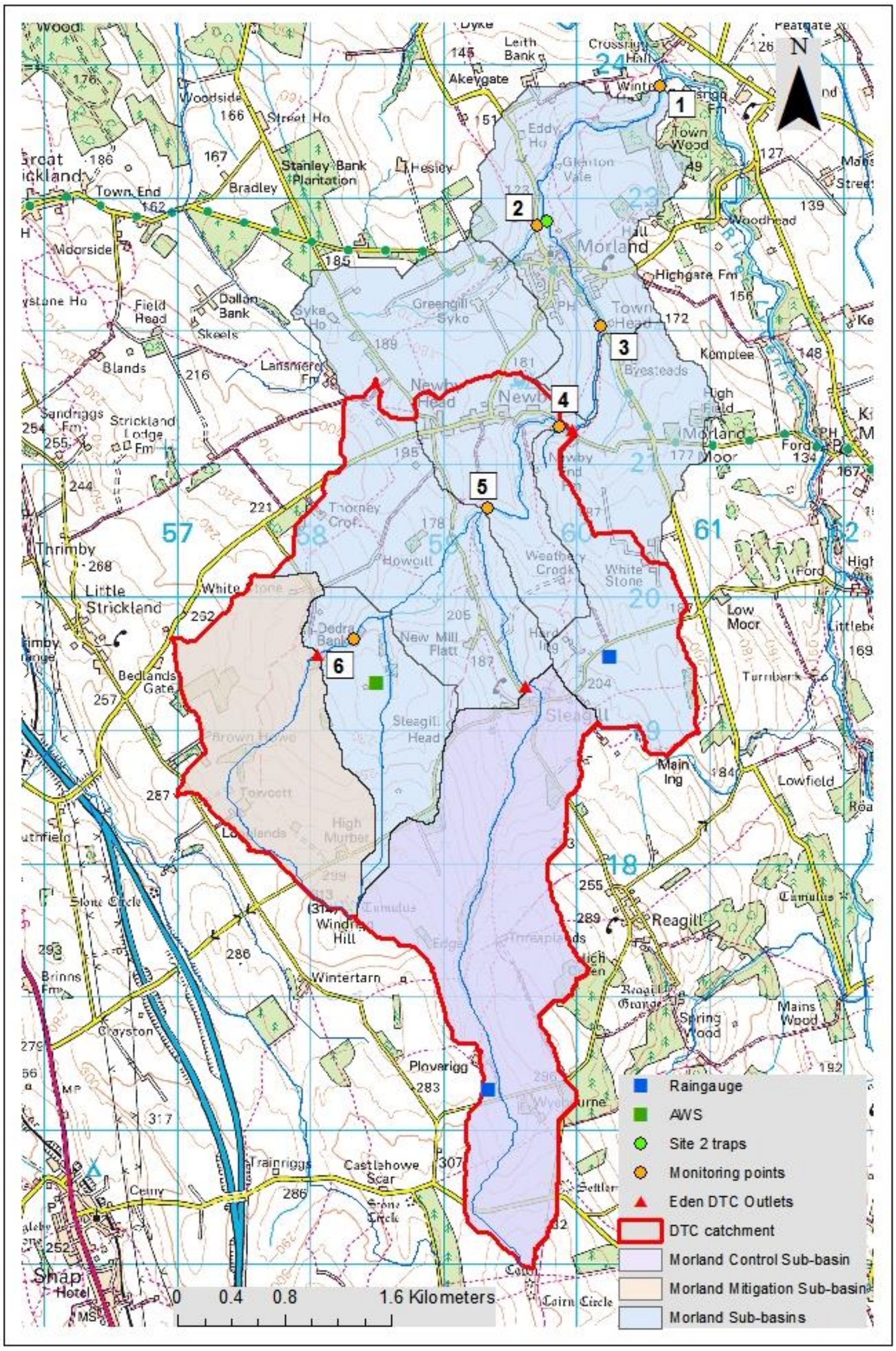

Figure 5.1 Map of the Newby Beck+ catchment, including the Eden DTC monitoring stations and original Newby Beck DTC catchment. AWS = Automatic Weather Station.

The Eden catchment bedrock consists of Permian and Triassic sandstones in the valley bottom, overlain by rocks of the Carboniferous Series (Ockenden et al., 2016). Newby Beck+ itself lies on the Carboniferous layers which dip under the sandstone at the valley bottom (Ockenden et al., 2016). There are likely to be localised aquifers across the catchment (Allen et al., 2010), however the degree of interconnection between bedrock and river is not currently known, and a borehole programme has been established to further investigate this.

Land use is largely improved grassland (76%), rough grazing (14%), with small areas of arable (6%), urban areas only comprise 0.7% of the land area (CEH, 2007; Ockenden et al., 2016). Morland village has a population of approximately 300 persons and has a small water treatment works beyond the village (~500 yards upstream of site 2 traps, Figure 5.1). Septic tanks do exist in the catchment but no map or data are currently available. Application rates of P fertiliser to grazed grassland fields are on average at 29 kg P ha^{-1} and nitrogen fertiliser at 63 kg N ha^{-1} reported for 2015 (Defra, 2016). Farm diary DTC data suggests in 2014 farm yard manure (FYM) applied to grassland was totalled to 285 kg ha^{-1} providing an additional estimated 5.9 kg P ha^{-1}. The soils are dominated by slowly permeable and seasonally waterlogged fine loams classified as Typic Haplaquept Inceptisols (Soil Survey Staff, 1999), or Chromic Eutric Albic Luvic Stagnosols (IUSS Working Group WRB, 2015), in the southern part of the catchment and well drained fine loams in the northern areas (NSRI, 2014). Average rainfall is 1203mm (1981-2000mm) and the catchment base flow index is 0.39 (Ockenden et al., 2016).

5.3.2 River data

At the six chosen sites flow or discharge (Q) was estimated for the days with corresponding nutrient data (bi-weekly sampling October 2014- July 2016) from the daily average of level data logged at 15-minute intervals using a barometric logger (In-Situ inc., Troll Series). Water level data was converted to flow using the application of a rating curve based on gauged flows (n=7) (Appendix 3 Figure 1). Flow was calculated using the equation:

$$\boldsymbol{Q} = \boldsymbol{C}(\boldsymbol{h} + \boldsymbol{a})^{\boldsymbol{n}} \qquad \textbf{(1)}$$

Where Q is flow, h is stage or level, a is the stage at zero flow, and C and n are constants calculated by the least squares procedure (Appendix 3 Table 1). No flow was recorded for 3 months in the spring of 2015 at all sites other than site 4 due to equipment failure. At the DTC outlet station level data are recorded at a 15-minute interval (converted here to 30-minute resolution), this data are converted to flow using the Velocity-Area Rating Extension (VARE) model (Ewen et al., 2010). It should be noted this is a different method of converting level to flow data used here; this method more accurately accounts for higher flows. However, high flows were not used in this study and there is good agreement ($r^2 = 0.89$) between the two methods for the lower flows which is visualised in Appendix 3 Figure 2 for site 4 which is the nearest site to the DTC outlet station (comparisons between DTC data and sites 5 and 6 are visualised in Appendix 3 Figure 3).

Stream chemistry data (chloride (Cl^-), total phosphorus (TP), soluble reactive phosphorus (SRP)) were collected at the 6 sites on a bi-weekly basis from October 2014 to August 2016. Two samples per site were collected in 50 mL centrifuge tubes; one was filtered at the site using a Whatman 0.45 µm syringe filter. Samples were then stored in a cool box until returning to the laboratory and stored at 4ºC until analysis within 48 h (see section 5.3.4.1). Samples were collected at the same place and in the same order (1-6) to ensure a consistent sampling technique. Whilst this technique may not be totally representative of the site, the consistent method allows the dynamics of the site to be sufficiently captured over time.

Total P and total reactive P (TRP) (30-minute resolution) were also recorded in-situ at the Newby Beck DTC outlet station with a Hach Lange Sigmatax sampling module and Phosphax analyser. A flow-through reservoir was refreshed at 30-minute intervals, from which samples were drawn for TP and TRP analysis. Total P and TRP are alternately measured by acid digestion (omitted on TRP cycle) and colorimetry by the Sigmatax-Phosphax analyser (Ockenden et al., 2016). The data (collected and validated by the DTC team) was accessed via an online sharing platform.

5.3.2.1 Chloride as a conservative tracer

Conservative tracers such as chloride (Cl^-) and boron (B^-) have been used to determine the retention and remobilisation of (non-conservative) P, especially effluent P, using extended end-member techniques (EMMA) (Jarvie et al., 2006; Jarvie et al., 2006; Jarvie et al., 2012; Neal et al., 2011; Tye et al., 2015). This analysis is possible when two distinct end-member chemistries which constrain the mixing series can be identified (Boyle et al., 1974; Burton 1988; Liss 1976). In this study, the two end-members would be 1) a dominant base-flow point source of elevated concentration of P and Cl^- from an effluent source, and 2) a high-flow and-member of low concentration of P and Cl^-. Providing these can be identified, a straight-line relationship between P and Cl^- indicates conservative mixing, whilst a non-linear or scattered relationship suggests non-conservative mixing (Jarvie et al., 1997), whereby P is subject to removal or addition via the stream-bed for example.

5.3.2.2 Phosphorus load apportionment modelling

The load apportionment model (LAM) described in Bowes et al. (2008) is used here to estimate the total annual load of P and the proportion of which are contributions from point or diffuse P sources. In this method, P concentration is modelled as a function of river flow rate, assuming that point (F_p) and diffuse (F_d) source loads (mg s^{-1}) can be modelled as a power-law function of flow, Q (m^3 s^{-1}).

$$\boldsymbol{F_p = A * Q^B \text{ and } F_d = C * Q^D} \qquad \textbf{(2)}$$

Total load (F_t, mg s^{-1}), of P is then a linear combination of the loads from point and diffuse sources:

$$\boldsymbol{F_t = F_p + F_d = A * Q^B + C * Q^D} \qquad \textbf{(3)}$$

where the parameters A, B, C and D are to be determined empirically. Phosphorus concentration (C_p, mg m^{-3}) at a given sampling point is equal to the load divided by flow, and so can be expressed as:

$$\boldsymbol{C_p = A * Q^{B-1} + C * Q^{D-1}} \qquad \textbf{(4)}$$

To test the model fit, the *Solver* function in Microsoft EXCEL© was used. Table 5.1 shows the parameter values used.

Table 5.1 Parameter values from the load apportionment modelling for the Newby Beck+ sites (1-6) for total phosphorus (TP) and soluble reactive phosphorus (SRP).

Site	Model parameter values TP				
	A	B	C	D	count
1	8.16	0	555.99	2.68	36
2	2.16	0	837.96	1.76	37
3	0.00	0	41.73	1.00	31
4	0.91	0	407.93	2.46	41
5	0.00	0	38.98	1.00	39
6	0.00	0	57.89	1.00	39
Site	Model parameter values SRP				
	A	B	C	D	count
1	7.12	0	196.03	2.00	36
2	1.87	0	313.99	1.42	35
3	0.00	0	29.51	1.00	31
4	0.83	0	184.85	2.19	38
5	0.00	0	34.28	1.00	36
6	0.00	0	42.75	1.00	36

5.3.2.3 Calculating mass balance

Catchment mass balance was calculated according to the standard expression as used by Teissier et al. (2008):

$$\boldsymbol{M_{dn}(\alpha) = M_{up}(\alpha) + M_t(\alpha) + \Delta m(\alpha)} \qquad \textbf{(5)}$$

Where $M_{dn}(\alpha)$ is the mass of the constituent α (phosphorus) at the downstream (dn) end of the reach in kg, $M_{up}(\alpha)$ is the mass upstream of the tributaries (M_t) in kg. The $\Delta m(\alpha)$ is the mass variation (kg) for α due to instream processes, therefore reflecting the net activity of the reach for in-stream processes. As $\Delta m(\alpha)$ was the unknown, the above equation was rearranged to make $\Delta m(\alpha)$ the subject. Each term $M\gamma$ (γ= dn, up,

t) is the total mass of the dissolved element, in this case P, crossing the sampling site during the sampled period. Each $M\gamma$ is characterised by the concentration (c_i) and discharge (q_i):

$$\boldsymbol{M_{(i)} = (c_i q_i + c_{i+1} q_{i+1})/2 \ * \Delta t} \tag{6}$$

$$\boldsymbol{M_\gamma = \sum M_{(i)}} \tag{7}$$

With $\Delta t = (t_{i+1} - t_i)$ as the time between the characterisation of $M_{(i)}$, it is therefore the frequency of sampling for each site. Mass balance is calculated between sites 4 and 1 (which include tributary sites 3 and 2) as further upstream not all the tributaries are accounted for as TP data is not available for the DTC mitigation sub-basins. Therefore, the mass at sites 6 and 5 is compared, but retention was not calculated. For summer and winter calculations, the mass variation was calculated for June, July, August and December, January, February respectively.

5.3.3 Sediment sampling

In the summer of 2015 sediment traps were installed at the 6 sampling locations. It should be noted that site 2 sediment samples were on the main Newby Beck before the site 2 (Figure 5.1) tributary entered the beck, this was due to inappropriate substrate for digging traps into the bed. These were 300 x 200 x 220 mm plastic boxes with wire mesh (10 mm square openings) tops 20 mm below the inside of the box, similar to the design in Bond (2002). Six boxes were initially dug into the stream bed at the beginning of July 2015, the lip of the box was flush with the stream bed and on top of the wire mesh clasts from the stream bed were used to create similar hydraulic conditions to the rest of the bed. Two boxes were then carefully retrieved from each site in October 2015. During the record breaking flows in Storm Desmond in December 2015, traps were lost and 6 across sites 1, 2 (one trap at each), 4 and 6 (two traps at each) were retrieved in February 2016. Two traps per site were then reinstalled in February. These traps were removed in April 2016, reinstalled, and then collected again in June 2016. Samples were stored at 6ºC and analysed for EPC_0 and total phosphorus (see sections 5.3.4.2 and 5.3.4.5).

In February 2016 bed sediment samples were collected at monthly intervals until August 2016 at the 6 sites. A transect at the monitoring site was chosen and 3 points were chosen across the stream. A metal cylinder (height= 100 cm, base area= 324 cm^2) was carefully placed and sealed to the stream bed, a plastic tube was then used to agitate the water (40 seconds) and the top 5 cm of the bed to mobilise fine sediment. This method is similar to that found in Ballantine et al. (2009). Two litres of the turbid water were then collected and stored at 6ºC before analysis of SRP according to the method in section 5.3.4.1. This was carried out at the 3 points across the stream. Results from this method are referred to as surface sediments. Sediments were analysed for EPC_0 and total phosphorus (see sections 5.3.4.2 and 5.3.4.5). Two litres of stream water from each site was collected on each occasion to calculate background total suspended solids (TSS) and to use in the sorption experiments.

5.3.4 Laboratory analysis

5.3.4.1 Stream samples collected on a bi-weekly basis

Unfiltered samples were digested in acid persulfate and analysed for TP, and filtered samples (Whatman 0.45 µm syringe filtered) were analysed for SRP according the method of Murphy and Riley (1962) using a SEAL AQ2 auto analyser in both instances. Chloride was analysed on filtered samples using ion chromatography (Dionex). In all analysis independent reference standards (Fisher Scientific Ion Chromatography –IC Standards) were used to ensure the accuracy of the calibration and their concentrations (e.g. for SRP 0.0375 and 0.15 mg P L^{-1}). In addition, control standards (e.g. 0.5 mg P L^{-1}) were used to check the instrument did not drift. Standards are also checked to see if they are within 10% of their known value or the run is repeated. Repeats of samples are also analysed to check they are within 10% of the reported value. Concentrations are reported by the machines to 4 decimal places, I report values to 2 decimal places.

5.3.4.2 Sediments: Equilibrium phosphorus concentration (EPC_0)

This method is an adaption from the method of Jarvie et al. (2005). All sediments were stored at 6ºC until analysis within one week of collection. I note the importance of the physiochemical changes that the sediment may undergo during sampling and storage. I have therefore attempted to recreate stream conditions where possible, e.g. by using stream water and the use of wet sediment, however the results are only used to assess the *potential* for SRP uptake or release, as advised by Palmer-Felgate et al. (2011). Sorption experiments were carried out using filtered (0.45 µm) stream water from each site, these were analysed for initial SRP concentration as above. Turbid water samples from the all sediment samples were centrifuged to remove the overlying water. Sediments (both trap and bed sediment samples) of <2 mm were analysed as this fraction is the most geochemically active (Jarvie et al., 2005). For each sediment sample (3 repeats per site) a known weight of wet sediment was placed in six 50 mL centrifuge tubes (108 samples). Stream water samples were then spiked with PO_4-P to provide a range of SRP concentrations (0, 2.5, 5, 10, 15, 20 µmol L^{-1}), 20 mL of each spiked sample was added to the sediment. Tubes were then placed on an over-end shaker in the dark for 24 h. After 24 h, tubes were centrifuged and the SRP concentration of the supernatant was analysed. Total dry mass was then determined by drying sediments to a constant weight.

EPC_0 (µmol L^{-1}) was then determined by plotting the relationship between the change in the amount of SRP sorbed after 24 h, relative to the initial amount (stream water concentration plus spike in µmol g^{-1}, ΔN_a), against the concentration of SRP in solution after 24 h (C_i, in µmol L^{-1}), and fitting an isotherm using the Freundlich model (House and Denison, 2000; Jarvie et al., 2005). The linear portion of the isotherm described by the sorption constant (K_d) was calculated using the *solver* function in Microsoft EXCEL©, the magnitude of which reflects the sorption affinity of sediments for SRP (House and Warwick, 1999; Jarvie et al., 2005).

5.3.4.3 Sediments: Extent of disequilibrium

When sediments are re-suspended in the water column, it can require a long time to obtain equilibrium with the ambient water due to a low solid to water ratio, consequently disequilibrium can be observed (Zhang and Huang, 2007). The extent of disequilibrium is given by the difference between water column SRP concentration and sediment EPC_0 (stream [SRP] – EPC_0) (Zhang and Huang, 2007). If the difference is negative, it will indicate that re-suspended sediment acts as a source, releasing P to the ambient water (Zhang and Huang, 2007). This is a similar concept to ‘EPC_0 Percentage Saturation’ used by Jarvie et al. (2005).

5.3.4.4 Sediments: Total suspended solids

Pre-weighed 1.2 µm filter discs were used to filter (using vacuum pump apparatus) 2 L of stream water samples per site. Each disc was dried at 105ºC for at least 1 hour, cooled in a desiccator and weighed. This was repeated until weight loss between two successive weighs was <0.5 mg. Total suspended solids were calculated as:

$$\frac{\boldsymbol{A-B}}{\boldsymbol{C}} * \mathbf{10^6}\ \boldsymbol{mg\ L^{-1}} \qquad \textbf{(8)}$$

Where;

A= weight of filter and solids (g)

B= weight of filter (g)

C= volume of sample filtered (mL)

5.3.4.5 Sediments: Total phosphorus

Sediment total phosphorus (S_{TP}) was determined by digesting sediment by a sulphuric-peroxide digestion mixture (Rowland and Grimshaw (1985) - modified Kjeldhal). Sediment samples (3 samples per site) were air-dried and sieved to <2 mm. Samples were then ground to a fine powder, and 0.2 g was weighed and placed in a 50 mL tube. In a fume cupboard 4.4 mL of the digestion mixture was added and the samples were digested (400ºC for 2 h). Samples were cooled, diluted to 50 mL, vortex mixed and left overnight. Samples were subsequently diluted (5-fold) and analysed for TP (Murphy and Riley, 1962) using a Seal AQ2. All sediment samples were dried in an oven at 105ºC to determine the total dry mass collected in both surface and trap sampling methods for each sampling date.

5.3.5 Statistical analysis

Simple linear regression was used to evaluate the relationship between sediment EPC_0, SRP and S_{TP}. It was also used to infer the relationship between stream load and concentration of TP and Cl^-. R^2 values are reported.

An F-test (two-sample for variances, alpha = 0.05) was used to determine whether surface and trap S_{TP} had equal variances. This was then used to justify the use of t-test (two-sample assuming equal variances, alpha = 0.05) to identify whether surface and trap S_{TP} was significantly different. Simple linear regression was then used to determine the relationship between surface and trap S_{TP} between months (r^2 values are reported). Frequency distributions of TP concentrations were determined by histogram plots.

5.4 Results

5.4.1 In-stream phosphorus, chloride and flow dynamics

Summary statistics of the bi-weekly samples of TP, Cl^- and high frequency flow at all sites for the sampling period October 2014 – July 2016 are reported in Table 5.2. Soluble reactive phosphorus concentrations are on average 78% of TP concentrations, and therefore show similar trends to TP during the sampling period (Figure 5.2). DTC outlet station data for TP and total reactive phosphorus (TRP) were compared to TP and SRP at site 4 for the same sampling period (Appendix 3 Figure 4). Total P shows good agreement and is within the daily range of TP recorded at the outlet station. Site 4 SRP data is higher than DTC TRP data, this difference may be due to the difference in analytical methodology and the timing of analyses giving rise to approximately 0.02 mg L-1 difference in concentration. Despite this, DTC TRP concentrations were on average ~80% of TP concentrations. Highest TP concentrations are most frequently observed at site 2 and site 6, and lowest TP values are most frequently observed at site 4 (Appendix 3 Figure 5). Total P and Cl^- ratios for the sampling period are described in Appendix 3 Figure 6.

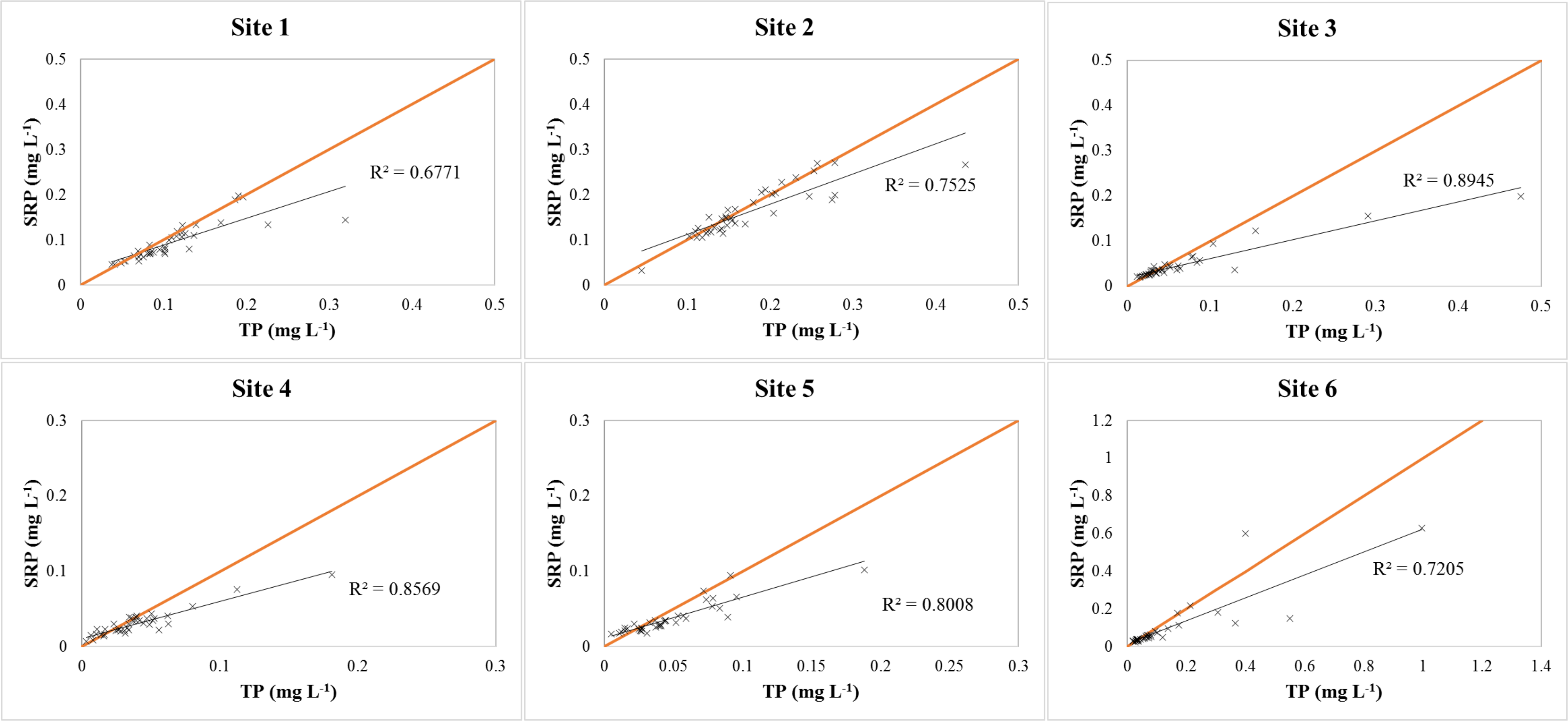

Figure 5.2 Soluble reactive phosphorus (SRP mg L^{-1}) versus total phosphorus (TP mg L^{-1}) including linear regression and R^2 values for the 6 sampling sites in the Newby Beck+ catchment for the time period October 2014 – July 2016. The orange line depicts a 1:1 relationship.

Table 5.2 Summary statistics of bi-weekly samples for the sampling period October 2014 – July 2016 of soluble reactive phosphorus (SRP mg L^{-1}); total phosphorus (TP mg L^{-1}); chloride (Cl$^-$ mg L^{-1}), and flow (m^3 s^{-1}). Flow data is the calculated daily flow for the sampling dates in which water samples were collected.

	Site 1				**Site 2**				**Site 3**			
	SRP (mg L^{-1})	TP (mg L^{-1})	Cl$^-$ (mg L^{-1})	Flow (m^3 s^{-1})	SRP (mg L^{-1})	TP (mg L^{-1})	Cl$^-$ (mg L^{-1})	Flow (m^3 s^{-1})	SRP (mg L^{-1})	TP (mg L^{-1})	Cl$^-$ (mg L^{-1})	Flow (m^3 s^{-1})
n	41	40	42	36	41	40	42	37	41	40	42	31
min	0.05	0.04	10.66	0.05	0.03	0.04	12.93	0.01	0.02	0.01	15.10	0.00
mean	0.09	0.11	18.52	0.19	0.16	0.17	21.87	0.06	0.05	0.06	21.82	0.02
median	0.08	0.10	17.41	0.17	0.15	0.15	21.42	0.05	0.04	0.04	19.49	0.02
max	0.20	0.32	30.08	0.69	0.27	0.44	37.86	0.29	0.20	0.48	52.05	0.04

	Site 4				**Site 5**				**Site 6**			
	SRP	TP	Cl$^-$	Flow	SRP	TP	Cl$^-$	Flow	SRP	TP	Cl$^-$	Flow
n	40	39	41	41	39	38	40	39	39	38	40	39
min	0.01	0.00	7.45	0.02	0.02	0.01	10.50	0.00	0.02	0.02	10.56	0.00
mean	0.03	0.04	14.63	0.16	0.04	0.05	14.77	0.04	0.09	0.13	15.77	0.02
median	0.03	0.03	14.26	0.13	0.03	0.04	14.04	0.03	0.05	0.06	15.00	0.01
max	0.10	0.18	25.92	0.59	0.10	0.19	32.83	0.11	0.63	1.00	35.75	0.08

Both TP and Cl$^-$ concentrations in each reach show some evidence of dilution with flow, sites 1 and 2 clearly show initial dilution with flow (Figure 5.3). Sites often exhibit high TP concentrations at low flows, specifically sites 1, 2, 5, and 6. Highest TP concentrations were observed at higher flows, however, the highest TP at site 6 was not observed at the highest flow.

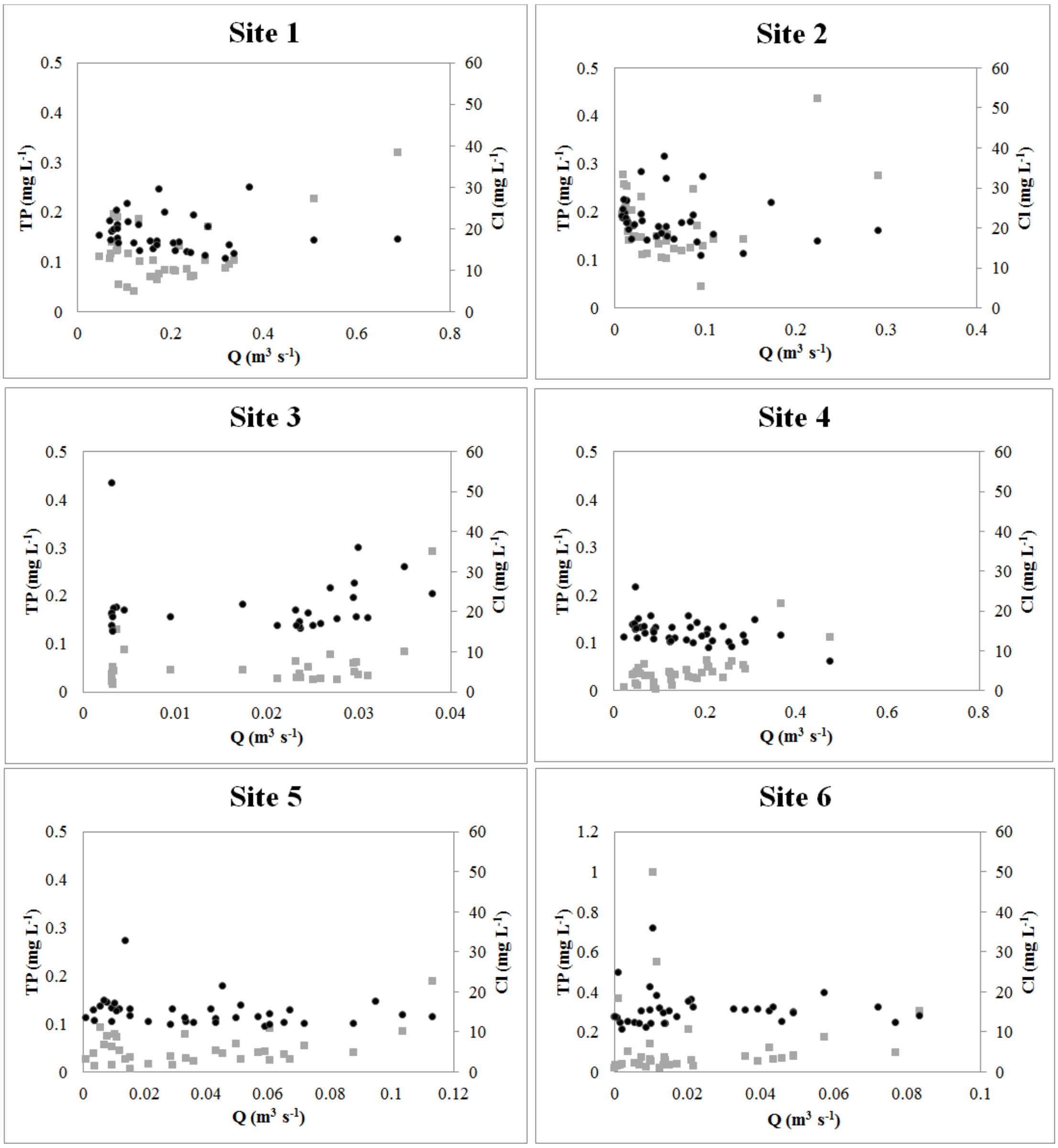

Figure 5.3 Stream total phosphorus (TP mg L^{-1}) (grey squares) and chloride (Cl$^-$ mg L^{-1}) (black circles) concentration versus stream flow (Q m^3 s^{-1}) for each site for the sampling period October 2014 - July 2017.

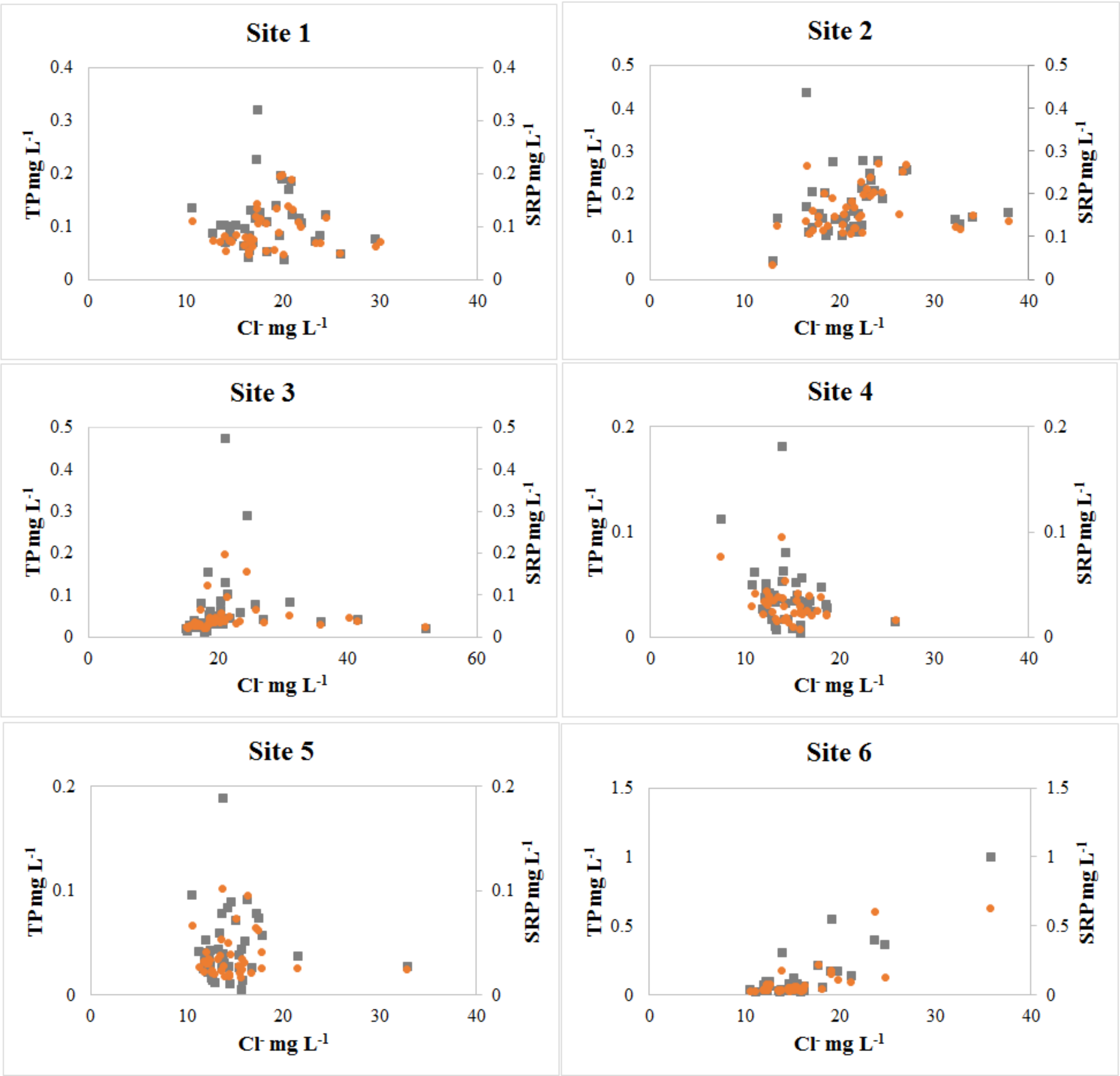

Figure 5.4 Stream total phosphorus (TP mg L^{-1}, grey squares) and soluble reactive phosphorus (SRP mg L^{-1}, orange circles) versus chloride (Cl^{-} mg L^{-1}) for each site for the sampling period October 2014 - July 2017. Note: each axis scale is different.

Figure 5.4 shows the non-conservative behaviour of TP and SRP as the relationship between phosphorus species and Cl^{-} concentration does not appear linear. There is some evidence at site 2 and 3 of two possible divergent straight lines. The scattered relationship at site 1 suggests there might not be distinct low-flow and high-flow endmember characteristics. This is not the case at site 6 suggesting there is a distinct ratio between P and Cl- at low-flows and high-flows, and that the low-flow signal is diluted under high-flow conditions. Appendix 3 Figure 7 shows the relationship of TP load and flow at the DTC Newby Beck outlet station for the same study time period, showing increased TP load at higher flows suggesting diffuse source inputs.

5.4.1.1 Phosphorus load apportionment modelling (LAM)

Phosphorus LAM results are reported in Table 5.3 (both TP and SRP), and Appendix 3 Figure 8 (TP) and Figure 9 (SRP). This catchment is primarily dominated by diffuse sources of TP, but downstream of Morland village at sites 1 and 2 point sources contribute more to the total TP load (18-34%). Site 4 near the Newby Beck DTC outlet also has contributions from point sources (8.5%). At site 1 point source contribution could dominate TP load 64% of the time. The model suggested similar results for SRP, although point source SRP was modelled as a slightly greater proportion of the overall load than TP. However, SRP point sources were calculated to contribute to the load less of the time comparative to TP, e.g. site 2 TP point sources predicted to dominate the load 46% of the time, whilst SRP 37% of the time. The LAM was also applied to the DTC high-resolution data but a poor model fit was found, perhaps due to the fact that such high-resolution dynamics identify hysteresis effects which mean the correlation is poor (Appendix 3 Figure 10). However, the model did suggest that from this site 100% of TP load was from diffuse sources.

Table 5.3 Results from load apportionment modelling for total phosphorus (TP) and soluble reactive phosphorus (SRP) load (t yr^{-1}) all sites (1-6) in the Newby Beck+ catchment.

Site	Load apportionment modelling TP				
	Point source TP load (t yr^{-1})	Diffuse source TP load (t yr^{-1})	Point source contribution to TP load (%)	Diffuse source contribution to TP load (%)	% of time point sources dominated TP load
1	0.26	0.49	34.2	65.8	64
2	0.07	0.31	18.0	82.0	46
3	0.00	0.02	0.1	99.9	0
4	0.03	0.31	8.5	91.5	32
5	0.00	0.05	0.0	100.0	0
6	0.00	0.04	0.0	100.0	0
Site	Load apportionment modelling SRP				
	Point source SRP load (t yr^{-1})	Diffuse source SRP load (t yr^{-1})	Point source contribution to SRP load (%)	Diffuse source contribution to SRP load (%)	% of time point sources dominated SRP load
1	0.22	0.36	40.0	60.0	61
2	0.06	0.24	19.4	80.6	37
3	0.00	0.02	0.1	99.9	0
4	0.03	0.16	14.5	85.5	32
5	0.00	0.04	0.0	100.0	0
6	0.00	0.03	0.0	100.0	0

5.4.1.2 Catchment mass balance

Mass balance calculations were carried out between sites 4 to 1 to fully account for the two tributaries at sites 2 and 3 (Figure 5.1) for the sampling period October 2014-July 2016 (Table 5.4). For this period the mass variation (Δm) (i.e. net retention or remobilisation) of P due to in-stream processes was calculated as 1410 kg (~822 kg yr^{-1}) and 335 kg (~195 kg yr^{-1}) for TP and SRP respectively. This calculation is an underestimate due to the missing 3 months of spring 2015 flow data (due to equipment failure), which could contribute >122 kg yr^{-1} more TP and >73 kg yr^{-1} more SRP according to 2016 spring calculations. The mass of TP was calculated for sites 6 and 5 as 1165 and 857 kg respectively for the sampling period October 2014-July 2016. Therefore, upstream of site 4 a total mass of ~1535 kg TP is not being accounted for. Mass variation of P (Δm) was calculated according to summer (June, July, August) and winter (December, January, February) months. In both the winters of 2015 and 2016, mass variation of TP was calculated as -392 and -132 kg respectively, indicating that TP mass was retained. Similarly, for SRP during the winters of 2015 and 2016, -283 and -131 kg were respectively calculated. During the summer of 2015 mass variation of TP and SRP was calculated as 275 and 299 kg respectively, indicating that the reach was gaining a greater mass of SRP than TP, i.e. that P was remobilised. Site 2 (tributary 1) contributes a greater mass downstream than the corresponding upstream site 4, it therefore contributes more than half of the mass to the downstream site 1.

Table 5.4 Results for calculating mass balance between sites 1 to 4 for total phosphorus (TP kg) and soluble reactive phosphorus (SRP kg). M_{dn} is site 1, M_{up} is site 4, M_{t1} is site 2 and M_{t2} is site 3. All numbers are rounded to the nearest whole number. Where mass variation (Δm) is positive mass is remobilised, and where negative mass is retained.

Total P (kg)	Mass balance TP				
	Mass downstream (M_{dn})	Mass upstream (M_{up})	Mass tributary 1 (M_{t1})	Mass tributary 2 (M_{t2})	Mass variation (Δm)
October 2014-July 2016	10408	3557	5046	395	+1410
kg yr^{-1}	6069	2074	2942	231	+822
Winter 2015	2667	1255	1598	207	-392
Summer 2015	642	145	174	49	+275
Winter 2016	1345	670	796	11	-132
Soluble reactive P (kg)	Mass balance SRP				
	Mass downstream (M_{dn})	Mass upstream (M_{up})	Mass tributary 1 (M_{t1})	Mass tributary 2 (M_{t2})	Mass variation (Δm)
October 2014-July 2016	7479	2615	4242	287	+335
kg yr^{-1}	4361	1525	2474	167	+195
Winter 2015	1975	762	1373	123	-283
Summer 2015	610	93	174	45	+299
Winter 2016	1021	481	667	4	-131

5.4.2 Sediments

Results of EPC_0 (µmol L^{-1}), stream SRP concentration (µmol L^{-1}) and S_{TP} (mg kg^{-1}) are reported in Figure 5.5; suspended solids (µmol L^{-1}) is reported in Appendix 3 Table 3. After December 2015 storm damage, only traps from 3 sites were recovered, data from 2016 is therefore only reported. Surface sediments were desorbing P at sites 1-4; trap sediment EPC_0 values were also closer to stream EPC_0.

Monthly surface sediment samples indicate that at downstream (sites 1 and 2) surface sediments are potentially more prone to alteration between absorbing and desorbing P, all other sites (upstream) show that surface sediments are desorbing P (Figure 5.5). Sediments in the traps however suggest that there is the potential for both the sorption and desorption of P.

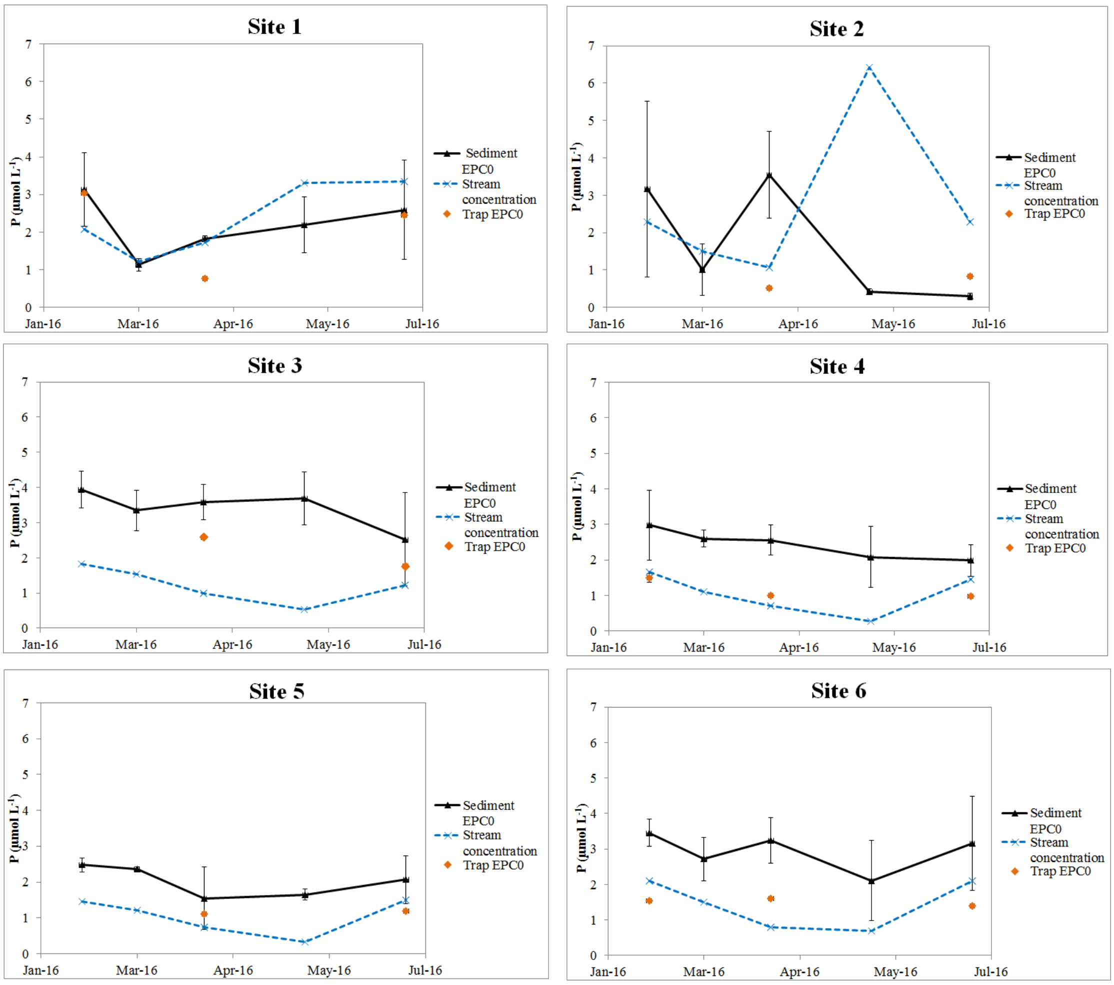

Figure 5.5 Equilibrium phosphorus concentration (EPC_0) for sediments and stream concentration (SRP µmol L^{-1}) for the sampling period February – July 2016. Error bars show the standard deviation of three sample repeats across the channel. When EPC_0>SRP in the surrounding water, the sediment will release SRP to the water column and when EPC_0<SRP, the sediment will take up SRP from the water column.

The extent of disequilibrium (Table 5.5) suggests that when surface sediments are re-suspended they will possibly act as a source to the ambient water at all sampled occasions at sites 3-6. At sites 1 and 2, re-suspended sediment is likely to act as a sink rather than a source on more sampled occasions. On average, site 3 surface re-suspended sediment is most likely to contribute the most to ambient water SRP concentrations, site 1 sediment is on the other hand least likely to contribute but rather act as a sink to water SRP concentrations.

Table 5.5 The extent of disequilibrium between average stream soluble reactive phosphorus concentration (stream [SRP]) and average surface sediment equilibrium phosphorus concentration (EPC_0) for the sampling period February –July 2016 (standard deviation). If the difference is negative, it will indicate that re-suspended sediment acts as a source, releasing P to the ambient water (Zhang and Huang, 2007).

	Feb 2016	**Mar 2016**	**Apr 2016**	**May 2016**	**Jul 2016**	**Average**
site	Extent of Disequilibrium (stream [SRP] – EPC_0)					
1	-1.05 (0.98)	0.10 (0.16)	-0.09 (0.08)	1.11 (0.74)	0.75 (1.31)	0.17 (0.83)
2	-0.87 (2.36)	0.50 (0.68)	-2.47 (1.16)	6.00 (0.07)	1.99 (0.09)	1.03 (3.23)
3	-2.12 (0.52)	-1.81 (0.58)	-2.59 (0.49)	-3.15 (0.75)	-1.31 (1.33)	-2.20 (0.71)
4	-1.31 (0.99)	-1.49 (0.23)	-1.85 (0.43)	-1.81 (0.86)	-0.53 (0.44)	-1.40 (0.54)
5	-1.01 (0.19)	-1.14 (0.06)	-0.81 (0.88)	-1.32 (0.15)	-0.58 (0.66)	-0.97 (0.29)
6	-1.35 (0.39)	-1.22 (0.61)	-2.44 (0.64)	-1.41 (1.13)	-1.07 (1.33)	-1.50 (0.54)

Total phosphorus in surface sediments is greatest at sites 3 and 6 from February to April 2016 (Figure 5.6). Sediment total phosphorus between trap and surface sediments is not significantly different across the catchment, p= 0.89, 0.99 for February and April, in July however a weaker relationship was observed (r^2 =0.5018, p= 0.27). There is no evidence to suggest correlation exists between S_{TP}, stream concentration and EPC_0 (Appendix 3 Figure 11-13). There is however a positive correlation between average trap S_{TP} and surface S_{TP} (Appendix 3 Figure 14), r^2= 0.93, 0.83, 0.50 for February, April and July 2016 respectively, indicating that this correlation weakens into the summer months. Linear regression analysis revealed that surface S_{TP} (mg) increased from February to July 2016 at all sites (r^2= 0.58, 0.65, 0.11, 0.80, 0.82, 0.94, for sites 1 to 6 respectively) (Figure 5.6).

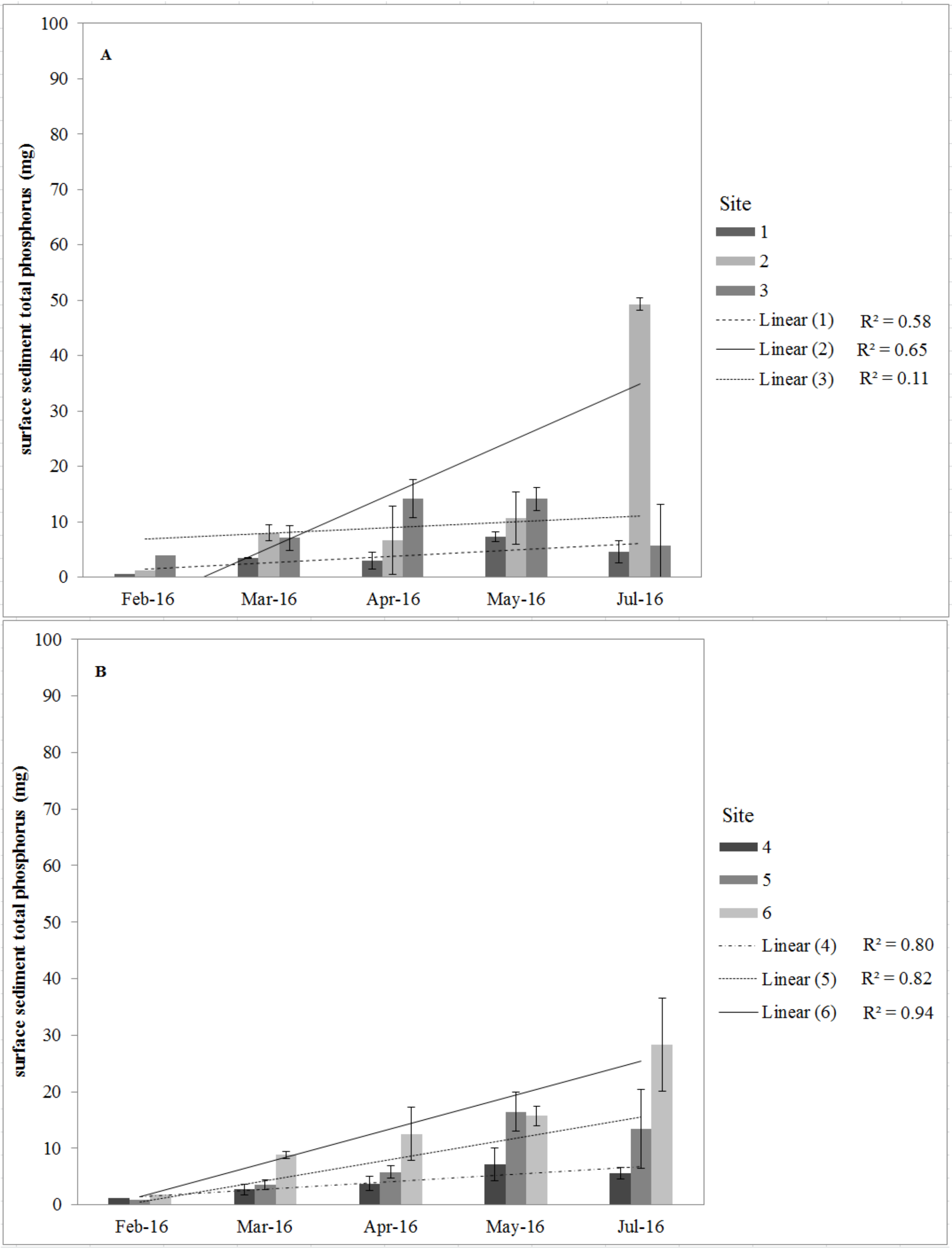

Figure 5.6 Surface sediment total phosphorus (mg) for Newby Beck+ sites A) 1-3 and B) 4-6 for the sampling period February – July 2016. Linear regression and r^2 values are included.

5.5 Discussion

5.5.1 In-stream phosphorus, chloride and flow dynamics

Within this headwater catchment it is notable that a significant proportion of observed TP is SRP (78%; 80% of TP is TRP for DTC outlet data); this headwater system is most likely impacted by the agricultural activities that occur. Ockenden et al. (2016) noted that at the DTC Newby Beck outlet higher proportions of TRP to TP were present at low flows, whilst particulate fractions were greater at high flows. The bi-weekly sampling regime has inadvertently favoured sampling during lower flows, which would likely explain the dominance of SRP. Nonetheless, although agricultural diffuse pollution is often particulate dominated (Kleinman et al., 2011), some evidence has suggested that low order streams have higher percentages of dissolved P than larger networks, due to biochemical transformations converting dissolved P to particulate P fractions in higher order streams (Dupas et al., 2015; Dupas et al., 2015). High proportions of dissolved P have also been observed in surface runoff in predominantly grassland systems (Haygarth and Jarvis, 1997; Heathwaite and Dils, 2000). This has been attributed to the high surface roughness of grassland which can consequently retain particulates, in addition to the preferential accumulation of P added in fertiliser and FYM at the surface of undisturbed soils, and thus yield high dissolved fractions of P (Heathwaite and Dils, 2000). Haygarth and Jarvis (1997) found that 70% of TP loss in grasslands was dissolved, primarily inorganic P, which is highly important for in-stream processes that control eutrophication issues. In addition, high dissolved fractions can be driven by subsurface flow sources and high groundwater connectivity (Dupas et al. 2015). The dominance of SRP is likely therefore due to the predominance of improved grassland within the catchment, which has good subsurface connectivity with the stream, especially at low flows.

There is some evidence to suggest the presence of point source contribution to each reach as TP and Cl^- concentrations show some evidence of dilution with flow, sites 1 and 2 in particular clearly show initial dilution with flow (Figure 5.3). Nonetheless, predominantly higher concentrations of TP are at higher flows which are indicative of diffuse source contributions. Total P and Cl^- ratios (TP:Cl^-) appear to fluctuate between those of un-impacted streams (0.0002- 0.0287), to levels comparable to sewage effluent contamination (e.g. >0.007 – 0.044) (Chen et al., 2015; Jarvie et al., 2012; Neal et al., 2005) (Appendix 3 Figure 6). In addition notable peaks in TP:Cl^- were observed (> 0.02), especially at site 6. In August 2015, the stream at site 6 had visible particulate matter present (Appendix 3 Photo 1); on September on the other hand slurry-like material was visible in the stream (Appendix 3 Photo 2 and 3) and TP concentrations remained elevated for at least a month from this date at this site. During these occasions comparatively lower SRP concentrations were observed, whilst Cl^- and TP concentrations were elevated and TP:Cl^- became comparable to effluent levels (Chen et al., 2015; Jarvie et al., 2012; Neal et al., 2005). Such evidence would imply some influence of sewage or slurry leakage to the system. Figure 5.4 suggests that TP acts conservatively at site 6, implying that the end-member effluent signal is diluted under high-flow conditions. This also suggested that there is mixing at which no transfer between phases is taking place (Jarvie et al., 1997), or that there is limited interaction with the streambed. The indication of divergent straight lines for site 2 and 3 in Figure 5.4 could suggest that catchment characteristics are having some influence on low-flow end-member composition (Jarvie et al., 1997). The scattered relationship at site 1 suggests there might not be distinct low-flow and high-flow endmember characteristics if not enough data has been collected to identify them, however Jarvie et al., (2007) suggests that such a relationship indicates the distinct non-conservative behaviour of a constituent. This would imply therefore the chemical and biological uptake of P throughout the reach.

5.5.1.1 Load apportionment modelling (LAM)

The phosphorus LAM implies that this catchment is dominated primarily by diffuse sources of P pollution (>60% TP and SRP), but that small villages such as Morland (approx. 350 people) can contribute significantly to point source pollution. Consequently, the importance of diffuse contributions downstream of the village could be potentially diminished as point sources can contribute to TP load 64% and nearly 50% of the time at sites 1 and 2 respectively. This means that although diffuse sources contribute to more of the TP load, of which 80% can be explained by high flow events (Ockenden et al., 2016), point sources are dominating more frequently and are therefore proportionally perhaps more important in terms of continuous downstream water quality.

At site 6, the model suggests there are no point sources dominating this site, for although a potential point source was observed at this site, a single point source may not be picked up by the data sufficiently to run the model. Frequency and timing of sampling can have a critical impact on how LAMs perform (Crockford et al., 2017). Using the high-resolution (30-minute) data from the DTC outlet performed poorly (high sum of squares), and is perhaps likely due to the fact a simple model is being used to describe a highly complex dataset.

5.5.1.2 Catchment mass balance

Calculating mass balance is a good way of accounting for net in-stream processing which would otherwise be immeasurable in this case. During the sampling period October 2014- July 2016, the mass variation between upstream site 4 and downstream site 1 suggest that TP and SRP mass increased along the reach, i.e. that P was remobilised, as a result of in-stream processing. Critically, the difference between TP and SRP mass gained (822 and 195 kg yr^{-1} respectively) implies sources of particulate P, which would support the predominance of diffuse inputs expressed by LAM. In addition, this gain in mass would suggest that in-stream processes are highly active in this headwater catchment, and can remobilise more P than a small tributary contributes (e.g. site 3). The remobilisation or transfer of P from the stream bed via abiotic (e.g. summer storms remobilising particles) and biotic transformations is especially important during the summer months. Sediment EPC_0 values at site 1 are correlated with stream SRP concentration and sediments at this site and have shown to fluctuate between desorbing and absorbing SRP. Therefore, it is perhaps possible that during low flow periods in the summer a high proportion of SRP mass could come from abiotic exchange from the sediments, thus contributing to the control of P concentrations during these periods (Van Der Perk et al., 2007). The significantly large mass of TP and SRP being contributed from the tributary at site 2 would suggest that farm-yard diffuse sources are critically important in this part of the catchment. This diffuse source is perhaps confirmed in its importance due to the higher SRP mass (and concentrations) measured during summer periods, which are characteristic of such sources (Withers et al., 2009).

During the winter months on the other hand, mass variation suggests that TP and SRP were being retained by the reach. It is most likely that this is due to over bank flooding retaining large amounts of P-rich sediment (Bowes and House, 2001), which was often visually observed between sites 4 and 1, especially during the winter of 2015. Snell et al. (2014) found that at the Newby DTC outlet site (beyond site 4), that trophic diatom index increased in winter months as TP concentration increased yielding a rise in nutrient tolerant taxa. Perhaps the proliferation of diatoms at these times can cause P to be absorbed, contributing to the retention of P. It is possible that sediments above the water line could have a greater affinity for absorbing SRP (House and Warwick, 1998), consequently when river level rises during the winter months bank sediments could absorb SRP, contributing to the retention of P.

There are always uncertainties in the measurement of flow (Di Baldassarre and Montanari, 2009), we can therefore over or under estimate how much this catchment is retaining or remobilising. In future, a greater frequency and range of flows associated with TP and SRP data would further reduce uncertainty. The incomplete accountancy of flow upstream of site 4 could account for the mass imbalance between sites 6 and 5 to 4; it is however possible that sediment could be contributing to the mass of P at site 4 as EPC_0 values suggest that upstream sediments are desorbing SRP. Nonetheless, it is important to estimate the variations in mass of P and therefore the behaviour of retention in this catchment.

5.5.2 Sediment phosphorus retention and release

Evidence here suggests that low order headwater streams are likely sources of P potentially contributing to P values further downstream. EPC_0 values show a clear spatial pattern whereby surface sediments have the potential to desorb P upstream of the village of Morland (sites 6-3), whilst surface sediments downstream of the village interchange between sorption, desorption and equilibrium (sites 1 and 2) (Figure 5.5). This would suggest that upstream reaches could be contributing to stream concentrations of P downstream, this differs from the mass balance results that imply remobilisation is critically occurring between sites 2 and 1. This also contrasts to the results from conservative mixing that suggests that upstream at site 6 P is not acting non-conservatively with the reach, implying that limited retention and remobilisation is occurring. However, previously, sediments impacted by point pollution have been found to absorb SRP especially during periods of low flow and ecological sensitivity due to elevated stream channel P concentrations downstream of sewage works (Jarvie et al., 2006). As upstream sediment EPC_0 does not correlate well with stream SRP concentration it is likely that these upstream sediments provide a vital source of SRP to the benthic community consequently retaining P within the reach during spring and summer (Weigelhofer, 2016). Headwater sites could also have high EPC_0 and S_{TP} values, due to the deposition of particles with high exchangeable P from diffuse sources (Jarvie et al., 2005). For example, sediments have been found to become anoxic due to the impact of dairy slurry consequently yielding high EPC_0 values (Reddy et al., 1998), which is likely to be occurring at these sites. Oxic conditions can critically control stream SRP concentrations by altering for example, Fe and Al to P ratios, and Fe^- and Al^- oxyhydroxide content (Hoffman et al., 2009; Klotz, 1988; Syers et al., 1973; Williams et al., 1971). Low redox potential (reducing conditions) for example, has been found to increase EPC_0 (House and Denison, 2000). If anoxic conditions have persisted over a long period of time the retention capacity of sediments would have likely been removed and consequently sediments act as a source of P rather than a sink due to the saturation of exchangeable P (Zhang and Huang, 2007). If sediments were re-suspended they would be in disequilibrium with the surrounding water column, subsequently acting as a source of P (Table 5.5). Exchange between SRP in sediments and stream water is likely to be more rapid during hydrological events (Hoffman et al., 2009; House et al., 1995), therefore desorption of SRP may contribute to high percentages of SRP to TP, and may also account for a rise in nutrient tolerant taxa (Snell et al., 2014).

Trap sediments are in this case more closely coupled to stream concentrations in that they appear to fluctuate between absorbing and desorbing P, whereas surface sediments at sites 3-6 do not fluctuate. This may be due the sampling method of surface sediments, disturbance and potential changes of temperature to sediment could have resulted in changes to true in-situ EPC_0 values (Palmer-Felgate et al., 2011). However, temperature was not controlled in either sampling method so the effect would be uniform. Nonetheless trap and surface sediment S_{TP} correlate well (Appendix 3 Figure 14), implying that P-rich sediment sources are mobilised and deposited throughout the year, re-affirming the dominance of diffuse sources in this catchment.

It is evident that the point source influence downstream of Morland alters the buffering capacity of sediments, as EPC_0 values suggest they can both absorb and desorb SRP. Effluent discharges high in SRP have been found to "swamp-out" release of SRP from sediments (Jarvie et al., 2005), for it is the stream water SRP concentrations which increase downstream rather than EPC_0 notably changing from upstream sites, especially at site 1. However, Smolders et al. (2017) found that low dissolved oxygen (DO) levels (<4 mg L^{-1}) combined with high P/Fe ratio (>0.4) sediments in lowland rivers was associated with the mobilization of P to the water column, despite river bed P concentration or locality to sources. This therefore yielded high concentrations of P in water column during summer months. Therefore, the interchange between absorption and desorption of P could be due to unmeasured DO and P/Fe ratios.

5.5.3 Considerations under climate change

Ockenden et al. (2017) found that under climate change (high emissions scenario, 2050s) winter P loads in the Newby Beck will increase up to 30%. To mitigate such increases they report that major agricultural changes would be required (20-80% reduction in P inputs). Such predictions will critically impact the retention of P in this small headwater catchment. Higher flows in winter will mean more overland flow from grasslands; it is likely that SRP concentrations will remain high throughout the year giving way to increased likelihoods of eutrophication pressures. It is perhaps unlikely that point sources will remain as significant in contributing more frequently to load in Newby Beck. As high loads in winter driven by diffuse source contribution will likely "outwash" (i.e. whereby point sources decrease in significance due to the combined effect of the dilution and removal of sediments exposed to point sources) point sources at Morland village. Such high loads will give way to more P being retained within the catchment, as more is mobilised, therefore overbank flooding (which was observed in this study) may become increasingly frequent and important for retaining P in the headwaters.

Ockenden et al. (2017) also show that lower flows and a decrease in P export (-20%) during summer is likely under climate change. This poses significant risk to eutrophication issues during the summer, as mass balance calculations suggest that bed sediments are likely to desorb P contributing to the P load. On the other hand, during increased precipitation and loads in winter months, increased loads of sediment are likely to enter the stream reach. Particles will be washed out the system or deposited as new, this flushing effect is likely to "re-set" the system, changing whether sediments absorb or desorb P which will have implications for stream SRP concentrations in summer.

Therefore, it might be hypothesised that climate change will yield extremes between nutrient quality in summer (high concentrations, low flows) and winter (high loads, high flows). Yet, Ockenden et al. (2017) found that mitigation measures farmers are likely to implement under climate change scenarios (e.g. increased livestock housing, covered slurry stores) are unlikely to be effective in reducing P loads. The likely disparities between summer and winter stream water quality, alongside the likely inefficiencies of mitigation measures calls for policy and regulation to reflect the urgency of the potential impacts of climate change on the riparian health in rural headwater communities.

5.6 Conclusion

There is evidence to suggest that this headwater system has been impacted by the activities occurring in the catchment such as agriculture. Flow and P data suggest that diffuse sources are critical sources upstream of Morland village, but downstream of this point sources increase in importance. Load apportionment modelling implies that diffuse sources dominate (>65%) TP load, but point sources downstream of Morland village contribute up to 64% of the time therefore potentially diminishing the importance of diffuse sources beyond this point. Mass balance calculations also suggest that bed sediments could play a critical role in the desorption and remobilisation of P to the river reach during summer contributing the P load downstream, whilst in winter results suggest the opposite is the case, that P is retained, most likely by P retention in floodplains. Sediment EPC_0 values suggest that there is possibly a limited or non-existent retention capacity for SRP within the headwaters, but that the influence of point sources downstream of Morland village alter this buffering capacity as sediments show the ability to absorb and desorb SRP. The hypothesis that anthropogenic point sources of P can alter the degree of retention of P even at the headwater scale where agricultural diffuse sources dominate can be accepted. In this case, this headwater catchment can potentially act as a source of P to downstream reaches, most likely due to anthropogenic inputs reduce the capacity of sediments to retain P. This remobilisation potential of P is especially critical during low flows when river ecological degradation is a more prevalent risk. Such low flow periods are likely to increase under climate change therefore, this headwater catchment may be at risk of further degradation. However, climate change will increase flows in Newby Beck by up to 30% in winter months. Such increases in flow may have the potential to “outwash” point sources at Morland village, and “re-set” instream sediment buffering capacity. It might be hypothesised therefore that climate change will yield extremes between nutrient quality in summer (high concentrations, low flows) and winter (high loads, high flows).

5.7 References

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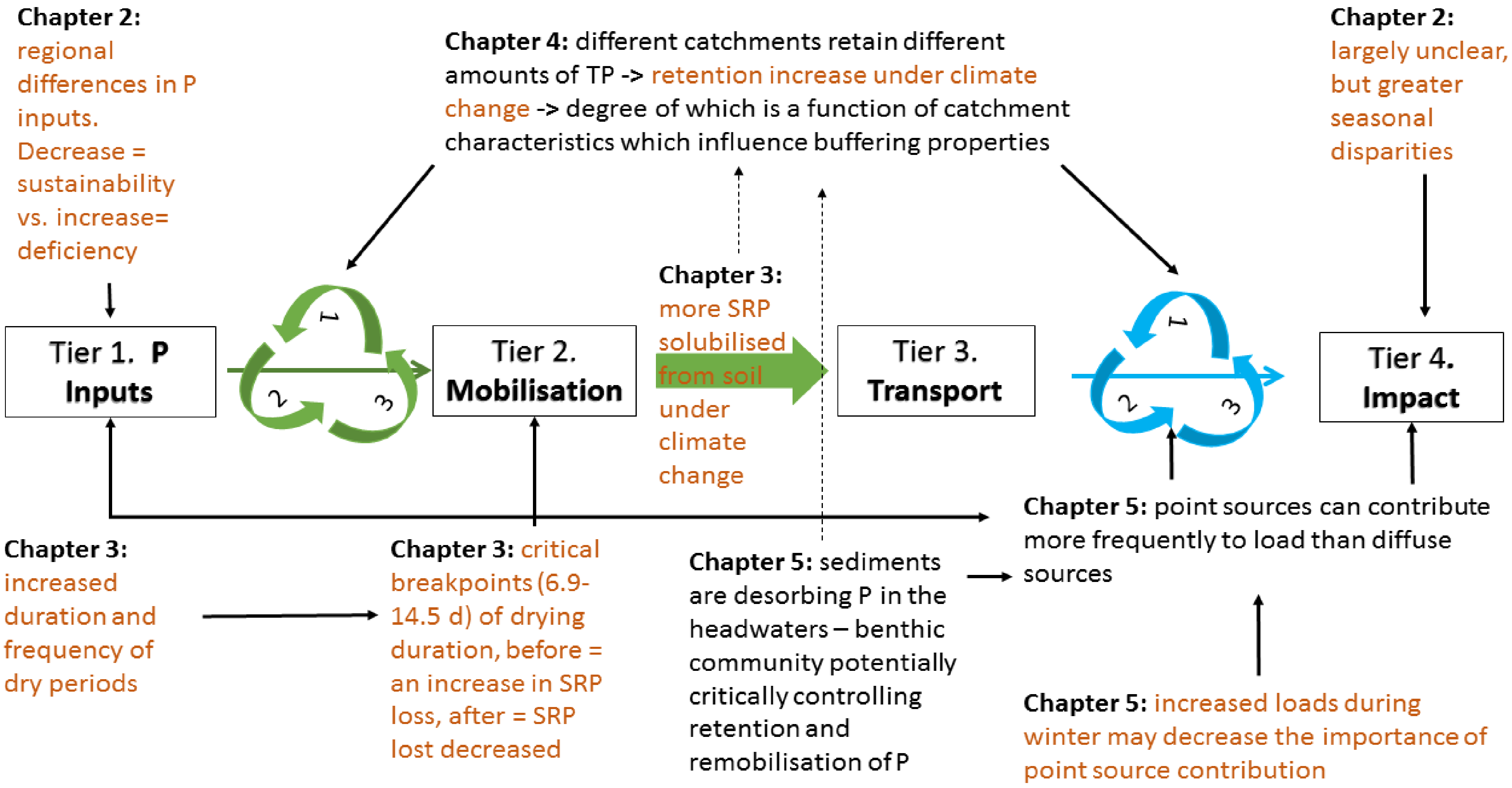
Chapter 6 Conclusions

In this chapter I firstly outline the specific conclusions reached from the work in this thesis. Secondly, I summarise and discuss the work completed and then outline future work which would be beneficial to enhance and progress my findings further.

6.1 Conclusions

My overall aim was to gain a better understanding of the possible changes which will be caused by climate change, including both individual processes (e.g. mobilisation) and catchment scale processes which encompass the P transfer continuum, in a rural headwater catchment (Newby Beck, Eden DTC).

I therefore highlight the possible risks of climate change exacerbating, rather than changing, the processes described in the P transfer continuum for the Newby Beck catchment (Figure 6.1 and Figure 6.2). This study has therefore encompassed a range of scales, from fine-scaled laboratory based experimentation; to small catchment scale monitoring; and multi-catchment coarse predictions; in order to bring together aspects of measuring and modelling to further our understanding of within catchment complexity (Neal, 2013). Objectives were achieved by analysis of current literature, laboratory experimentation, high and low- resolution river quality (P, chloride), flow, and sediment P data, and the modelling of process-based model predictions for P and flow for future climatic conditions. The work was underpinned by existing work being carried out on the national DTC framework, and research under the NUTCAT project.



Chapter 2: regional differences in P inputs. Decrease = sustainability vs. increase= deficiency

Chapter 4: different catchments retain different amounts of TP -> retention increase under climate change -> degree of which is a function of catchment characteristics which influence buffering properties

Chapter 2: largely unclear, but greater seasonal disparities

Chapter 3: more SRP solubilised from soil under climate change

Chapter 5: point sources can contribute more frequently to load than diffuse sources

Chapter 3: increased duration and frequency of dry periods

Chapter 3: critical breakpoints (6.9-14.5 d) of drying duration, before = an increase in SRP loss, after = SRP lost decreased

Chapter 5: sediments are desorbing P in the headwaters – benthic community potentially critically controlling retention and remobilisation of P

Chapter 5: increased loads during winter may decrease the importance of point source contribution

Figure 6.1 A conceptual diagram of the main conclusions of the thesis based on the phosphorus (P) transfer continuum diagram outlined in Chapter 2. The recycling arrows represent buffering properties on land (green) and within the river reach (blue). Writing in orange depicts changes under climate change. Bold arrows show linkages that influence the next process/component, dashed arrows show result links between chapters.

The following conclusions, relevant to the research objectives, have been drawn from this thesis and are highlighted in Figure 6.1 and Figure 6.2:

Objective 1: To appraise the likely changes to the P transfer continuum under climate change in regions of the world which already have extensive P issues and challenges by exploring the current literature.

- Conclusion 1: Global regions will have increased disparity in P inputs as agricultural land use and management strategies will either focus on sustainability and decrease inputs, or increase inputs to close deficiency gaps.
- Conclusion 2: Overall, impacts of P under climate change are perhaps largely unclear and will most likely exhibit greater seasonal extremes if combined summer temperatures increase and precipitation decreases, whilst winter precipitation increases.

Objective 2: To identify whether extreme summer conditions predicted in the UK will yield and increase of mobilisation of P via solubilisation from three DTC soils. I hypothesise that changes in the future patterns of DRW affect the amount of SRP solubilised.

- Conclusion 1: Under climate change projections, the duration and frequency of dry periods will increase compared with present day conditions in three contrasting UK catchments.
- Conclusion 2: For three soils critical breakpoints (6.9-14.5 d) of drying duration have been identified; before the breakpoint an increase in SRP loss with the number of dry days was observed; after this point the amount of SRP lost decreased or stayed fairly constant. The frequency of these breakpoints

occurring under climate change was predicted to increase and therefore yield an increase in SRP solubilisation in only two of the studied soils.

- Conclusion 3: As the frequency of longer dry periods will increase under climate change, the solubilisation of SRP from soil (-1 to +13%) will also change. Therefore, we can accept our original hypothesis that changes in the future patterns of DRW affect the amount of SRP solubilised (Figure 6.1).
- Conclusion 4: The study highlighted the need for more research with a greater range of soils to affirm results.

Objective 3: To explore the impact of climate change on catchment P retention in the three DTC catchments as a function of: (a) hydrological regime and residence time, (b) net biogeochemical retention, and (c) ecological response. I hypothesise that climate change will alter catchment P retention in these three contrasting UK catchments. I postulate that the degree of change experienced as a result of perturbation by climate change is determined by the sensitivity of a catchment to changes in hydrology, biogeochemistry and ecology which influence the retention of P in the land-water continuum.

- Conclusion 1: Results suggest that three contrasting UK catchments retain different amounts of TP for both observed and baseline conditions.
- Conclusion 2: Under climate change scenarios (UKCP09) each catchment retains more TP, consequently the hypothesis a) that P retention under climate change will alter can be accepted.
- Conclusion 3: The degree of retention was found to be a function of TP export, and influenced primarily by landscape characteristics that determined hydrological regime and residence time. Therefore, the hypothesis b) the

degree or sensitivity of change experienced will be determined by individual catchment characteristics (e.g. hydrology, biogeochemistry and ecology) and pressures which influence the retention of P in the land-water continuum can be accepted.

- Conclusion 4: As each catchment response to nutrient loadings under climate change is different, its response to remediation will be highly specific in nature, and therefore calls for policy and regulation to reflect this.

Objective 4: To improve understanding of in-stream retention of P and the influence of anthropogenic sources of P at the headwater scale (Newby Beck+). I hypothesise that anthropogenic point sources of P can alter the degree of retention of P even at the headwater scale where agricultural diffuse sources dominate.

- Conclusion 1: Flow and P data suggest that diffuse sources are critical P sources upstream of Morland village, but downstream of this point sources increase in importance.
- Conclusion 2: Load apportionment modelling implies that diffuse sources dominate (>65%) TP load, but point sources downstream of Morland village contribute up to 64% of the time therefore potentially diminishing the importance of diffuse sources beyond this point.
- Conclusion 3: Mass balance calculations suggest that bed sediments could play a critical role in the desorption and remobilisation of P to the river reach during summer contributing the P load downstream, whilst in winter results suggest the opposite is the case, that P is retained, most likely by P retention in floodplains.

- Conclusion 4: Sediment EPC_0 values suggest that there is limited potential for SRP retention within the headwaters, and indeed potential for SRP release from bed sediments, but that the influence of point sources downstream of Morland village alter this buffering capacity as sediments show the ability to absorb SRP.
- Conclusion 5: The hypothesis that anthropogenic point sources of P can alter the degree of retention of P even at the headwater scale where agricultural diffuse sources dominate can be accepted.
- Conclusion 6: Increased flows in Newby Beck (30%) in winter months may have the potential to "outwash" point sources at Morland village, and "re-set" instream sediment buffering capacity. Climate change may therefore yield extremes between nutrient quality in summer (high concentrations, low flows) and winter (high loads, high flows) (Figure 6.2).

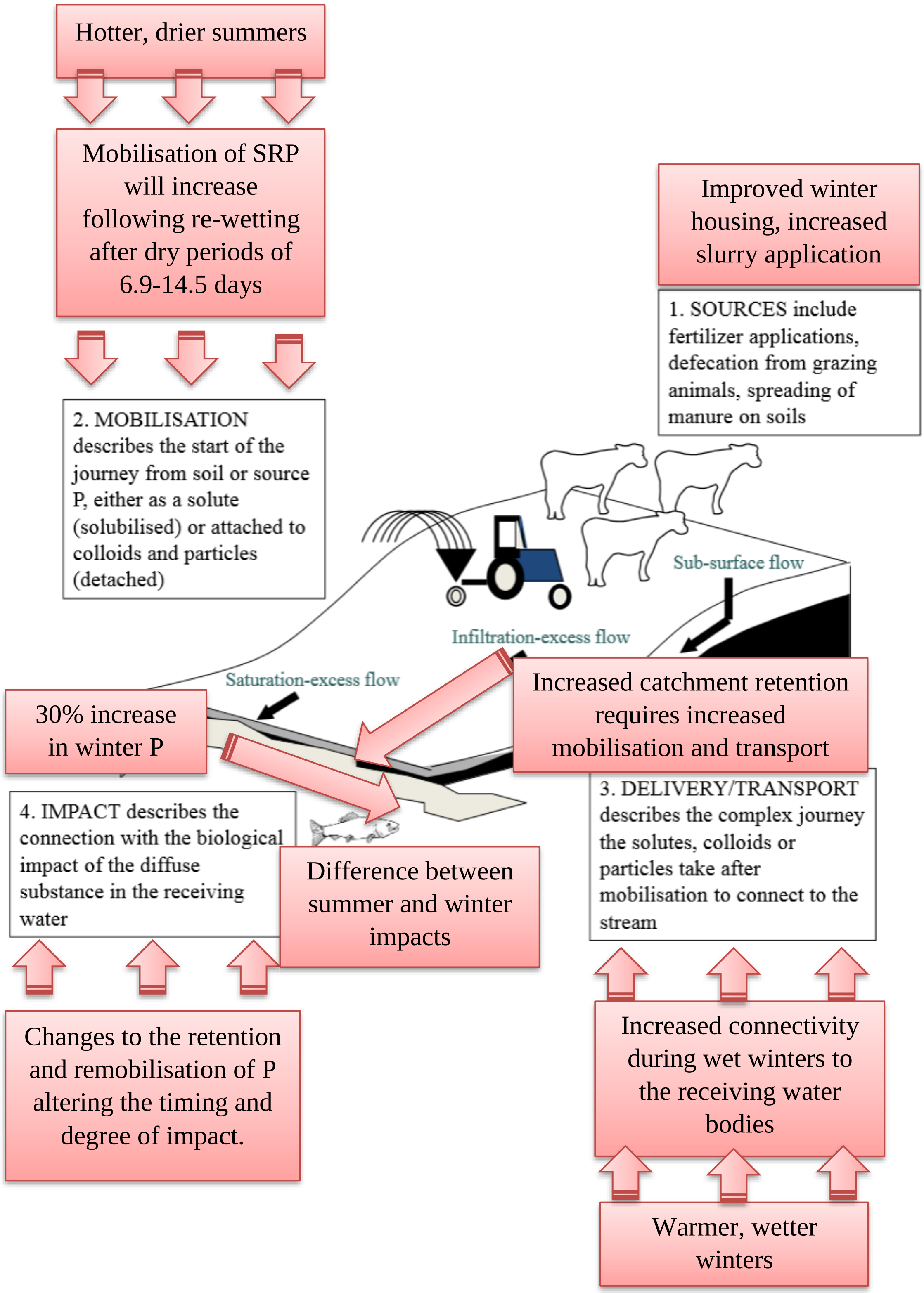


Figure 6.2 The phosphorus (P) transfer continuum under climate change in the Newby Beck catchment, Eden DTC, Cumbria. Heavily amended from Withers and Haygarth (2007) to show how 1) sources are unlikely to change radically, 2) mobilisation will likely increase as a result of hotter, drier summers, 3) catchment retention will increase as a result of increased mobilisation and transport, 4) changes to in-stream retention will alter the timing and degree of impact.

6.2 Summary of work

The fate and behaviour of phosphorus (P) in the catchment environment is critical not only to water quality but it underpins the sustainability of agriculture, and as the global climate shifts our continued understanding of this matter is ever more pressing. In general, current studies have raised considerable concern to the future impact of climate change on specific tiers of the P transfer continuum. Whether it be considering future agricultural crop yields and fertiliser applications (Lobell and Gourdji, 2012; Ray et al., 2015) or P security (Cordell and White, 2011) and sustainability (Withers et al., 2015); increased potential for mobilisation and transfer of P due to precipitation changes (Ockenden et al., 2016) and land use change (Wu et al., 2012); or changes to eutrophication pressures and costs due to climate change (Schindler et al., 2012). But this study uniquely attempts to encompass a range of scales, and techniques in order to explore some of the potential changes posed to catchment P fluxes (i.e. multiple tiers of the P transfer continuum) under climate change.

Although not fully addressed in this thesis, P inputs to the environment under climate change was synthesised and discussed under a global outlook in chapter 2. Phosphorus inputs are the only part of the continuum critically controlled by human behaviours. Therefore, under climate change it is the tier we might consider most easily curbed and controlled as fertiliser application rates, and improvements in plant P use and P recycling for example, can be influenced by choice. This is not to say it is simple, changes in weather patterns will alter the timing and rates of applications (Lobell and Gourdji, 2012), in addition to the pressures of producing high yields for a rising global population whilst the link between nutrient requirement and crop production prevails (Sylvester-Bradley and Withers, 2011), will likely lead to increased P use. But it is the only tier, I suggest, we directly control, and control gives way to opportunity. In the Eden DTC it is perhaps unlikely that P inputs will decrease in the near future as farmers suggested that slurry applications will increase (Ockenden et al. (2017), Figure 6.1). To reduce P use is in this catchment would likely require innovative recycling of slurry (e.g. biogas production supported by funding) as it is considered the most likely to increase under climate change.

The mobilisation of P from soil includes solubilisation and detachment (Haygarth et al., 2005), and is regulated by temperature, moisture, biology, carbon and nitrogen speciation, soil physical structure and geochemical arrangement, and is thus thoroughly complex and dynamic in space and time. In understanding the ‘start of the journey’ we can intercept, hinder or utilise P movement at this stage, preventing it from continuing its journey ‘downstream’. By testing the solubilisation of P from soils under climatic extremes which are predicted under UKCP09 (temperature and dry day length) in Chapter 3, it was realised that shorter dry spells which are predicted to increase in frequency, followed by extreme precipitation events, are critical in the solubilisation of P from the soils tested. Although no mechanism was identified to cause the breakpoint relationship (whereby SRP solubilisation increased until 6.9-14.5 d then subsequently decreased) found in two of the (Eden DTC) soils tested, it was a critical observation which has potential implications for the movement of P in soil. For if more P is solubilised then it is possible that soil water which is leached or mobilised and transported in laminar flow, has a higher concentration of P, consequently increasing the potential impact of P in watercourses or even increasing availability of P to plants. The results therefore support other observations which suggest more P may be mobilised from soils under climate change (Blackwell et al., 2009; Blackwell et al., 2012; Turner and Haygarth, 2001). However, caution should always be used when examining P speciation in soils that have undergone processing and storage as P can exchange between P pools (Haygarth et al., 1995; Haynes and Swift, 1985; Schlichting and Leinweber, 2002), therefore soils will act differently in the environment. Nonetheless, this research has highlighted a process which warrants further investigation at both the laboratory and field scale. If such an effect was observable at a larger scale this would put a potential strain on the second tier of the transfer continuum. If more P is mobilised under increased length and frequency of dry events followed by intense storms, it will likely result in increased transfer of P and therefore impact in the Newby Beck catchment (Figure 6.1). Perhaps with our current understanding we could not mitigate against this effect, other than avoiding P application and slurry addition during critical days of drying.

The ability for a catchment to buffer (i.e. retain and remobilised) P inputs or sources determines how sensitive it is to P pollution. Buffering properties encompass a) hydrological regime and residence time, b) net biogeochemical retention and c) ecological response. These properties govern the mobilisation, transport (or delivery), and impact of P within the transfer continuum. Understanding how a catchment retains P can lead us to consider which tier of the continuum is consequently vulnerable to changes such as climate change. By using E-EMMA analysis the amount of P which has been mobilised and subsequently retained can be quantified (Jarvie et al., 2011). This method has a similar concept to that of Behrendt and Opitz (1999) in that retention is explained by specific runoff i.e., P that is mobilised and transported. The difference being that E-EMMA can capture catchment retention rather than the retention within the river reach as Behrendt and Opitz (1999) do. Both methods critically rely on the quality of data that is used; there is consequently inherent uncertainty in the data used in Chapter 4 to quantify catchment retention both under current conditions and under climate change using the output from the HYPE model. High resolution data can enable dynamics of daily and temporal nutrient behaviours which would otherwise be omitted from lower frequency monitoring strategies (Bieroza et al., 2014). These sampling strategies are highly labour intensive due to equipment complexity and maintenance which can therefore sometimes limit the continuous nature of these strategies. As a result, models such as HYPE can be calibrated with fragmented data yielding poor model agreement, or simply calibrated to a parameter set which has a limited reflection of the true environmental conditions. Using methods such as GLUE (Beven and Binley, 1992; Beven and Freer, 2001) can help us assign a likelihood weight as to whether a parameter set is an acceptable representation of the true system, using both quantitative and qualitative evidence. It addresses both driving data uncertainty and model uncertainty. Therefore, HYPE is constrained by its known uncertainties yet it enables us to postulate possible effects to the P transfer continuum and is therefore an essential tool in understanding the likely effects of climate change.

The results in Chapter 4 indicate that under current conditions three UK catchments, which are considered to be representative of the different farming systems in the UK (McGonigle et al., 2014), each show a positive relationship between catchment TP export and TP retention. The properties of each of these catchments in terms of buffering determine the degree of this relationship. The retention of TP is also predicted to increase under climate change, this means that more TP will be mobilised in each catchment, therefore the effects of increased mobilisation shown in chapter 3 are also seen here. The degree of change to retention under climate is different between each catchment, supporting the hypothesis that catchment properties define how sensitive it is to climatic changes. It is also likely that the *impact* of retained TP will alter as buffering properties respond. This is especially important for these headwater catchments studied, as headwaters have been considered as transport mechanisms of P to downstream reaches (Dodds and Oakes, 2008). So although more TP is retained, more TP is exported from each catchment, transferring increasing loads further downstream, moving and exacerbating potential issues further downstream (Figure 6.1).

Consequently, climate change will likely yield changes that are disparate among catchments, i.e. that the P transfer continuum is unlikely to respond uniformly between catchments. This will raise further questions as to why catchments are not achieving water quality standards despite continued effort and investment in mitigation measures. But our ability to predict a catchment’s response to climate pressures is a challenging task (Thompson et al., 2011) especially in the case of P, as this research has highlighted. We are also not only dealing with the complexity of climate but also societal and policy-driven complexities which are difficult to disentangle, in order to inform effective intervention measures (Withers et al., 2014) to reduce the impact of P in our watercourses. There has been discussion recently as to whether some water bodies should be given over as “casualties”, and the prioritisation of societal goals should to be taken into account in order to do this (Doody et al., 2014; Sharpley et al., 2015; Withers et al., 2014). Such statements will have to be seriously considered as the mobilisation and impact of P will vary between catchments under the effects of climate change. Therefore, we will require management strategies to reflect these highly dynamic systems.

Chapter 5 highlights more deeply the impact of anthropogenic activities on the retention and therefore the retention of P in the small headwater catchment of Newby Beck+, Cumbria (Eden DTC). From this evidence, it was affirmed that diffuse sources of P dominate in the upstream reaches of the beck, and that sediments have the potential to source SRP to the benthic community and the water column. This highlights the importance of headwaters to act as transport mechanisms to downstream reaches (Dodds and Oakes, 2008). As diffuse sources dominate in the upstream reaches, this causes the catchment to be exceptionally vulnerable to increased mobilisation and transport/delivery of P into the reach under climate change. As sediments are currently acting as sources of SRP, the addition of greater loads of TP in surface runoff or attached to particles predicted in this catchment (Ockenden et al., 2016), will alter their buffering capacity. In the light of chapter 3, this mobilised P may be more greatly saturated in soluble P forms, consequently fuelling the benthic community present, rather than being absorbed and buffered by sediments as observed in other catchments (Jarvie et al., 2006). It is known that benthic communities dominate headwater ecosystems (Kupe et al., 2008) and are consequently influenced by the dynamic changes in flow and P additions (Snell et al., 2014). Snell et al. (2014) found in Newby Beck that benthic diatom communities were resilient to event-driven disturbances, recovering to an underlying equilibrium with water quality. But they also found that between the two catchments studied in the Eden DTC (Newby Beck and Pow Beck), that catchment specific factors influenced the benthic community. Newcomer Johnson et al. (2016) in a synthesis of studies also recognised positive relationships between nutrient concentrations and chlorophyll-*a* which were considered to be linked to high retention rates. In addition, results of sediment EPC_0 values at the headwaters in Chapter 5 also slightly contrast to those results implied by Chapter 4, as EPC_0 suggests that sediments remobilise P to the reach (although this did not correlate with stream SRP concentration) whilst E-EMMA and the Brehndt and Optiz comparison suggest that in-stream retention is critical to overall catchment retention. This comparison potentially highlights the stream benthic community as a missing important link in considering P retention. Therefore, it is perhaps essential to gain greater understanding of the long-term influence of benthic communities on the retention of P in headwaters with different catchment sensitivities as they clearly play a vital role.

Interestingly, water companies are thought to likely invest in rural catchment diffuse mitigation measures rather than improving rural treatment works as it is considered a better use of the investment required. Yet, it was found that mitigation measures which are likely to occur in this catchment are unlikely to have a significant impact in reducing TP loads under climate change (Ockenden et al., 2017). This therefore implies that the mobilisation and transport of P is unlikely to be slowed in this catchment unless intervention measures can account for or be tailored to the buffering capacity of this catchment accounting for its resilience into the future under climate change (Figure 6.1). The mitigation measures required might however be currently financially unfeasible for a lot of farmers in the Eden (and elsewhere). Such change would require state and community investment and support. Chapter 5 also highlighted the impact of winter flooding and the transfer of P. As this study extended beyond the boundaries of the DTC Newby Beck outlet and mass balance implied that during the exceptional wet winter of 2015 P was retained in this headwater. The ability for land being given over to flooding in the winter changed this small headwater from transporting P further downstream to it being retained in the flood plain. Our alterations to headwater systems clearly have a vital impact on the P transfer continuum, introducing tier one (sources) and exacerbating the rest.

Chapter 5 also highlights the different results found in Chapter 4, for the mass balance results in Chapter 5 imply that the reach in Newby Beck was primarily remobilising

TP in the observed years beyond the village of Morland (sites 4 to 1). Whilst Chapter 4 highlights the ability of this catchment to retain TP across the land-water continuum within the headwaters (sites 6 to 4 in Chapter 5). Critically, Chapter 5 extends the Newby Beck catchment beyond the village of Morland, and thus highlights how the impacts of a small rural community can potentially alter the retention of TP in the river reach. These slight differences in scale potentially emphasize the importance and thus regulation scale has on the observable functioning of a system, that an element eliminated at the small scale has a greater importance at the larger scale.

To conclude, the impact of climate change will likely put strain on each tier of the P transfer continuum in the Newby Beck, Eden DTC (Figure 6.1). Therefore, the hypothesis that the P transfer continuum will alter under climate change, as the rates of P mobilisation, transfer and efficiency of delivery will likely increase, specifically in the Newby Beck catchment, and that intervention will be required to slow processes at each tier and mitigate the impacts of eventual P pollution, can be accepted as a result of this research. This work highlights the benefit of using the P transfer continuum to frame research as its simplicity allows it to be transferred and applied to different catchments. Consequently, it can be used as a tool to highlight where research is needed and which tier is likely to be more vulnerable under the impacts of climate change.

6.3 Future work

It would be rewarding to further build on this work by, for example:

- Repeating the experiment in chapter 3 with more soil. This would enable a greater range of soil types to be covered to test whether the same change-point response is seen in sandy, silty and clay soils.

- Repeating the experiment in chapter 3 using undisturbed soil cores instead of sieved soils would enable the natural cracking process to be incorporated.
- Identifying the cause of the breakpoint in SRP solubilisation observed in chapter 3, in order that it's possible effects in real-time may be investigated and perhaps included in process-based catchment models. This might be achieved by scaling the experiment to box and plot size.
- It would also be valuable to further explore the relationship of P retention and export to catchment buffering properties: a) hydrological regime and residence time, b) net biogeochemical retention, c) ecological response, in a greater variety of catchments where P eutrophication issues are currently present. This would either require use of a process based model which allows for each buffering property to be quantified, or the use of a long term comprehensive datasets.
- It would be beneficial to further investigate the role of sediments in the retention of P in headwaters and to explore the change in retention/remobilisation flux as a result of winter flow extremes.
- It would be useful to gain further insight into the role of benthic communities in the regulation of P retention in headwaters at a long-term scale. This would provide insight into the resilience of benthic P uptake under climate change. This could be achieved by establishing relationships between uptake lengths and degree of perturbation, such as high flow events.
- It would also be useful to engage headwater communities in their role of P retention and stream health, and how their interaction with their riparian environment can impact downstream communities. This might be achieved by, for example, improving communication of scientific outputs with the

relevant community, or using stakeholder engagement to design and implement research outcomes.

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Appendix 1

Weather Generator

The UKCP09 Weather Generator provides plausible multiple daily and hourly time series of weather data from 30 to 1000 years in duration, which are statistically equivalent and stationary (Jones et al., 2010). For each of these locations the weather generator produced a hundred 30-year long simulations of daily rainfall and the mean daily temperature (average of daily max. and daily min.) to represent present day conditions and 2050s conditions. Dry periods were identified from the rainfall time series as the number of consecutive days with no rain. For each of the dry periods recorded, the mean average daily temperature was also calculated. The characteristics of extremes for temperature and dry period duration were used to inform DRW cycles in our experiment.

Appendix 1 Table 1 Annual and seasonal rainfall (mm) (the rainfall time series were used to calculate annual rainfall, winter rainfall (December, January, February) and summer rainfall (June, July, August)) predicted by UK Climate Predictions Weather Generator for present day and scenario periods (medium emissions 2050), for the Newby, Pow (previously published in (Ockenden et al., 2016) and Blackwater sub-catchments, mean and (standard deviation) (UKCP, 2009).

	Newby Beck				Pow Beck				Blackwater			
	present day		scenario		present day		scenario		present day		scenario	
Annual rainfall	1056	(134)	1083	(158)	831	(96)	850	(110)	650	(90)	643	(104)
Winter rainfall DJF	334	(83)	372	(101)	217	(50)	250	(63)	165	(39)	184	(47)
Summer rainfall JJA	202	(46)	170	(53)	203	(45)	171	(51)	161	(47)	128	(52)

Appendix 1 Table 2 Duration of dry periods (95th, 99th, 100th percentiles), and temperature (95th percentile) during dry periods for present day and scenario periods (medium emissions 2050), for the Newby, Pow and Blackwater sub-catchments. Each value is the mean over 100 time series.

	Newby Beck				Pow Beck				Blackwater			
	present day		scenario		present day		scenario		present day		scenario	
95th percentile of length of dry period (days, mean of 100 runs)	10.4	(0.6)	11.6	(1.4)	9.3	(0.5)	10.2	(1.1)	12.6	(0.6)	14.9	(2.1)
99th percentile of length of dry period (days, mean of 100 runs)	16.7	(0.9)	19.4	(2.7)	14.5	(0.8)	16.8	(2.0)	21.0	(1.4)	27.0	(5.0)
Maximum length of dry period (days, mean of 100 runs)	29.4	(5.3)	33.9	(6.5)	25.2	(4.7)	31.4	(5.8)	38.1	(6.3)	50.3	(13.2)
95th percentile of temperature during dry periods (mean, °C)	15.2	(0.1)	18.1	(0.2)	15.7	(0.1)	18.3	(0.2)	17.1	(0.1)	20.2	(0.3)

Statistics and calculations

Statistical analysis was performed in R using the Segmented package (Muggeo, 2015) to estimate breakpoints between duration of dry days and SRP solubilised. Breakpoints are reported in R with relevant standard error and multiple R^2 values. Increased SRP which can be potentially solubilised after re-wetting at the breakpoint under climate change scenario was calculated using the percentage increase in frequency of drying events with the duration of the breakpoint between the present day and the future period. The concentration of SRP at the Blackwater breakpoint was calculated using the equation for the line of the first slope in the segmented model as no data was collected at the identified breakpoint.

Appendix 1 Table 3 Soil characteristics including soil classification (USDA Soil Taxonomy, IUSS WG World Reference Base (Cranfield University, 2017)) , pH, carbon (C) and nitrogen (N) percent and ratio, total soil phosphorus (TP), matric potential (standard deviation), and bulk density as reported by National Soil Research Institute (NSRI) of the Newby, Pow (Eden, Cumbria, UK) and Blackwater (Wensum, East Anglia, UK) soils.

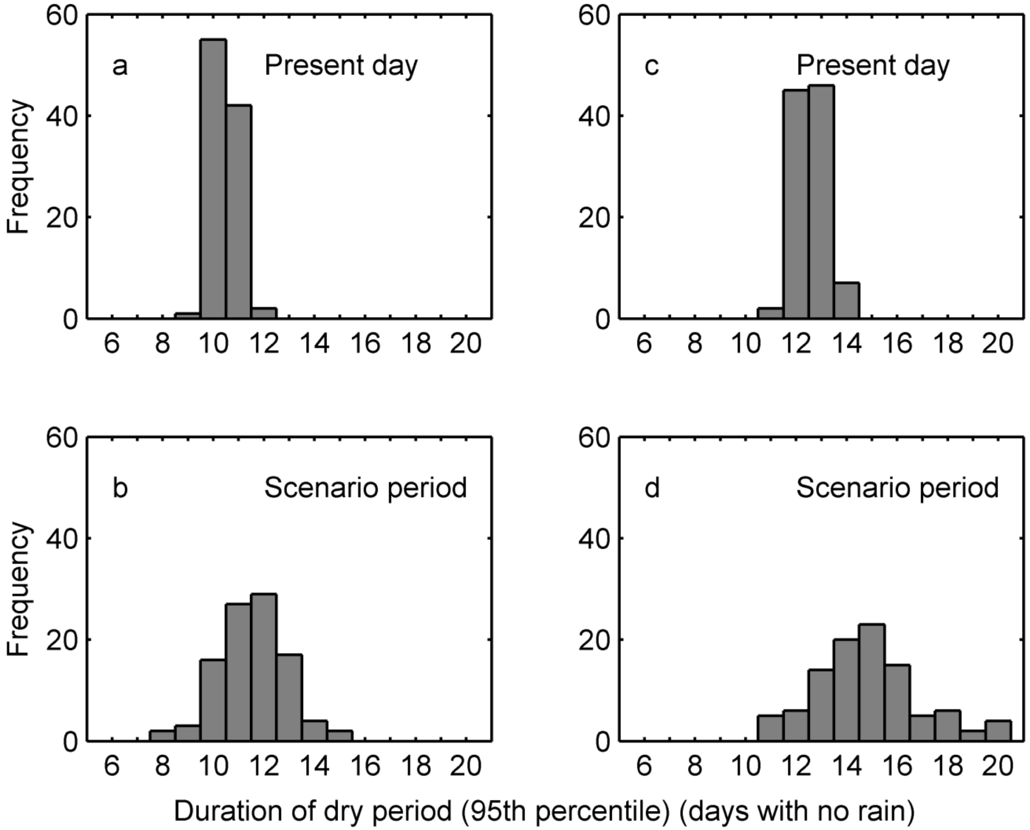
		Eden		Wensum
		Newby	Pow	Blackwater
Soil Classification	USDA Soil Taxonomy	Typic Haplaquept Inceptisol	Typic Haplaquept Inceptisol	Aquic Dystrochept Inceptisol
	IUSS WG World Reference Base	Chromic Eutric Albic Luvic Stagnosols	Chromic Eutric Albic Luvic Stagnosols	Endostagnic Luvisols
Catchment area (km^2)		12.5	10.5	19.7
Soil pH		5.84	5.56	5.78
C%, N%		4.18, 0.47	6.43, 0.62	1.47, 0.17
C:N		8.89	10.37	8.65
TP (mg kg^{-1})		1600	1200	780
Olsen's P (mg kg^{-1})		3.4	12.8	3.4
Initial matric potential (at 0 days) (MPa)		-0 (0)	-0.24 (0.11)	-0.46 (0.095)
Moisture content (%)		32.93 (2.13)	34.97 (1.36)	14.65 (1.11)
Bulk density (g cm^{-3}) (NSRI database)		1.22	1.2	1.4

The Blackwater soil used was an arable soil, crop rotations have been reported for 3 years in Outram et al. (2016) and are as follows: 2011-2012 sugar beet (0 P kg ha^{-1}), 2012-2013 spring barley (malt) (1-49 P kg ha^{-1}), and 2013-2014 spring bean (dried) (1-49 P kg ha^{-1}). In 2014 spring beans were the second most common crop grown in land area. The Newby Beck soil was collected from improved grassland field, farm diary data includes application rate of P_2O_5 fertiliser to grazed grassland fields at 28.76 kg P ha^{-1} and nitrogen fertiliser at 62.77 kg N ha^{-1} for 2014. Farm yard manure (FYM) and slurry was totalled to 356.12 tonnes and 727375 L, respectively for 2014. For the Pow Beck soil, limited data was available from the farm diaries, no P fertiliser was recorded as applied but 64 kg N ha^{-1} was applied to grazed grassland fields at this site. No slurry or manure data was collected for this farm.

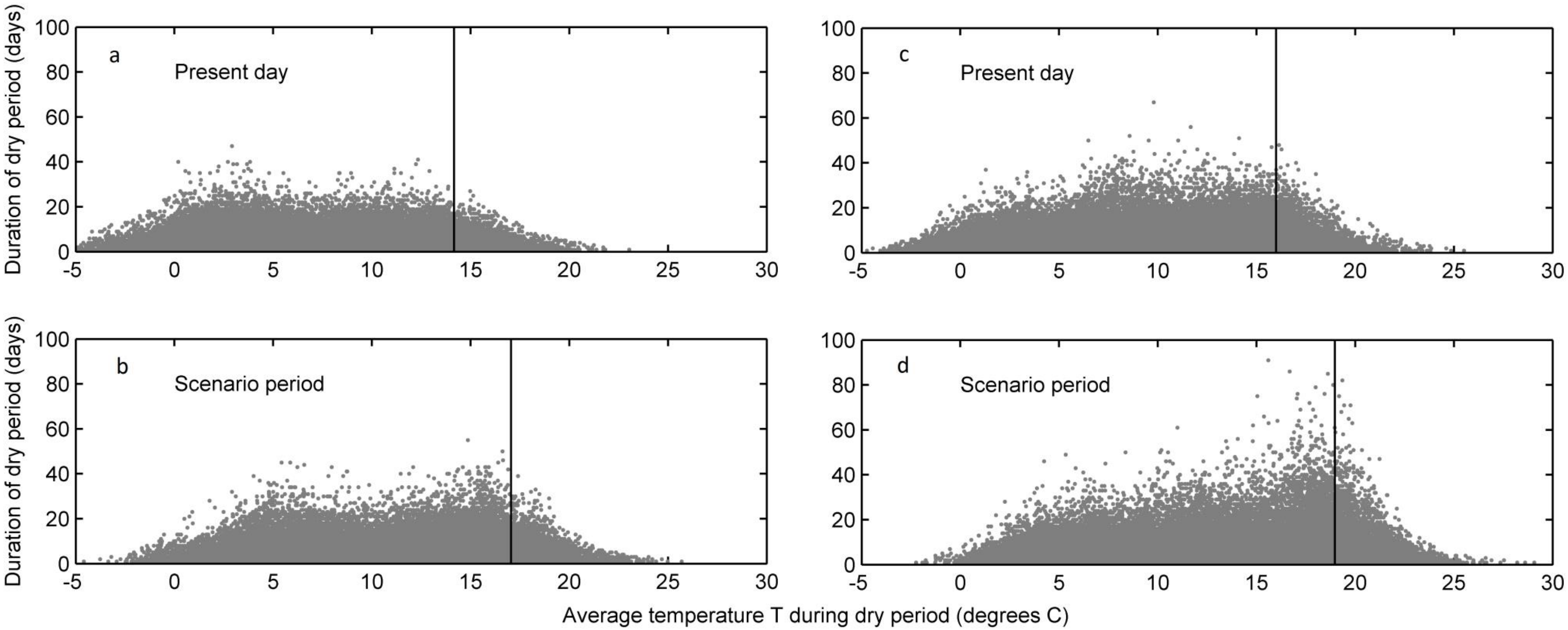
Appendix 1 Table 4 Results for all soils: leachate collected (mL), soluble reactive phosphorus (SRP) (μg L^{-1}) and matric potential (-Mpa). (Standard deviation of five replicates, three replicates for matric potential). Results are given to 1 decimal place.

	Eden								Wensum			
	Newby				Pow				Blackwater			
Days Dried	Leachate collected (mL)	SRP load (μg P)	SRP concentration (μg L^{-1})	Matric Potential (-Mpa)	Leachate collected (mL)	SRP load (μg P)	SRP concentration (μg L^{-1})	Matric Potential (-Mpa)	Leachate collected (mL)	SRP load (μg P)	SRP concentration (μg L^{-1})	Matric Potential (-Mpa)
0	41.8 (3.0)	0 (0.0)	0 (0.0)	0 (0.0)	43.1 (4.5)	0 (0.0)	0 (0.0)	0.2 (0.1)	40.9 (1.1)	9.0 (0.6)	222.7 (20.7)	0.5 (0.1)
2	36.6 (3.2)	0.3 (0.4)	8.3 (9.3)	10.5 (0.5)	43.7 (2.0)	0 (0.0)	0 (0.0)	1.2 (0.1)	-	-	-	-
4	39.5 (3.0)	0.0 (0.1)	0.7 (1.2)	139.3 (1.1)	38.4 (3.1)	0.3 (0.4)	10.3 (8.8)	139.0 (0.6)	-	-	-	-
5	34.9 (1.2)	1.7 (0.4)	48.4 (11.1)	128.7 (0.4)	36.1 (1.1)	1.4 (0.4)	37.4 (9.8)	138.9 (1.0)	39.6 (2.4)	11.5 (1.7)	290.4 (61.3)	146.3 (2.0)
6	36.0 (1.5)	1.1 (0.4)	36.7 (11.0)	147.0 (1.3)	36.7 (1.2)	1.0 (0.4)	26.1 (10.0)	146.1 (3.2)	-	-	-	-
8	38.1 (2.6)	1.2 (0.5)	30.4 (9.9)	151.5 (0.7)	36.9 (1.1)	1.6 (0.7)	41.6 (18.8)	157.6 (2.7)	-	-	-	-
10	37.2 (1.9)	3.5 (0.6)	93.0 (17.6)	145.3 (2.0)	36.8 (0.9)	2.5 (0.9)	68.1 (23.2)	152.7 (2.0)	40.7 (1.9)	11.9 (3.1)	291.6 (90.4)	147.3 (1.7)
15	33.3 (1.2)	4.3 (0.4)	129.7 (7.7)	148.0 (2.18)	36.5 (1.2)	1.4 (1.0)	38.5 (27.4)	155.5 (6.2)	38.9 (2.0)	11.4 (2.6)	299.1 (60.2)	148.6 (1.1)

20	31.3 (1.4)	4.0 (0.6)	127.9 (25.5)	152.2 (2.5)	36.2 (0.9)	2.1 (0.6)	56.3 (14.5)	153.7 (3.0)	39.2 (1.6)	12.1 (2.9)	305.9 (67.8)	147.8 (0.3)
25	33.6 (2.1)	2.7 (0.5)	81.5 (15.7)	149.2 (0.8)	36.6 (2.7)	2.2 (0.3)	61.3 (11.5)	154.4 (0.1)	40.3 (2.6)	6.5 (1.6)	158.3 (32.9)	147.2 (1.0)
30	36.5 (2.9)	2.6 (1.2)	72.0 (30.7)	146.4 (1.3)	42.2 (2.5)	1.8 (0.5)	41.5 (11.7)	158.0 (3.0)	42.0 (2.3)	9.9 (2.4)	235.9 (67.2)	152.0 (2.1)
60	34.1 (1.4)	2.1 (0.8)	63.4 (24.1)	148.4 (2.1)	40.6 (2.0)	1.4 (0.3)	34.6 (8.3)	157.5 (0.8)	40.6 (2.0)	10.7 (2.8)	263.5 (78.7)	151.9 (3.1)
90	34.4 (1.2)	3.0 (1.5)	86.6 (30.0)	144.6 (1.0)	38.9 (2.5)	2.0 (0.9)	49.4 (25.1)	151.2 (2.2)	40.4 (2.2)	9.8 (1.6)	242.8 (39.3)	141.7 (7.1)



Appendix 1 Figure 1 Duration of dry periods (days with no rain), 95th percentile, in Newby Beck (Eden) catchment (a present day period, b scenario period) and Blackwater (Wensum) catchment (c present day period, d scenario period).

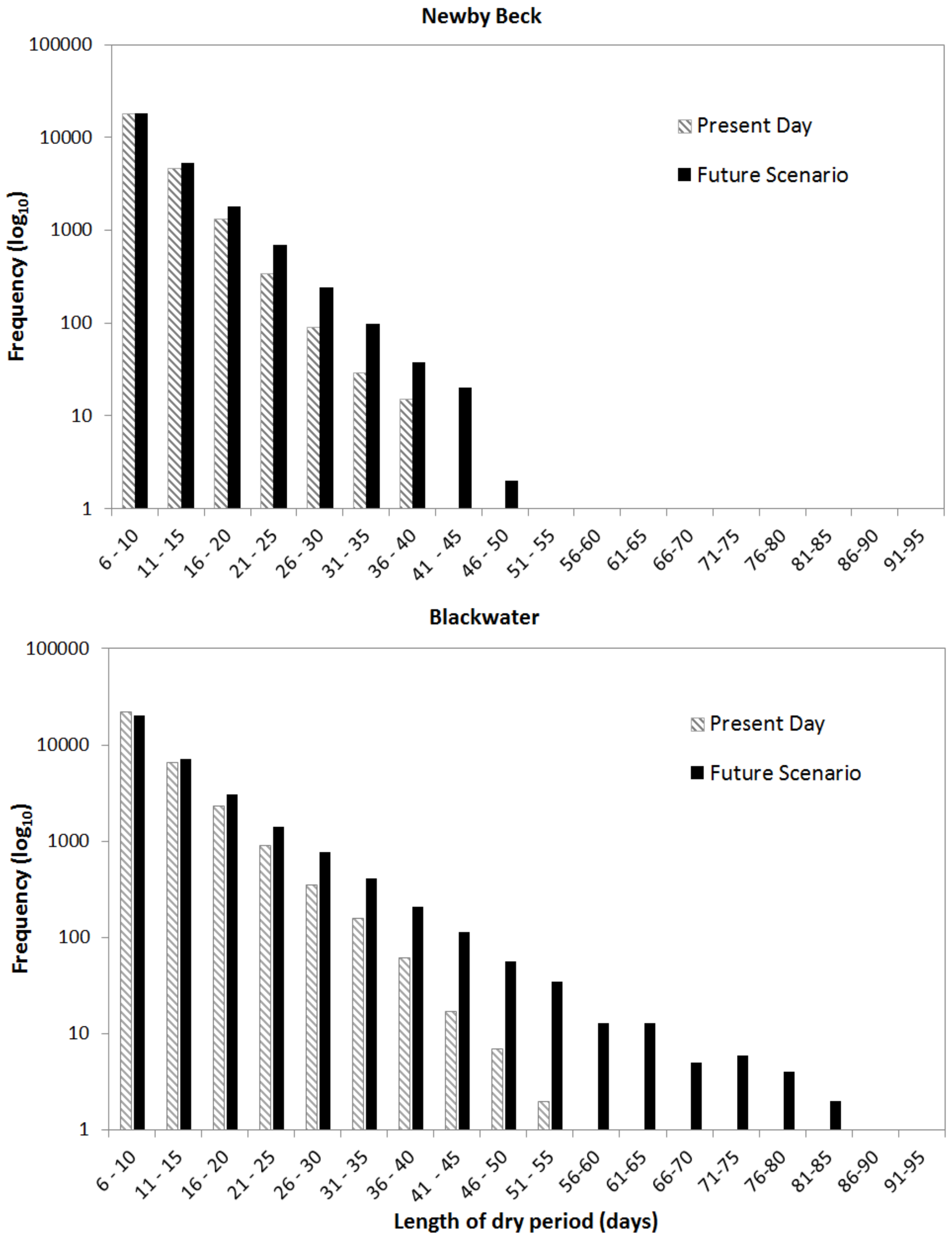


Appendix 1 Figure 2 Duration of dry period and average temperature during dry periods for the Newby Beck (Eden) catchment (a present day period, b scenario period) and Blackwater (Wensum) catchment (c present day period, d scenario period), vertical lines marking the 90th percentile.

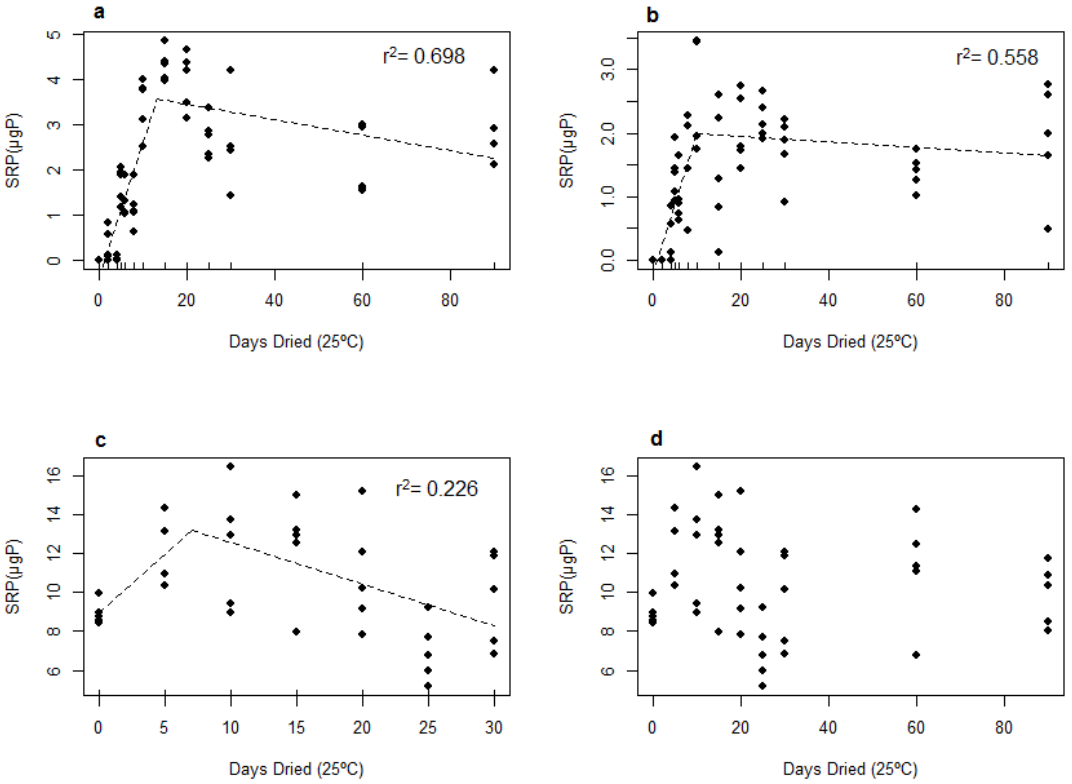
Interpretation

The annual rainfall and seasonal rainfall in the present day period and the scenario period (2050s), as predicted by the UKCP weather generator are shown in Table 1. Although the mean annual rainfall totals are similar between the present day and the scenario periods, the seasonal rainfall totals show the trend of wetter winters, drier summers. The scenario period also shows more variation in the data (higher standard deviations) reflecting the greater uncertainty in the probabilistic data.

The distribution of the 95th percentile duration of dry period, for both the present day and scenario periods is shown for Newby Beck and the Blackwater catchment in Figure 1, and indicates the spread of the data from the 100 time series. The range of predicted average temperature during dry periods is shown for Newby Beck and Blackwater in Figure 2. These show the predicted range of temperatures, from negative values during some winter dry periods in the present day period, to average temperatures in excess of 25°C in the scenario period. As every dry period for all 100 runs is represented here, it also indicates the full range of the length of dry periods, including occasional dry periods up to 90 d in the Blackwater in the scenario period.



Appendix 1 Figure 3 Frequency of dry periods (d) (no rain) on a $\log_{10}$ scale for present day and scenario periods across all simulations for the Newby Beck (Eden) (top) and the Blackwater (Wensum) (bottom) catchments.



Appendix 1 Figure 4 Soluble reactive phosphorus (SRP) load (µg P) (five replicates) plotted against time dried in days at 25°C for Newby (a), Pow (b) and Blackwater (c, 0-30 d data, and d complete dataset) soils. The segmented model prediction (dashed line) suggests that the significant breakpoint in the data is at 13.1 ± 1.4 (r^2= 0.698), 9.9 ± 1.4 (r^2= 0.558), 7.1 ± 2.4 (r^2= 0.226) d, for Newby, Pow and Blackwater respectively, where the relationship between the duration of time (days) dried and SRP solubilisation changes.

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Appendix 2

HYPE results and model description

The results from the Hydrological Predictions for the Environment (HYPE) model driven by the Weather Generator (UKCP09) are the same as those reported in Ockenden et al. (2017), but are included here for information.

Appendix 2 Table 1 Rainfall from the UKCP09 Weather Generator (mm), discharge (total annual mm, m^3 s^{-1}* s yr^{-1} / area in m^2 * 1000 mm m^{-1}) and total phosphorus load (kg through catchment outlet) predicted by HYPE for 2050s and 2080s, low, medium and high emission scenarios. Results for each realisation (30 years) are a mean average over years 5-30, with 5th, 50th (median) and 95th percentiles from 100 realisations and % change (%Δ) of the median from the baseline median value as in Ockenden et al. (2017).

UKCP Driving data ->		Baseline			2050s				2050s				2050s				2080s				2080s				2080s			
Emission scenario ->					LOW				MEDIUM				HIGH				LOW				MEDIUM				HIGH			
Percentile		5th	50th	95th	5th	50th	95th	%Δ	5th	50th	95th	%Δ	5th	50th	95th	%Δ	5th	50th	95th	%Δ	5th	50th	95th	%Δ	5th	50th	95th	%Δ
Newby Rainfall (mm)	Annual	1010	1051	1097	983	1083	1187	3	995	1085	1197	3	990	1102	1221	5	1005	1102	1196	5	997	1088	1200	4	1004	1111	1256	6
	Winter	306	332	363	318	360	431	8	314	367	429	11	328	382	440	15	326	379	450	14	323	375	455	13	340	402	488	21
	Summer	186	201	217	143	179	239	-11	126	168	226	-16	129	172	237	-14	136	179	234	-11	120	166	225	-17	101	159	216	-21
Newby Q (mm)	Annual	482	513	549	425	507	588	-1	430	506	601	-1	425	520	625	1	439	509	584	-1	421	505	589	-2	420	523	647	2
	Winter	213	234	265	202	242	297	4	202	246	300	5	205	259	311	11	209	255	303	9	208	205	312	7	217	270	354	15
	Summer	39	47	56	24	40	68	-16	22	32	61	-31	22	35	62	-27	25	36	62	-24	18	32	63	-32	17	30	50	-37
Newby TP (kg)	Annual	1076	1180	1325	1089	1356	1681	15	1099	1364	1721	16	1135	1452	1798	23	1137	1371	1721	16	1148	1411	1748	20	1191	1564	2003	33
	Winter	498	581	687	512	677	921	16	518	693	933	19	565	764	981	31	542	740	972	27	561	733	1012	26	624	840	1253	45
	Summer	54	72	101	26	70	178	-3	24	70	138	-3	29	67	151	-8	31	71	174	-2	21	62	190	-14	18	65	159	-10
Blackwater Rainfall (mm)	Annual	629	659	689	600	651	734	-1	585	642	727	-3	594	664	722	1	587	659	730	0	579	651	716	-1	568	637	742	-3
	Winter	154	165	178	160	181	214	10	152	183	211	11	168	189	214	15	162	187	211	13	162	192	230	16	168	199	239	21
	Summer	146	162	178	101	141	202	-13	94	128	189	-21	95	139	184	-14	83	138	203	-15	78	123	169	-24	65	119	189	-27
Blackwater Q (mm)	Annual	104	119	135	88	111	153	-6	87	112	143	-6	90	114	148	-4	92	114	150	-14	85	115	148	-3	79	110	147	-7
	Winter	36	44	52	33	43	60	-3	30	44	61	0	32	46	62	3	30	43	62	-3	29	45	70	1	28	44	71	0
	Summer	17	20	24	10	17	35	-14	8	15	28	-22	10	17	29	-16	9	17	33	-13	8	15	25	-26	5	14	30	-30
Blackwater TP (kg)	Annual	201	227	259	187	234	334	3	184	237	312	4	181	250	323	10	191	250	323	10	193	249	330	10	183	248	343	9
	Winter	59	72	87	56	78	115	9	56	80	113	12	59	85	121	18	57	81	120	13	55	86	136	20	58	85	150	19
	Summer	34	42	55	19	39	90	-9	17	36	72	-14	21	40	77	-6	17	43	84	-13	18	36	66	-15	10	34	86	-19
Wylye Rainfall (mm)	Annual	954	994	1031	909	1006	1119	1	913	1008	1123	1	916	1011	1104	2	918	1017	1142	2	898	1027	1158	3	925	1051	1210	6
	Winter	266	287	309	275	322	368	12	276	329	404	15	277	327	411	14	294	342	408	19	285	348	452	21	280	366	501	28
	Summer	185	204	224	96	178	272	-13	107	165	224	-19	102	165	241	-19	107	166	258	-19	89	160	435	-22	80	156	246	-24
Wylye Q (mm)	Annual	126	137	153	116	140	177	2	111	142	194	3	112	138	193	0	114	146	194	6	110	152	211	10	1202	160	258	16
	Winter	45	52	60	41	58	79	12	42	60	96	16	41	57	97	10	47	61	93	19	44	64	105	24	45	69	129	34
	Summer	19	22	24	13	20	32	-10	14	18	25	-15	13	18	28	-16	14	19	30	-13	12	19	29	-13	13	19	32	-13
Wylye TP (kg)	Annual	1018	1123	1298	1025	1312	1767	17	1038	1357	1984	21	1013	1365	2047	22	1036	1433	2052	28	1079	1530	2392	36	1178	1719	2851	53
	Winter	389	479	587	404	615	889	28	423	635	1125	33	395	608	1205	27	4575	698	1161	46	438	724	1393	51	489	858	1741	79
	Summer	105	142	184	66	146	319	3	66	123	225	-13	67	120	301	-15	71	132	284	-7	64	124	284	-13	62	140	312	-2

Appendix 2 Table 2 HYPE model: Description, evaluation criteria and parameter ranges used in HYPE behavioural runs as reported in Ockenden et al. (2017)

Parameter ranges for Newby Beck, Eden:

Parameter Name	Parameter description	Min Value	Max Value
mperc1_sol1	Max percolation capacity from soil layer 1 to 2 (For soil class 1)	11	99
mperc1_sol2	Max percolation capacity from soil layer 1 to 2 (For soil class 2)	5	99
mperc1_sol3	Max percolation capacity from soil layer 1 to 2 (For soil class 3)	5	96
mperc2_sol1	Max percolation capacity from soil layer 2 to 3 (For soil class 1)	7	96
mperc2_sol2	Max percolation capacity from soil layer 2 to 3 (For soil class 2)	9	99
mperc2_sol3	Max percolation capacity from soil layer 2 to 3 (For soil class 3)	6	99
wcep_sol1	Effective porosity as a fraction for all soil layers (soil class 1)	0.05	0.10
wcep_sol2	Effective porosity as a fraction for all soil layers (soil class 2)	0.05	0.07
wcep_sol3	Effective porosity as a fraction for all soil layers (soil class 3)	0.05	0.29
wcfc_sol1	Fraction of soil water available for evapotranspiration and not runoff - same for all soil layers (soil class 1)	0.05	0.29
wcfc_sol2	Fraction of soil water available for evapotranspiration and not runoff - same for all soil layers (soil class 2)	0.10	0.28
wcfc_sol3	Fraction of soil water available for evapotranspiration and not runoff - same for all soil layers (soil class 3)	0.04	0.30
wcwp_sol1	Wilting point as a fraction - same for all soil layers (soil class 1)	0.10	0.20
wcwp_sol2	Wilting point as a fraction - same for all soil layers (soil class 2)	0.11	0.19
wcwp_sol3	Wilting point as a fraction - same for all soil layers (soil class 3)	0.11	0.20
rrcs1_sol1	Recession coefficient for uppermost soil layer (soil class 1)	0.22	0.74
rrcs1_sol2	Recession coefficient for uppermost soil layer (soil class 2)	0.05	0.53
rrcs1_sol3	Recession coefficient for uppermost soil layer (soil class 3)	0.11	0.74
rrcs2_sol1	Recession coefficient for lowest soil layer (soil class 1)	0.00	0.39
rrcs2_sol2	Recession coefficient for lowest soil layer (soil class 2)	0.00	0.27
rrcs2_sol3	Recession coefficient for lowest soil layer (soil class 3)	0.01	0.39
srrate_sol1	Fraction for surface runoff (soil class 1)	0.24	0.78

srrate_sol2	Fraction for surface runoff (soil class 2)	0.70	0.98
srrate_sol3	Fraction for surface runoff (soil class 3)	0.34	0.98
soilcoh_sol1	Characteristic of soil for erosion calculation - kPa (soil class 1)	0.27	0.96
soilcoh_sol2	Characteristic of soil for erosion calculation - kPa (soil class 2)	0.21	0.95
soilcoh_sol3	Characteristic of soil for erosion calculation - kPa (soil class 3)	0.28	0.94
soilerod_sol1	Characteristic of soil for calculation of erosion (erodibility) - g/J (soil class 1)	0.24	1.00
soilerod_sol2	Characteristic of soil for calculation of erosion (erodibility) - g/J (soil class 2)	0.31	0.97
soilerod_sol3	Characteristic of soil for calculation of erosion (erodibility) - g/J (soil class 3)	0.21	0.97
kc_past	Crop coefficient for PET models (pasture land class)	0.41	0.97
kc_rgrs	Crop coefficient for PET models (rough grazing land class)	0.22	4.17
kc_agrl	Crop coefficient for PET models (arable land class)	0.05	4.95
cevp_past	Evapotranspiration parameter - mm/degree/d (pasture land class)	0.12	0.28
cevp_rgrs	Evapotranspiration parameter - mm/degree/d (rough grazing land class)	0.13	0.30
cevp_agrl	Evapotranspiration parameter - mm/degree/d (arable land class)	0.13	0.29
degradhp_past	Decay of humus to fastP - d-1 (pasture land class)	1.7E-06	2.4E-05
degradhp_rgrs	Decay of humus to fastP - d-1 (rough grazing land class)	3.8E-06	2.4E-05
degradhp_agrl	Decay of humus to fastP - d-1 (arable land class)	1.7E-06	2.2E-05
minerfp_past	Mineralisation of fastP to SRP - d-1 (pasture land class)	1.1E-02	2.1E-02
minerfp_rgrs	Mineralisation of fastP to SRP - d-1 (rough grazing land class)	7.5E-03	2.8E-02
minerfp_agrl	Mineralisation of fastP to SRP - d-1 (arable land class)	6.6E-03	3.0E-02
dissolfp_past	Decay of fastP to dissolved PP - d-1 (pasture land class)	1.7E-05	1.4E-04
dissolfp_rgrs	Decay of fastP to dissolved PP - d-1 (rough grazing land class)	2.3E-05	1.5E-04
dissolfp_agrl	Decay of fastP to dissolved PP - d-1 (arable land class)	1.6E-05	1.5E-04
dissolhp_past	Decay of humusP to dissolved PP - d-1 (pasture land class)	8.5E-07	2.9E-06
dissolhp_rgrs	Decay of humusP to dissolved PP - d-1 (rough grazing land class)	8.2E-07	2.9E-06
dissolhp_agrl	Decay of humusP to dissolved PP - d-1 (arable land class)	1.4E-06	3.0E-06
humusP0_past	Starting value for pool in soil of humus P - mg/m3 (pasture land class)	5762	181025

humusP0_rgrs	Starting value for pool in soil of humus P - mg/m3 (rough grazing land class)	26370	198661
humusP0_past	Starting value for pool in soil of humus P - mg/m3 (arable land class)	30606	191150
partP0_past	Starting value for pool in soil of partP - mg/m3 (pasture land class)	24778	145460
partP0_rgrs	Starting value for pool in soil of partP - mg/m3 (rough grazing land class)	1633	146590
partP0_agrl	Starting value for pool in soil of partP - mg/m3 (arable land class)	3788	138615
damp	Fraction of delay in water course which also causes damping	0.09	0.96
wprodp	Production/decay of P in water - kgm-3d-1	1.9E-05	4.6E-05
fastP0	Starting value for pool in soil of fastP - mg/m3	53	494
lp	Limit for Potential evapotranspiration	0.04	0.99
rcgrw	Recession coefficient for regional groundwater flow from soil layers	5.7E-05	9.2E-03
cevpph	Phase of sinus function that corrects potential evapotranspiration - days	3	44
cevpam	Amplitude of sinus function that corrects potential evapotranspiration	0.16	1.44
mwind	Average windspeed - m/s	3.1	4.8
epotdist	coefficient in exponential function for potential evapotranspiration depth dependency	2.1	4.9

Appendix 2 Table 2 continued

Parameter ranges for Blackwater, Wensum:

Parameter Name	**Parameter description**	**Min Value**	**Max Value**
mperc1_sol1	Max percolation capacity from soil layer 1 to 2 (For soil class 1)	19	91
mperc1_sol2	Max percolation capacity from soil layer 1 to 2 (For soil class 2)	9	93
mperc1_sol3	Max percolation capacity from soil layer 1 to 2 (For soil class 3)	21	95
mperc1_sol4	Max percolation capacity from soil layer 1 to 2 (For soil class 4)	28	88
mperc2_sol1	Max percolation capacity from soil layer 2 to 3 (For soil class 1)	13	97
mperc2_sol2	Max percolation capacity from soil layer 2 to 3 (For soil class 2)	14	99
mperc2_sol3	Max percolation capacity from soil layer 2 to 3 (For soil class 3)	22	96

mperc2_sol4	Max percolation capacity from soil layer 2 to 3 (For soil class 4)	19	97
wcep_sol1	Effective porosity as a fraction for all soil layers (soil class 1)	0.32	0.49
wcep_sol2	Effective porosity as a fraction for all soil layers (soil class 2)	0.21	0.48
wcep_sol3	Effective porosity as a fraction for all soil layers (soil class 3)	0.11	0.41
wcep_sol4	Effective porosity as a fraction for all soil layers (soil class 4)	0.08	0.48
wcfc_sol1	Fraction of soil water available for evapotranspiration and not runoff - same for all soil layers (soil class 1)	0.13	0.45
wcfc_sol2	Fraction of soil water available for evapotranspiration and not runoff - same for all soil layers (soil class 2)	0.06	0.42
wcfc_sol3	Fraction of soil water available for evapotranspiration and not runoff - same for all soil layers (soil class 3)	0.06	0.15
wcfc_sol4	Fraction of soil water available for evapotranspiration and not runoff - same for all soil layers (soil class 4)	0.08	0.35
wcwp_sol1	Wilting point as a fraction - same for all soil layers (soil class 1)	0.11	0.20
wcwp_sol2	Wilting point as a fraction - same for all soil layers (soil class 2)	0.11	0.19
wcwp_sol3	Wilting point as a fraction - same for all soil layers (soil class 3)	0.10	0.19
wcwp_sol4	Wilting point as a fraction - same for all soil layers (soil class 4)	0.10	0.20
rrcs1_sol1	Recession coefficient for uppermost soil layer (soil class 1)	0.06	0.73
rrcs1_sol2	Recession coefficient for uppermost soil layer (soil class 2)	0.09	0.57
rrcs1_sol3	Recession coefficient for uppermost soil layer (soil class 3)	0.17	0.74
rrcs1_sol4	Recession coefficient for uppermost soil layer (soil class 4)	0.15	0.61
rrcs2_sol1	Recession coefficient for lowest soil layer (soil class 1)	0.00	0.02
rrcs2_sol2	Recession coefficient for lowest soil layer (soil class 2)	0.00	0.01
rrcs2_sol3	Recession coefficient for lowest soil layer (soil class 3)	0.21	0.40
rrcs2_sol4	Recession coefficient for lowest soil layer (soil class 4)	0.24	0.40
srrate_sol1	Fraction for surface runoff (soil class 1)	0.21	0.26
srrate_sol2	Fraction for surface runoff (soil class 2)	0.20	0.24
srrate_sol3	Fraction for surface runoff (soil class 3)	0.21	0.30
srrate_sol4	Fraction for surface runoff (soil class 4)	0.21	0.42
soilcoh_sol1	Characteristic of soil for erosion calculation - kPa (soil class 1)	0.36	1.00
soilcoh_sol2	Characteristic of soil for erosion calculation - kPa (soil class 2)	0.24	0.87

soilcoh_sol3	Characteristic of soil for erosion calculation - kPa (soil class 3)	0.24	0.98
soilcoh_sol4	Characteristic of soil for erosion calculation - kPa (soil class 4)	0.22	0.99
soilerod_sol1	Characteristic of soil for calculation of erosion (erodibility) - g/J (soil class 1)	0.22	0.84
soilerod_sol2	Characteristic of soil for calculation of erosion (erodibility) - g/J (soil class 2)	0.21	0.81
soilerod_sol3	Characteristic of soil for calculation of erosion (erodibility) - g/J (soil class 3)	0.29	0.83
soilerod_sol4	Characteristic of soil for calculation of erosion (erodibility) - g/J (soil class 4)	0.42	0.97
kc_agrl	Crop coefficient for PET models (arable land class)	1.20	1.43
kc_past	Crop coefficient for PET models (pasture land class)	0.13	0.22
kc_rgrs	Crop coefficient for PET models (rough grazing land class)	0.08	4.94
cevp_agrl	Evapotranspiration parameter - mm/degree/d (arable land class)	0.16	0.30
cevp_past	Evapotranspiration parameter - mm/degree/d (pasture land class)	0.11	0.30
cevp_rgrs	Evapotranspiration parameter - mm/degree/d (rough grazing land class)	0.13	0.30
degradhp_agrl	Decay of humus to fastP - d-1 (arable land class)	6.0E-06	2.5E-05
degradhp_past	Decay of humus to fastP - d-1 (pasture land class)	1.9E-06	2.5E-05
degradhp_rgrs	Decay of humus to fastP - d-1 (rough grazing land class)	2.8E-06	2.3E-05
minerfp_agrl	Mineralisation of fastP to SRP - d-1 (arable land class)	8.5E-03	2.8E-02
minerfp_past	Mineralisation of fastP to SRP - d-1 (pasture land class)	8.5E-03	2.7E-02
minerfp_rgrs	Mineralisation of fastP to SRP - d-1 (rough grazing land class)	8.3E-03	2.8E-02
dissolfp_agrl	Decay of fastP to dissolved PP - d-1 (arable land class)	3.3E-05	1.3E-04
dissolfp_past	Decay of fastP to dissolved PP - d-1 (pature land class)	2.3E-05	1.4E-04
dissolfp_rgrs	Decay of fastP to dissolved PP - d-1 (rough grazing land class)	5.0E-05	1.4E-04
dissolhp_agrl	Decay of humusP to dissolved PP - d-1 (arable land class)	9.1E-07	3.0E-06
dissolhp_past	Decay of humusP to dissolved PP - d-1 (pasture land class)	9.5E-07	3.0E-06
dissolhp_rgrs	Decay of humusP to dissolved PP - d-1 (rough grazing land class)	1.0E-06	3.0E-06
humusP0_agrl	Starting value for pool in soil of humus P - mg/m3 (arable land class)	7904	168105
humusP0_past	Starting value for pool in soil of humus P - mg/m3 (pasture land class)	9712	176377
humusP0_rgrs	Starting value for pool in soil of humus P - mg/m3 (rough grazing land class)	35465	163663

partP0_agrl	Starting value for pool in soil of partP - mg/m3 (arable land class)	1247	7937
partP0_past	Starting value for pool in soil of partP - mg/m3 (pasture land class)	113765	145968
partP0_rgrs	Starting value for pool in soil of partP - mg/m3 (rough grazing land class)	27846	145453
damp	Fraction of delay in water course which also causes damping	0.07	0.97
wprodp	Production/decay of P in water - kgm-3d-1	1.6E-05	4.9E-05
fastP0	Starting value for pool in soil of fastP - mg/m3	39	437
lp	Limit for Potential evapotranspiration	0.75	1.00
rcgrw	Recession coefficient for regional groundwater flow from soil layers	3.4E-03	1.8E-02
cevpph	Phase of sinus function that corrects potential evapotranspiration - days	4	44
cevpam	Amplitude of sinus function that corrects potential evapotranspiration	0.26	1.48
mwind	Average windspeed - m/s	3.1	4.9
epotdist	coefficient in exponential function for potential evapotranspiration depth dependency	1.1	4.4

Appendix 2 Table 2 continued

Parameter ranges for Wylye, Avon:

Parameter Name	**Parameter description**	**Min Value**	**Max Value**
mperc1_sol1	Max percolation capacity from soil layer 1 to 2 (For soil class 1)	22	90
mperc1_sol2	Max percolation capacity from soil layer 1 to 2 (For soil class 2)	15	95
mperc1_sol3	Max percolation capacity from soil layer 1 to 2 (For soil class 3)	11	99
mperc2_sol1	Max percolation capacity from soil layer 2 to 3 (For soil class 1)	19	83
mperc2_sol2	Max percolation capacity from soil layer 2 to 3 (For soil class 2)	11	96
mperc2_sol3	Max percolation capacity from soil layer 2 to 3 (For soil class 3)	17	97
wcep_sol1	Effective porosity as a fraction for all soil layers (soil class 1)	0.35	0.74
wcep_sol2	Effective porosity as a fraction for all soil layers (soil class 2)	0.05	0.42
wcep_sol3	Effective porosity as a fraction for all soil layers (soil class 3)	0.06	0.48

wcfc_sol1	Fraction of soil water available for evapotranspiration and not runoff - same for all soil layers (soil class 1)	0.18	0.37
wcfc_sol2	Fraction of soil water available for evapotranspiration and not runoff - same for all soil layers (soil class 2)	0.16	0.48
wcfc_sol3	Fraction of soil water available for evapotranspiration and not runoff - same for all soil layers (soil class 3)	0.30	0.49
wcwp_sol1	Wilting point as a fraction - same for all soil layers (soil class 1)	0.11	0.20
wcwp_sol2	Wilting point as a fraction - same for all soil layers (soil class 2)	0.11	0.20
wcwp_sol3	Wilting point as a fraction - same for all soil layers (soil class 3)	0.12	0.20
rrcs1_sol1	Recession coefficient for uppermost soil layer (soil class 1)	0.05	0.20
rrcs1_sol2	Recession coefficient for uppermost soil layer (soil class 2)	0.06	0.51
rrcs1_sol3	Recession coefficient for uppermost soil layer (soil class 3)	0.09	0.74
rrcs2_sol1	Recession coefficient for lowest soil layer (soil class 1)	0.00	0.01
rrcs2_sol2	Recession coefficient for lowest soil layer (soil class 2)	0.00	0.01
rrcs2_sol3	Recession coefficient for lowest soil layer (soil class 3)	0.01	0.27
srrate_sol1	Fraction for surface runoff (soil class 1)	0.27	0.38
srrate_sol2	Fraction for surface runoff (soil class 2)	0.23	0.40
srrate_sol3	Fraction for surface runoff (soil class 3)	0.26	0.69
soilcoh_sol1	Characteristic of soil for erosion calculation - kPa (soil class 1)	0.23	0.99
soilcoh_sol2	Characteristic of soil for erosion calculation - kPa (soil class 2)	0.40	0.98
soilcoh_sol3	Characteristic of soil for erosion calculation - kPa (soil class 3)	0.28	0.87
soilerod_sol1	Characteristic of soil for calculation of erosion (erodibility) - g/J (soil class 1)	0.46	0.99
soilerod_sol2	Characteristic of soil for calculation of erosion (erodibility) - g/J (soil class 2)	0.26	0.98
soilerod_sol3	Characteristic of soil for calculation of erosion (erodibility) - g/J (soil class 3)	0.43	0.98
kc_agrl	Crop coefficient for PET models (arable land class)	2.34	4.89
kc_past	Crop coefficient for PET models (pasture land class)	1.09	4.39
kc_rgrs	Crop coefficient for PET models (rough grazing land class)	0.14	2.64
cevp_agrl	Evapotranspiration parameter - mm/degree/d (arable land class)	0.11	0.28
cevp_past	Evapotranspiration parameter - mm/degree/d (pasture land class)	0.11	0.24
cevp_rgrs	Evapotranspiration parameter - mm/degree/d (rough grazing land class)	0.11	0.29

degradhp_agrl	Decay of humus to fastP - d-1 (arable land class)	1.9E-06	2.0E-05
degradhp_past	Decay of humus to fastP - d-1 (pasture land class)	1.9E-06	2.2E-05
degradhp_rgrs	Decay of humus to fastP - d-1 (rough grazing land class)	5.5E-06	2.3E-05
minerfp_agrl	Mineralisation of fastP to SRP - d-1 (arable land class)	1.3E-02	3.0E-02
minerfp_past	Mineralisation of fastP to SRP - d-1 (pasture land class)	7.1E-03	3.0E-02
minerfp_rgrs	Mineralisation of fastP to SRP - d-1 (rough grazing land class)	7.8E-03	3.0E-02
dissolfp_agrl	Decay of fastP to dissolved PP - d-1 (arable land class)	3.2E-05	1.5E-04
dissolfp_past	Decay of fastP to dissolved PP - d-1 (pature land class)	2.1E-05	1.4E-04
dissolfp_rgrs	Decay of fastP to dissolved PP - d-1 (rough grazing land class)	1.6E-05	1.4E-04
dissolhp_agrl	Decay of humusP to dissolved PP - d-1 (arable land class)	9.1E-07	2.7E-06
dissolhp_past	Decay of humusP to dissolved PP - d-1 (pasture land class)	1.2E-06	2.7E-06
dissolhp_rgrs	Decay of humusP to dissolved PP - d-1 (rough grazing land class)	8.5E-07	2.5E-06
humusP0_agrl	Starting value for pool in soil of humus P - mg/m3 (arable land class)	10567	184007
humusP0_past	Starting value for pool in soil of humus P - mg/m3 (pasture land class)	24397	190219
humusP0_rgrs	Starting value for pool in soil of humus P - mg/m3 (rough grazing land class)	101747	191793
partP0_agrl	Starting value for pool in soil of partP - mg/m3 (arable land class)	21482	128280
partP0_past	Starting value for pool in soil of partP - mg/m3 (pasture land class)	30704	140191
partP0_rgrs	Starting value for pool in soil of partP - mg/m3 (rough grazing land class)	3413	146845
damp	Fraction of delay in water course which also causes damping	0.01	0.98
wprodp	Production/decay of P in water - kgm-3d-1	1.5E-05	4.8E-05
fastP0	Starting value for pool in soil of fastP - mg/m3	113	483
lp	Limit for Potential evapotranspiration	0.00	0.38
rcgrw	Recession coefficient for regional groundwater flow from soil layers	7.6E-03	1.5E-01
cevpph	Phase of sinus function that corrects potential evapotranspiration - days	5	48
cevpam	Amplitude of sinus function that corrects potential evapotranspiration	0.24	1.36
mwind	Average windspeed - m/s	1.6	4.8
epotdist	coefficient in exponential function for potential evapotranspiration depth dependency	1.1	4.7

Appendix 2 Table 3 HYPE model fit statistics

This table of model fit statistics from Ockenden et al. (2017) includes the observed and modelled median (Q50 or TP50), and ranges (Q10, Q90 or TP10, TP90) for discharge Q and total phosphorus load TP. Nash Sutcliffe Efficiency (NSE) and model bias (PBIAS) are given for the calibration period (1 October 2011 – 30 September 2013) and the validation period (1 October 2013 – 30 September 2014).

Catchment	Newby Beck									
	Calibration		0.0	% data missing		Validation		0.0	% data missing	
	Q10	Q50	Q90	NSE	PBIAS %	Q10	Q50	Q90	NSE	PBIAS %
Observations	0.033	0.108	0.510			0.023	0.135	1.051		
Model	0.025	0.133	0.634	0.60	9.7	0.022	0.139	1.030	0.72	-1.9
n = 14	0.033	0.114	0.537	0.61	-5.6	0.031	0.126	0.920	0.72	-12.4
	0.041	0.149	0.557	0.64	5.4	0.038	0.165	0.891	0.72	-5.9
	0.030	0.129	0.614	0.60	3.3	0.030	0.138	0.962	0.70	-8.1
	0.033	0.151	0.648	0.61	13.7	0.026	0.171	1.012	0.71	0.7
	0.042	0.149	0.576	0.61	9.1	0.039	0.163	0.959	0.71	-2.4
	0.067	0.150	0.515	0.61	3.7	0.059	0.153	0.942	0.71	-5.3
	0.066	0.188	0.610	0.60	21.3	0.062	0.206	0.963	0.71	4.7
	0.034	0.141	0.591	0.61	6.3	0.028	0.149	0.971	0.72	-5.1
	0.031	0.104	0.493	0.60	-12.5	0.030	0.105	0.879	0.69	-18.7
	0.023	0.147	0.635	0.61	10.1	0.016	0.157	1.004	0.71	-1.9
	0.045	0.116	0.616	0.61	1.5	0.048	0.129	0.951	0.69	-8.6
	0.077	0.185	0.607	0.60	18.8	0.079	0.203	0.960	0.72	4.2
	0.051	0.136	0.510	0.60	-2.1	0.049	0.144	0.873	0.70	-11.4

Appendix 2 Table 3 continued

Catchment	Newby Beck									
	Calibration		17.2	% data missing		Validation		34.5	% data missing	
	TP10	TP50	TP90	NSE	PBIAS %	TP10	TP50	TP90	NSE	PBIAS %
Observations	0.116	0.509	8.610			0.026	0.743	18.776		
Model	0.053	0.558	6.802	0.44	-43.0	0.034	0.512	14.556	0.47	-33.4
n=14	0.112	0.716	11.162	0.50	15.7	0.121	0.748	26.387	0.45	35.4
	0.135	1.103	9.242	0.60	-18.6	0.112	1.074	19.808	0.59	-7.4
	0.084	0.543	4.433	0.48	-47.2	0.083	0.568	11.111	0.44	-43.1
	0.234	1.553	13.844	0.62	19.0	0.158	1.539	27.331	0.59	31.2
	0.094	0.662	8.250	0.59	-19.5	0.087	0.661	19.764	0.57	-6.5
	0.155	0.770	8.426	0.60	-15.2	0.172	0.859	20.166	0.64	3.7
	0.222	1.248	9.313	0.54	-19.5	0.202	1.379	19.144	0.56	-8.4
	0.123	0.956	9.522	0.60	-15.6	0.103	0.978	20.524	0.64	-5.1
	0.066	0.762	11.714	0.62	2.1	0.091	0.777	26.016	0.63	22.1
	0.186	1.878	17.442	0.56	44.7	0.095	1.784	31.768	0.47	54.9
	0.057	0.295	5.502	0.52	-38.8	0.073	0.336	15.306	0.46	-33.9
	0.224	0.876	6.160	0.49	-35.0	0.238	0.974	15.142	0.57	-20.4
	0.177	1.066	10.742	0.57	-2.6	0.185	1.106	23.188	0.59	17.4

Appendix 2 Table 3 continued

Catchment	Blackwater									
	Calibration		14.9	% data missing		Validation		1.9	% data missing	
	Q10	Q50	Q90	NSE	PBIAS %	Q10	Q50	Q90	NSE	PBIAS %
Observations	0.025	0.062	0.236			0.025	0.067	0.210		
Model	0.013	0.048	0.251	0.57	-10.4	0.016	0.041	0.162	-0.18	-21.7
n=12	0.013	0.046	0.260	0.57	-10.8	0.017	0.040	0.170	-0.32	-18.6
	0.011	0.046	0.249	0.55	-13.6	0.014	0.042	0.154	-0.22	-24.4
	0.012	0.048	0.254	0.56	-11.6	0.016	0.043	0.175	-0.21	-20.7
	0.012	0.045	0.244	0.55	-12.5	0.014	0.039	0.163	-0.39	-22.7
	0.013	0.053	0.263	0.57	-3.4	0.017	0.048	0.181	-0.28	-13.3
	0.011	0.042	0.236	0.56	-19.9	0.014	0.037	0.145	-0.19	-28.4
	0.011	0.049	0.262	0.55	-9.6	0.015	0.044	0.181	-0.38	-17.6
	0.010	0.044	0.248	0.56	-11.3	0.013	0.038	0.182	-0.68	-18.7
	0.013	0.048	0.236	0.57	-13.8	0.015	0.042	0.153	-0.26	-23.1
	0.011	0.051	0.264	0.55	-7.2	0.014	0.043	0.176	-0.42	-15.8
	0.012	0.051	0.249	0.56	-10.2	0.015	0.043	0.166	-0.34	-20.8

Appendix 2 Table 3 continued

Catchment	Blackwater									
	Calibration		40.2	% data missing		Validation		12.3	% data missing	
	TP10	TP50	TP90	NSE	PBIAS %	TP10	TP50	TP90	NSE	PBIAS %
Observations	0.188	0.500	1.688			0.177	0.428	1.275		
Model	0.079	0.372	1.868	0.53	-17.2	0.153	0.328	1.019	-0.22	-10.6
n=12	0.072	0.381	1.985	0.53	-16.1	0.155	0.317	0.972	-0.21	-12.2
	0.080	0.456	1.883	0.53	-12.4	0.147	0.381	1.176	-0.37	-3.8
	0.084	0.459	1.943	0.54	-10.9	0.168	0.378	1.176	-0.28	-1.2
	0.070	0.419	1.970	0.55	-12.4	0.151	0.336	1.131	-0.30	-6.0
	0.079	0.428	1.714	0.53	-17.2	0.145	0.338	1.091	0.06	-14.4
	0.063	0.390	1.901	0.53	-18.0	0.140	0.317	1.007	-0.11	-11.3
	0.065	0.408	1.625	0.53	-23.4	0.137	0.328	1.043	-0.27	-15.0
	0.061	0.368	1.640	0.54	-23.6	0.125	0.282	1.031	-0.13	-20.3
	0.091	0.444	1.723	0.54	-15.8	0.153	0.352	1.116	-0.09	-9.9
	0.063	0.437	1.910	0.53	-12.6	0.132	0.321	1.133	-0.58	-2.9
	0.079	0.474	2.085	0.55	-8.1	0.155	0.381	1.146	-0.22	-1.5

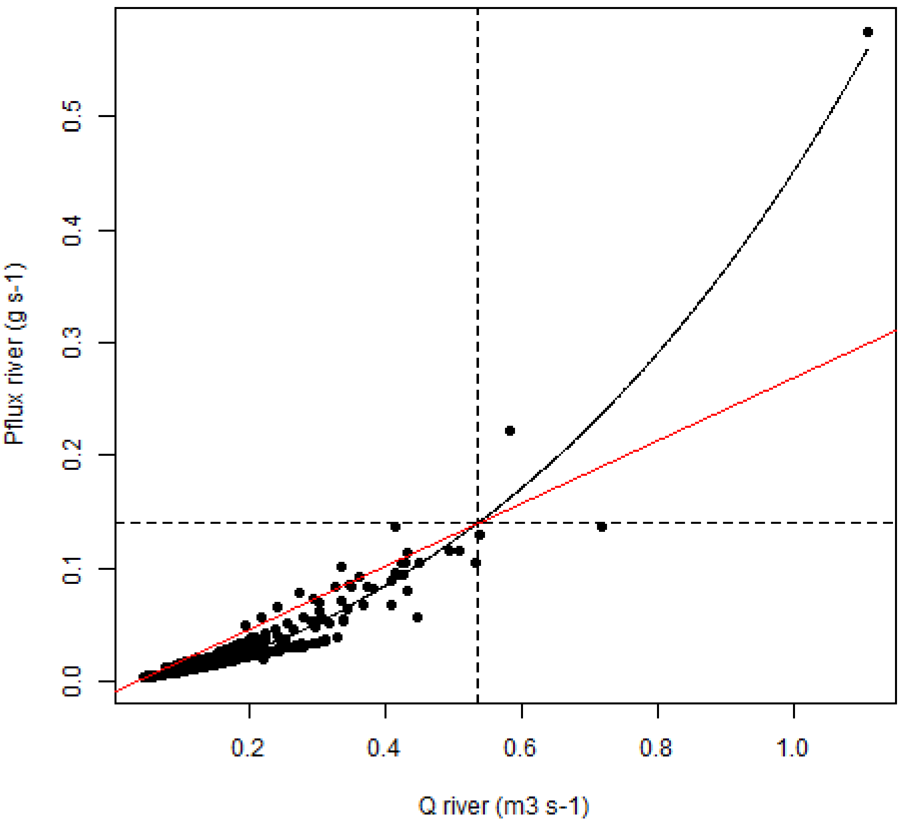
Appendix 2 Table 3 continued

Catchment	Wylye									
	Calibration		0.0	% data missing		Validation		38.4	% data missing	
	Q10	Q50	Q90	NSE	PBIAS %	Q10	Q50	Q90	NSE	PBIAS %
Observations	0.082	0.184	0.784			0.069	0.366	1.765		
Model	0.098	0.232	0.653	0.65	-4.8	0.189	0.472	1.885	0.53	21.6
n=11	0.076	0.210	0.625	0.64	-3.8	0.160	0.452	2.271	0.39	29.0
	0.082	0.192	0.680	0.61	-5.0	0.157	0.453	2.195	0.28	29.0
	0.044	0.131	0.535	0.60	-30.5	0.102	0.259	1.396	0.42	-14.8
	0.056	0.168	0.649	0.65	-16.2	0.156	0.364	1.969	0.52	13.9
	0.070	0.197	0.686	0.66	-9.0	0.156	0.487	2.089	0.27	28.8
	0.075	0.163	0.560	0.64	-19.6	0.147	0.364	1.525	0.43	-4.0
	0.033	0.135	0.690	0.62	-17.2	0.109	0.365	2.194	0.52	19.4
	0.079	0.218	0.620	0.64	-4.8	0.180	0.420	2.262	0.37	28.6
	0.053	0.153	0.654	0.62	-19.1	0.137	0.329	2.246	0.31	21.0
	0.128	0.250	0.645	0.65	-0.5	0.206	0.547	1.740	0.43	19.7

Appendix 2 Table 3 continued

Catchment	Wylye									
	Calibration		49.9	% data missing		Validation		67.7	% data missing	
	TP10	TP50	TP90	NSE	PBIAS %	TP10	TP50	TP90	NSE	PBIAS %
Observations	0.817	3.048	12.117			1.089	1.353	30.979		
Model	0.635	2.473	8.418	0.64	-29.3	0.783	10.954	28.537	-0.07	22.8
n=11	0.628	3.014	12.428	0.62	-8.4	1.641	14.443	43.730	-0.21	67.6
	0.516	2.580	10.951	0.63	-15.7	1.136	14.317	45.954	-0.42	72.9
	0.475	2.245	10.118	0.66	-21.1	0.333	9.822	29.753	-0.06	25.1
	0.565	2.864	11.661	0.65	-7.0	0.513	14.758	42.935	-0.69	76.0
	0.561	2.775	9.903	0.62	-17.8	0.643	15.087	41.401	-0.87	66.0
	0.718	2.314	8.058	0.62	-29.7	0.657	8.198	26.101	-0.11	15.0
	0.554	2.409	12.201	0.65	-8.1	0.461	8.628	43.431	0.03	54.0
	0.578	2.641	10.255	0.63	-19.5	0.706	11.841	34.036	0.25	31.7
	0.429	2.324	10.452	0.68	-17.7	0.339	11.013	46.752	-1.86	74.8
	0.886	2.979	9.733	0.63	-16.2	1.649	13.377	37.148	-0.70	51.9

E-EMMA analysis for observed catchment data



Appendix 2 Figure 1 An example year of Extended End Member Mixing Analysis for the Avon catchment by plotting phosphorus flux in the river (Pflux river g s^{-1}) versus river discharge (Qriver m^3 s^{-1}). The red line depicts the conservative mixing series and the black line depicts the LOESS regression. The dashed lines indicate the 99th percentile of Qriver.

Appendix 2 Table 4 Results for calculating catchment retention using E-EMMA analysis in 'R' for the Newby Beck (Eden), Blackwater (Wensum) and Wylye (Avon) catchments for observed data of the year 2012

Newby 2012	Bins	Frequency in bin	lower bound	upper bound	integration linear model	area under curve linear model	integration loes model	area under curve loess model	retention (g s-1)
1	[0.0298,0.14)	180	0.029838	0.139629	2.40E-05	0.004325	6.02E-06	0.001083	3.24E-03
2	[0.14,0.249)	61	0.139629	0.249419	7.02E-05	0.004284	2.09E-05	0.001273	3.01E-03
3	[0.249,0.359)	26	0.249419	0.35921	1.16E-04	0.003028	5.22E-05	0.001358	1.67E-03
4	[0.359,0.469)	11	0.35921	0.469	1.63E-04	0.001789	1.23E-04	0.001351	4.39E-04
5	[0.469,0.579)	15	0.469	0.578791	2.09E-04	0.003133	1.89E-04	0.002829	3.04E-04
6	[0.579,0.689)	3	0.578791	0.688581	2.55E-04	0.000765	2.40E-04	0.000721	4.44E-05
7	[0.689,0.798)	6	0.688581	0.798372	3.01E-04	0.001808	2.93E-04	0.001756	5.14E-05
8	[0.798,0.908)	4	0.798372	0.908162	3.48E-04	0.00139	3.46E-04	0.001385	5.26E-06
9	[0.908,1.02)	3	0.908162	1.017953	3.94E-04	0.001181	4.00E-04	0.001201	-2.02E-05
10	[1.02,1.13)	1	1.017953	1.127744	4.40E-04	0.00044	4.55E-04	0.000455	-1.54E-05
11	[1.13,1.24)	1	1.127743	1.237534	4.86E-04	0.000486	5.11E-04	0.000511	-2.44E-05
12	[1.24,1.35)	3	1.237534	1.347325	5.32E-04	0.001597	5.66E-04	0.001698	-1.01E-04
13	[1.35,1.46)	0	1.347325	1.457115	5.79E-04	0	6.21E-04	0	0.00E+00
14	[1.46,1.57)	0	1.457115	1.566906	6.25E-04	0	6.76E-04	0	0.00E+00
15	[1.57,1.68)	1	1.566906	1.676696	6.71E-04	0.000671	7.31E-04	0.000731	-6.00E-05
16	[1.68,1.79)	0	1.676696	1.786487	7.17E-04	0	7.85E-04	0	0.00E+00
17	[1.79,1.9)	1	1.786487	1.896277	7.63E-04	0.000763	8.38E-04	0.000838	-7.46E-05
18	[1.9,2.01)	1	1.896277	2.006068	8.10E-04	0.00081	8.90E-04	0.00089	-8.03E-05
19	[2.01,2.12)	0	2.006068	2.115858	8.56E-04	0	9.41E-04	0	0.00E+00
20	[2.12,2.23)	0	2.115858	2.225649	9.02E-04	0	9.90E-04	0	0.00E+00
21	[2.23,2.34)	1	2.225649	2.335439	9.48E-04	0.000948	1.04E-03	0.001037	-8.89E-05
22	[2.34,2.45)	0	2.335439	2.44523	9.94E-04	0	1.08E-03	0	0.00E+00
23	[2.45,2.56)	0	2.44523	2.55502	1.04E-03	0	1.13E-03	0	0.00E+00
24	[2.56,2.66)	0	2.55502	2.664811	1.09E-03	0	1.17E-03	0	0.00E+00
25	[2.66,2.77)	0	2.664811	2.774602	1.13E-03	0	1.21E-03	0	0.00E+00
26	[2.77,2.88)	1	2.774602	2.884392	1.18E-03	0.001179	1.24E-03	0.001241	-6.17E-05
27	[2.88,2.99)	0	2.884392	2.994183	1.23E-03	0	1.27E-03	0	0.00E+00
28	[2.99,3.1)	0	2.994183	3.103973	1.27E-03	0	1.30E-03	0	0.00E+00
29	[3.1,3.21)	0	3.103973	3.213764	1.32E-03	0	1.33E-03	0	0.00E+00

Appendix 2 Table 4 continued

Blackwater 2012	Bins	Frequency in bin	lower bound	upper bound	integration linear model	area under curve linear model	integration loes model	area under curve loess model	retention (g s-1)
1	[0.0206,0.039	34	0.020563	0.039711	7.86E-07	2.67E-05	6.19E-07	2.10E-05	5.69E-06
2	[0.0397,0.058	47	0.039711	0.05886	1.38E-06	6.47E-05	9.78E-07	4.60E-05	1.87E-05
3	[0.0589,0.078)	17	0.05886	0.078009	1.97E-06	3.34E-05	1.30E-06	2.21E-05	1.13E-05
4	[0.078,0.0972)	11	0.078009	0.097158	2.56E-06	2.81E-05	1.58E-06	1.74E-05	1.07E-05
5	[0.0972,0.116)	7	0.097158	0.116307	3.15E-06	2.20E-05	1.79E-06	1.25E-05	9.48E-06
6	[0.116,0.135)	14	0.116307	0.135456	3.74E-06	5.23E-05	1.93E-06	2.71E-05	2.52E-05
7	[0.135,0.155)	5	0.135456	0.154604	4.33E-06	2.16E-05	2.10E-06	1.05E-05	1.11E-05
8	[0.155,0.174)	3	0.154604	0.173753	4.92E-06	1.47E-05	2.39E-06	7.16E-06	7.58E-06
9	[0.174,0.193)	11	0.173753	0.192902	5.50E-06	6.06E-05	2.79E-06	3.07E-05	2.99E-05
10	[0.193,0.212)	6	0.192902	0.212051	6.09E-06	3.66E-05	3.23E-06	1.94E-05	1.72E-05
11	[0.212,0.231)	10	0.212051	0.2312	6.68E-06	6.68E-05	3.65E-06	3.65E-05	3.04E-05
12	[0.231,0.25)	9	0.2312	0.250349	7.27E-06	6.55E-05	4.05E-06	3.64E-05	2.90E-05
13	[0.25,0.269)	5	0.250349	0.269497	7.86E-06	3.93E-05	4.47E-06	2.23E-05	1.70E-05
14	[0.269,0.289)	6	0.269497	0.288646	8.45E-06	5.07E-05	4.90E-06	2.94E-05	2.13E-05
15	[0.289,0.308)	5	0.288646	0.307795	9.04E-06	4.52E-05	5.34E-06	2.67E-05	1.85E-05
16	[0.308,0.327)	5	0.307795	0.326944	9.63E-06	4.82E-05	5.81E-06	2.91E-05	1.91E-05
17	[0.327,0.346)	2	0.326944	0.346093	1.02E-05	2.04E-05	6.35E-06	1.27E-05	7.74E-06
18	[0.346,0.365)	2	0.346093	0.365241	1.08E-05	2.16E-05	6.95E-06	1.39E-05	7.73E-06
19	[0.365,0.384)	0	0.365241	0.38439	1.14E-05	0.00E+00	7.60E-06	0.00E+00	0.00E+00
20	[0.384,0.404)	0	0.38439	0.403539	1.20E-05	0.00E+00	8.30E-06	0.00E+00	0.00E+00
21	[0.404,0.423)	2	0.403539	0.422688	1.26E-05	2.52E-05	9.07E-06	1.81E-05	7.03E-06
22	[0.423,0.442)	2	0.422688	0.441837	1.32E-05	2.63E-05	9.88E-06	1.98E-05	6.58E-06
23	[0.442,0.461)	1	0.441837	0.460986	1.38E-05	1.38E-05	1.07E-05	1.07E-05	3.01E-06
24	[0.461,0.48)	0	0.460986	0.480134	1.44E-05	0.00E+00	1.17E-05	0.00E+00	0.00E+00
25	[0.48,0.499)	1	0.480134	0.499283	1.49E-05	1.49E-05	1.26E-05	1.26E-05	2.31E-06
26	[0.499,0.518)	2	0.499283	0.518432	1.55E-05	3.11E-05	1.37E-05	2.73E-05	3.75E-06
27	[0.518,0.538)	2	0.518432	0.537581	1.61E-05	3.22E-05	1.47E-05	2.94E-05	2.80E-06
28	[0.538,0.557)	0	0.537581	0.55673	1.67E-05	0.00E+00	1.58E-05	0.00E+00	0.00E+00
29	[0.557,0.576)	1	0.55673	0.575879	1.73E-05	1.73E-05	1.70E-05	1.70E-05	3.01E-07

Appendix 2 Table 4 continued

Wylye 2012	Bins	Frequency in bin	lower bound	upper bound	integration linear model	area under curve linear model	integration loes model	area under curve loess model	retention (g s-1)
1	[0.0716,0.115)	31	0.071552	0.114793	0.0006206	0.019238	0.00047262	0.014651	0.004587
2	[0.115,0.158)	28	0.114793	0.158034	0.0012522	0.035062	0.00084348	0.023617	0.011444
3	[0.158,0.201)	20	0.158034	0.201275	0.0018838	0.037676	0.00122591	0.024518	0.013158
4	[0.201,0.245)	0	0.201275	0.244516	0.0025154	0	0.00162083	0	0
5	[0.245,0.288)	0	0.244516	0.287757	0.003147	0	0.00200789	0	0
6	[0.288,0.331)	5	0.287757	0.330998	0.0037786	0.018893	0.002345	0.011725	0.007168
7	[0.331,0.374)	8	0.330998	0.374239	0.0044103	0.035282	0.00257408	0.020593	0.01469
8	[0.374,0.417)	9	0.374239	0.41748	0.0050419	0.045377	0.00264069	0.023766	0.021611
9	[0.417,0.461)	35	0.41748	0.460721	0.0056735	0.198572	0.0028965	0.101378	0.097195
10	[0.461,0.504)	8	0.460721	0.503962	0.0063051	0.050441	0.00350276	0.028022	0.022419
11	[0.504,0.547)	3	0.503962	0.547203	0.0069367	0.02081	0.00416582	0.012497	0.008313
12	[0.547,0.59)	2	0.547203	0.590444	0.0075683	0.015137	0.00480591	0.009612	0.005525
13	[0.59,0.634)	0	0.590444	0.633685	0.0081999	0	0.00540125	0	0
14	[0.634,0.677)	1	0.633685	0.676926	0.0088316	0.008832	0.00593004	0.00593	0.002902
15	[0.677,0.72)	1	0.676925	0.720166	0.0094632	0.009463	0.00637327	0.006373	0.00309
16	[0.72,0.763)	2	0.720166	0.763407	0.0100948	0.02019	0.00679002	0.01358	0.00661
17	[0.763,0.807)	1	0.763407	0.806648	0.0107264	0.010726	0.0072616	0.007262	0.003465
18	[0.807,0.85)	1	0.806648	0.849889	0.011358	0.011358	0.00779355	0.007794	0.003564
19	[0.85,0.893)	2	0.849889	0.89313	0.0119896	0.023979	0.00838702	0.016774	0.007205
20	[0.893,0.936)	1	0.89313	0.936371	0.0126212	0.012621	0.00904318	0.009043	0.003578
21	[0.936,0.98)	2	0.936371	0.979612	0.0132528	0.026506	0.00976318	0.019526	0.006979
22	[0.98,1.02)	0	0.979612	1.022853	0.0138845	0	0.01054818	0	0
23	[1.02,1.07)	1	1.022853	1.066094	0.0145161	0.014516	0.01139934	0.011399	0.003117
24	[1.07,1.11)	3	1.066094	1.109335	0.0151477	0.045443	0.01231783	0.036953	0.00849
25	[1.11,1.15)	2	1.109335	1.152576	0.0157793	0.031559	0.01330479	0.02661	0.004949
26	[1.15,1.2)	2	1.152576	1.195817	0.0164109	0.032822	0.0143614	0.028723	0.004099
27	[1.2,1.24)	1	1.195817	1.239058	0.0170425	0.017043	0.0154888	0.015489	0.001554
28	[1.24,1.28)	1	1.239058	1.282299	0.0176741	0.017674	0.01668816	0.016688	0.000986
29	[1.28,1.33)	0	1.282299	1.32554	0.0183057	0	0.01796065	0	0

Calculating TP load and TP input ratio

Behrendt and Opitz (1999) use the following equation to calculate the ratio of P load to the sum of P inputs (named emissions):

$$\frac{L_P}{E_P} = \frac{1}{1 + R_{L_P}} \quad (9)$$

Where L_P is the mean annual transport or load of P in a river system within a certain time period, and E_P is the sum of all the point and diffuse P emissions. R_{LP} is the transport weighted sum of all retention and losses (retention divided by load). The right hand side of the equation was used to calculate TP load to TP emission ratio for each catchment. R_{LP} was calculated by dividing the average retention (100 realisations for the sampled year) by the average load for that same year (100 realisations for the sampled year).

Appendix 2 Table 5 Transport emission ratio for TP each catchment, Newby Beck (Eden), Blackwater (Wensum), Wylye (Avon). The average is calculated over 100 realisations for 28 years.

TP transport: TP emission						
	Newby Beck		Blackwater		Wylye	
	Average	Std.d	Average	Std.d	Average	Std.d
Baseline	0.973	0.002	0.996	0.001	0.984	0.002
Low 2050s	0.970	0.001	0.995	0.002	0.975	0.004
Low 2080s	0.970	0.001	0.994	0.002	0.971	0.004
Medium 2050s	0.970	0.002	0.995	0.002	0.973	0.005
Medium 2080s	0.970	0.002	0.994	0.002	0.968	0.004
High 2050s	0.969	0.001	0.994	0.002	0.973	0.004
High 2080s	0.968	0.002	0.994	0.002	0.962	0.004

References

Behrendt, H. and D. Opitz. 1999. Retention of nutrients in river systems: Dependence on specific runoff and hydraulic load. Hydrobiologia 410: 111-122. doi:10.1023/a:1003735225869.

Ockenden, M.C., M.J. Hollaway, K.J. Beven, A.L. Collins, R. Evans, P.D. Falloon, et al. 2017. Major agricultural changes required to mitigate phosphorus losses under climate change. Nature Comm. 8: 161. doi:10.1038/s41467-017-00232-0.

Appendix 3

Calculation of discharge

At the 6 chosen sites flow or discharge (Q) was estimated from level data logged at 15-minute intervals using a barometric logger (In-Situ inc., Troll Series), converted to flow using the application of a rating curve based on gauged flows (n=7). Flow was calculated using the equation:

$$\boldsymbol{Q = C(h + a)^{n}} \tag{10}$$

Where *Q* is flow, *h* is stage or level, *a* is the stage at zero flow, and C and n are constants calculated by the least squares procedure. The values of C and n are obtained by:

$$\boldsymbol{\sum Y - N(logC) - n\sum X = 0} \tag{11}$$

$$\boldsymbol{\sum(XY) - \sum(X)\,(logC) - n\sum(X^{2}) = 0} \tag{12}$$

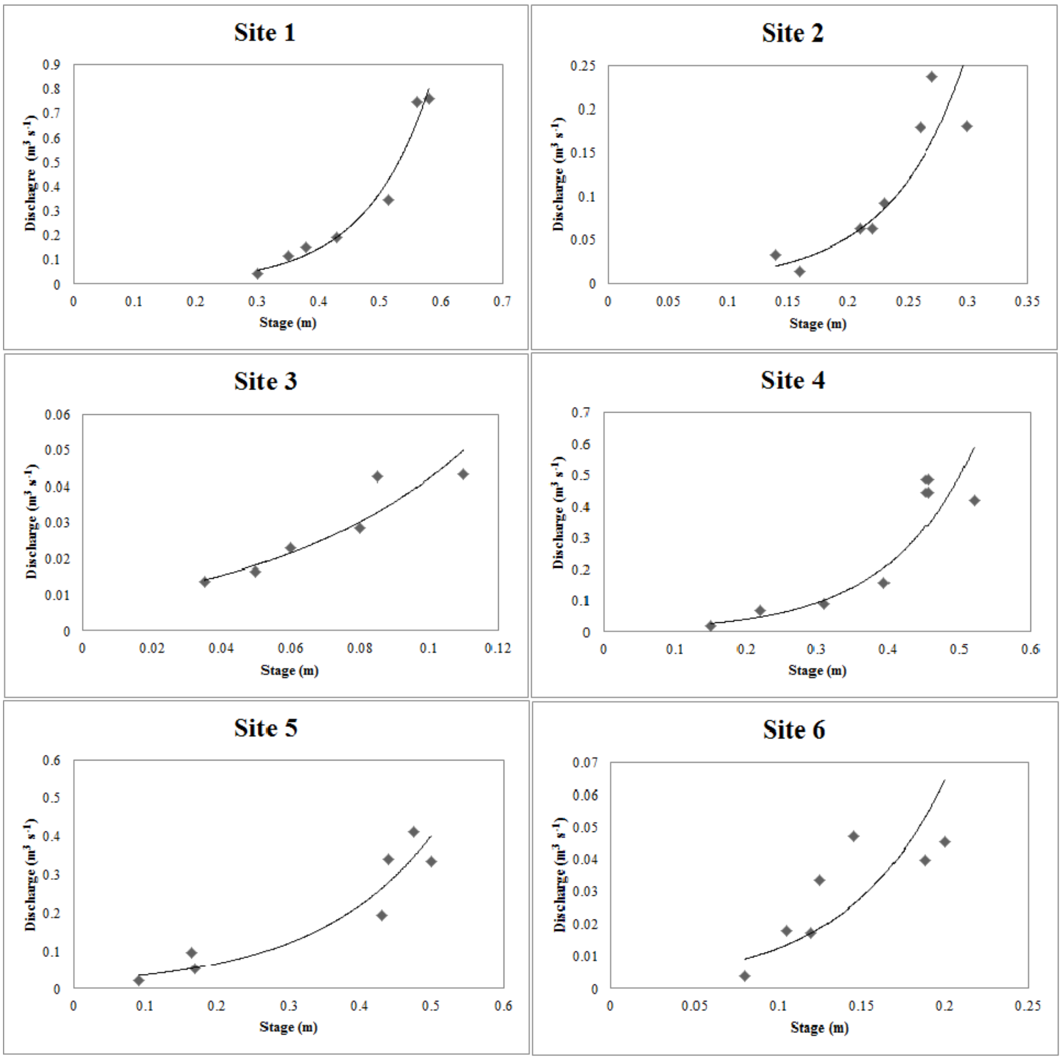
Where ΣY is the sum of all the values of logQ; ΣX is the sum of all the values of log(h+a); Σ(X^2) is the sum of all the values of the square of X; Σ(XY) is the sum of all the values of the product of X and Y; and N is the number of current meter observations.

For all sites values were calculated as:

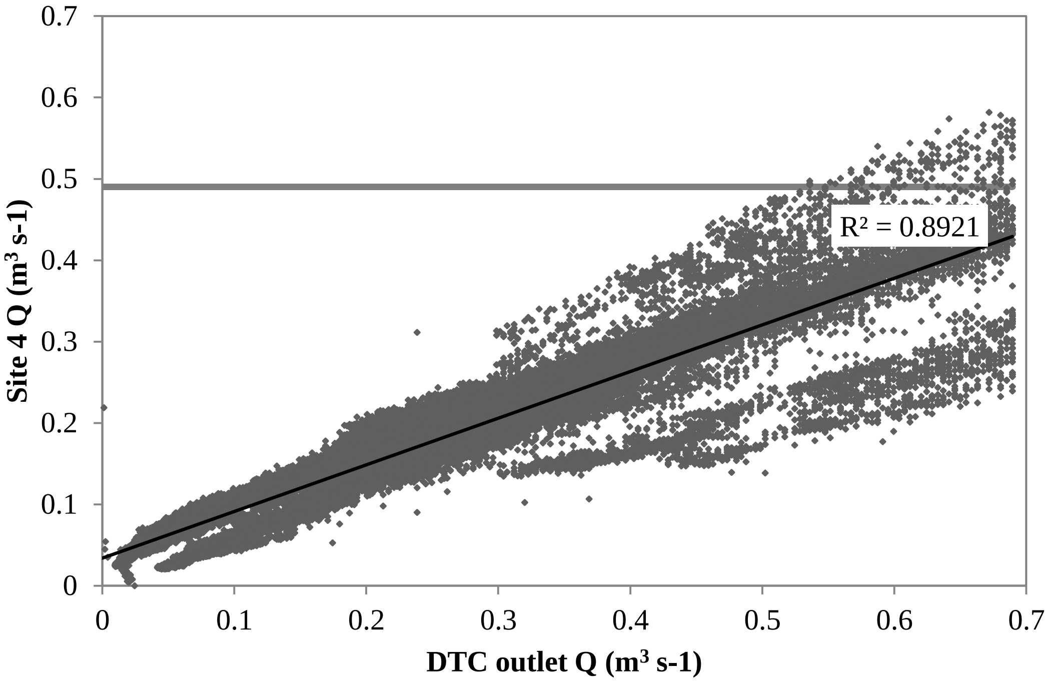
Appendix 3 Table 1 Calculation of flow for each of the six sample sites in Newby Beck+.

Site	ΣY	ΣX	Σ(X^2)	Σ(XY)	N	n	logC	C
1	-4.592	-2.542	0.995	1.963	7	4.140	0.848	7.040
2	-8.889	-5.300	3.601	6.186	8	3.323	1.091	12.319
3	-9.566	-7.105	8.574	11.506	6	1.114	-0.275	0.531
4	-5.765	-3.362	1.847	3.357	7	2.526	0.390	2.452
5	-6.005	-3.945	2.755	4.214	7	1.562	0.023	1.054
6	-9.737	-5.184	4.585	8.686	6	2.577	0.603	4.013

The following graphs show the rating curves for each site:



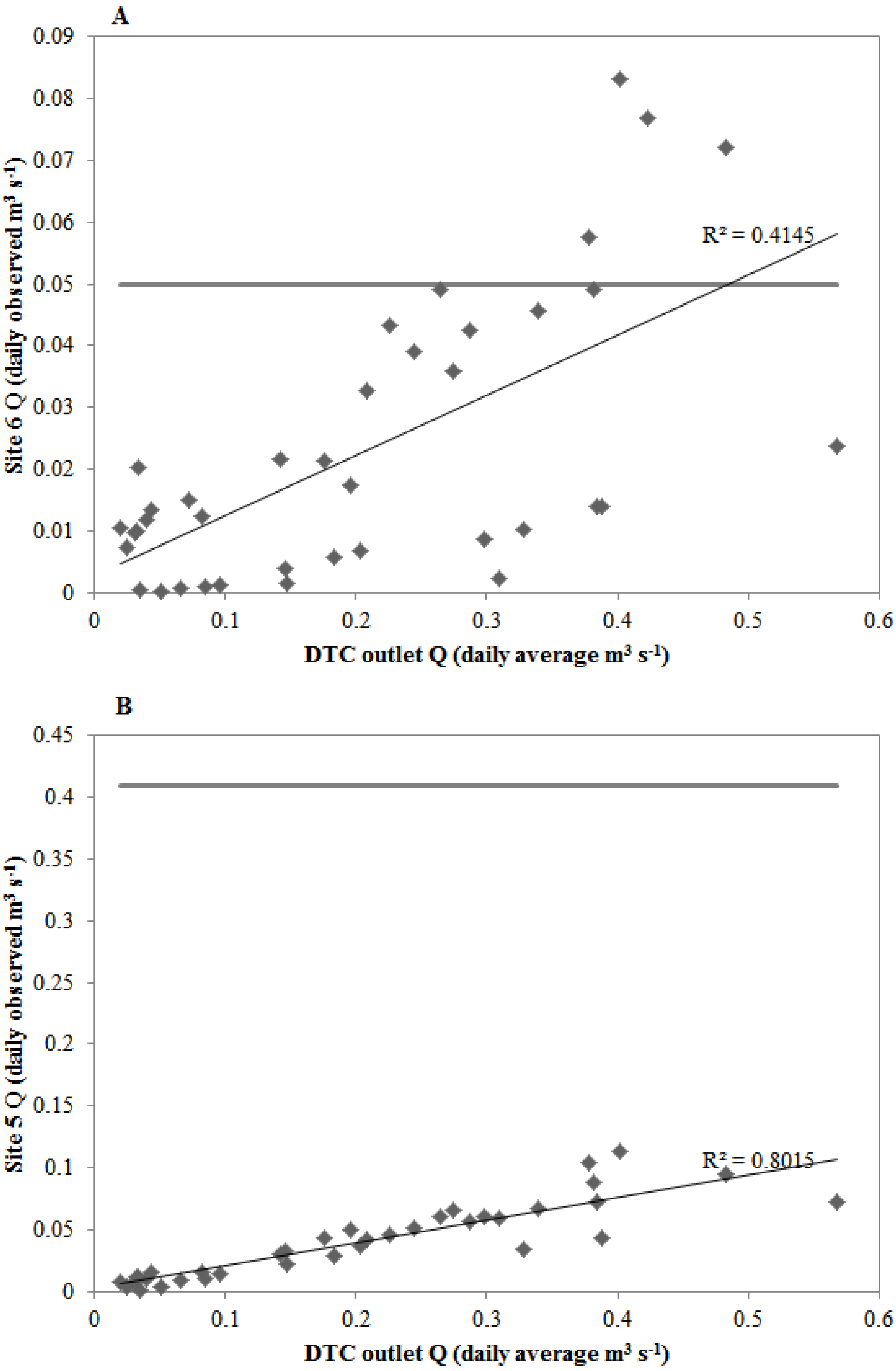
Appendix 3 Figure 1 Newby Beck+ rating curves for sites 1-6.



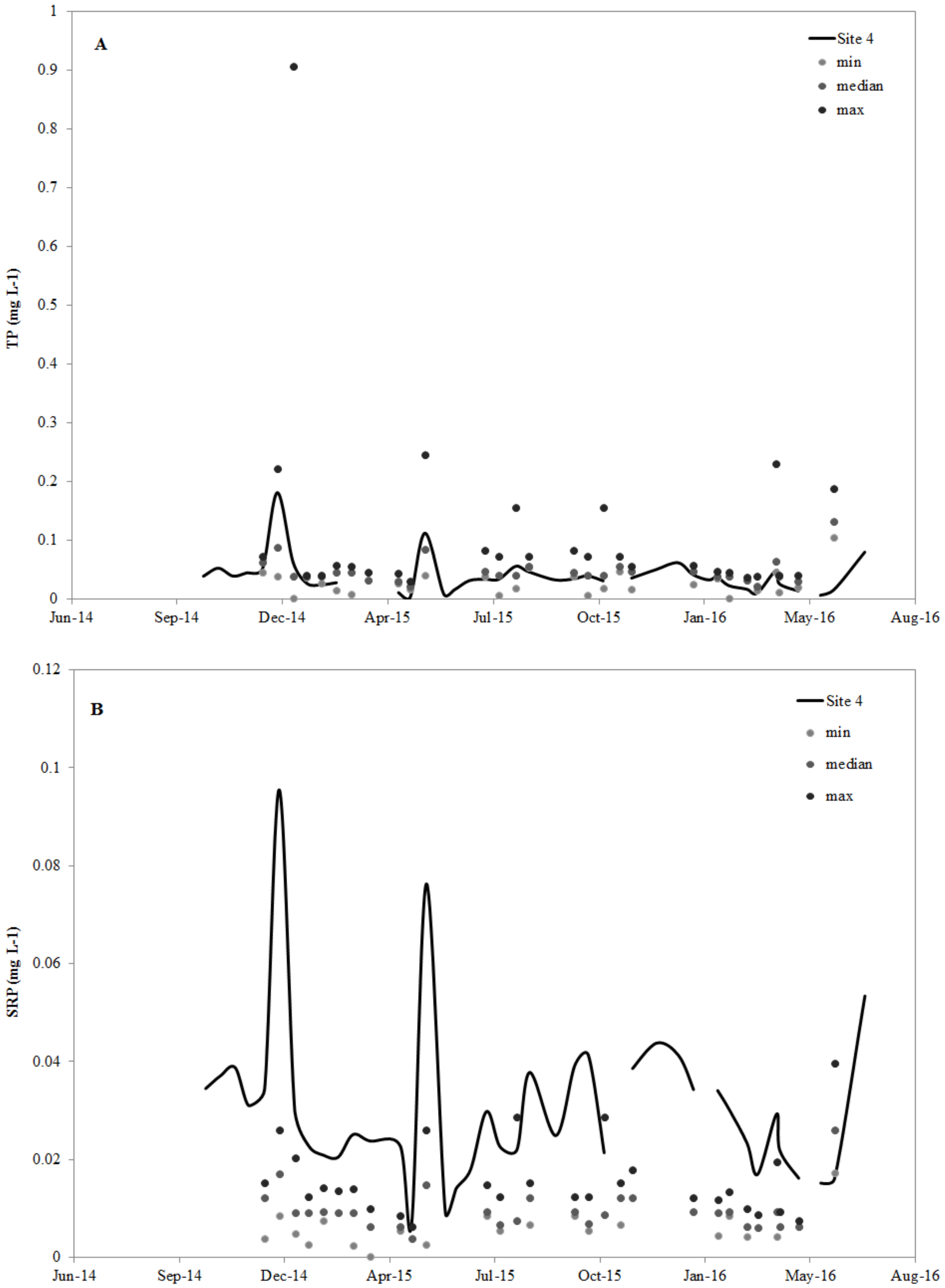
Appendix 3 Figure 2 Newby Beck+ Site 4 flow (Q) plotted against DTC outlet Q data for the maximum observed flow at site 4 (0.59 m^3 s^{-1}). Maximum gauged discharge for site 4 (0.49 m^3 s^{-1}) is the grey line. Linear regression (black line) result r^2= 0.89 (two decimal figures).

Appendix 3 Table 2 Maximum gauged flow (Q m^3 s^{-1}) for sites 1-6 at Newby Beck+ and the maximum daily average flow for the observed data (which has corresponding phosphorus data).

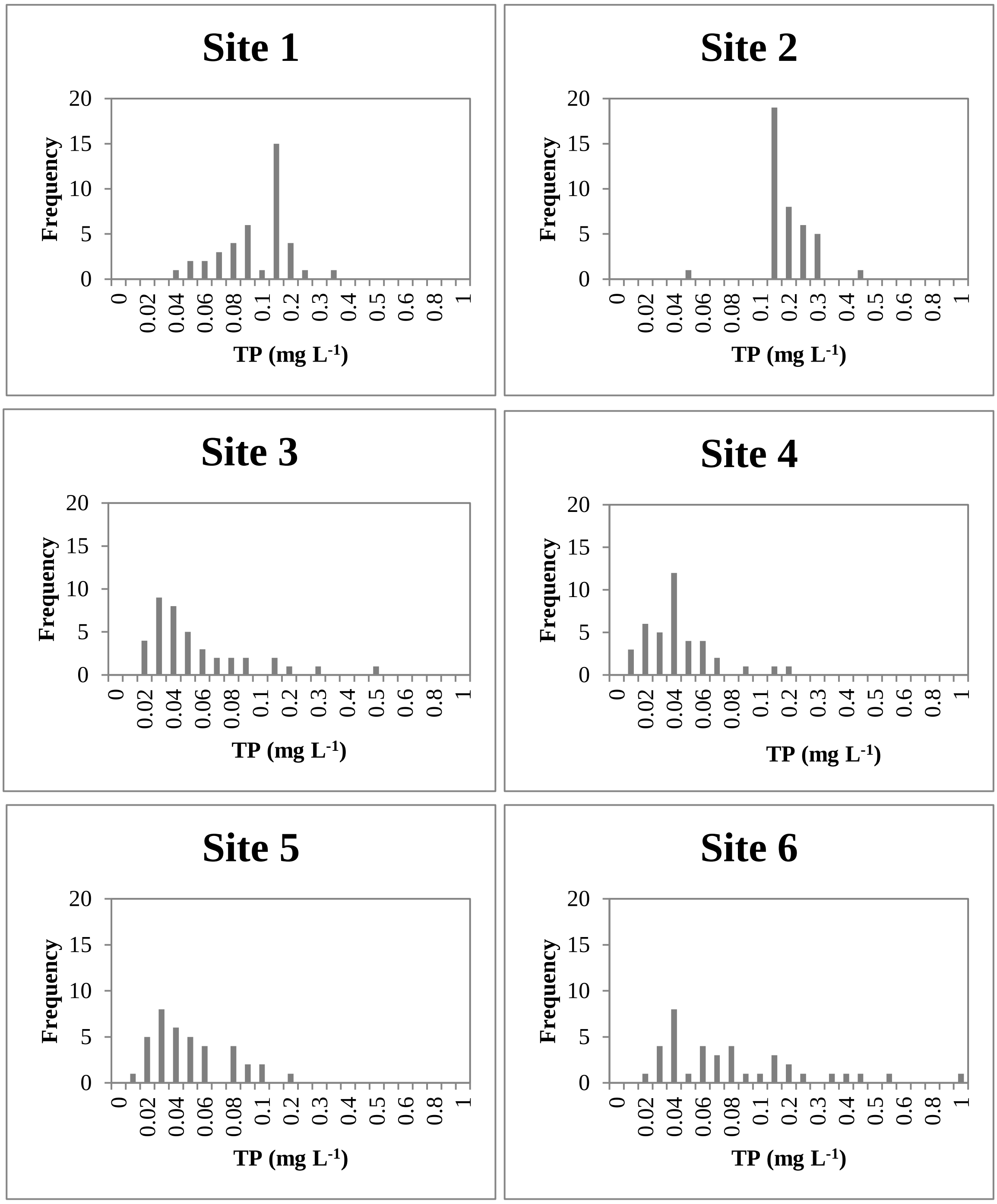
Site	Max gauged Q (m^3 s^{-1})	Max dataset Q (m^3 s^{-1})
1	0.76	0.69
2	0.18	0.29
3	0.04	0.04
4	0.49	0.59
5	0.41	0.11
6	0.05	0.08



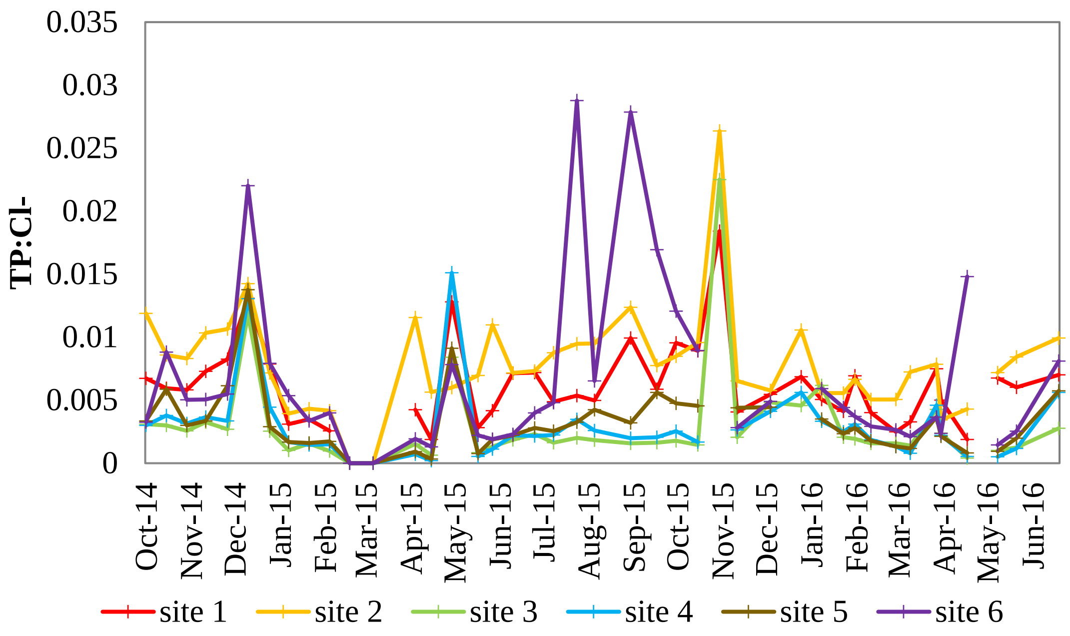
Appendix 3 Figure 3 Site 6 (A) and site 5 (B) (Newby Beck+) average daily observed Q (m^3 s^{-1}) plotted against DTC outlet daily average Q (m^3 s^{-1}) for the same bi-weekly sampling period from October 2014- July 2016. The grey line shows the maximum gauged flow at site 6 (A, 0.05 m^3 s^{-1}) and site 5 (B, 0.41 m^3 s^{-1}). R^2 values are 0.41 and 0.80 for site 6 and site 5 respectively (two decimal figures).



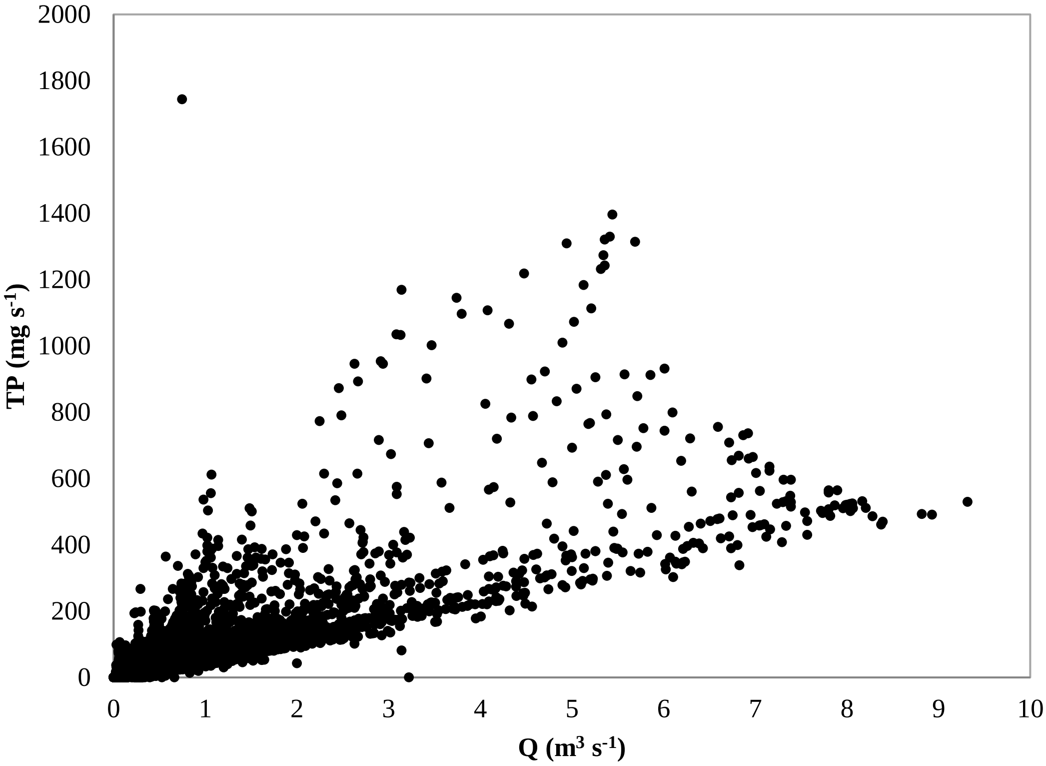
Appendix 3 Figure 4 DTC outlet station data (daily min, median and max) for TP and total reactive phosphorus (TRP) was compared to TP (A) and SRP (B) at site 4 (Newby Beck+) for the period October 2014- July 2016.



Appendix 3 Figure 5 Frequency analysis of total phosphorus concentration (mg L^{-1}) for the 6 sites in the Newby Beck+ catchment for the bi-weekly sampling during the period October 2014- July 2016.



Appendix 3 Figure 6 Total phosphorus (TP) and chloride (Cl^-) ratio for the sampling period October 2014- July 2016 for each site.



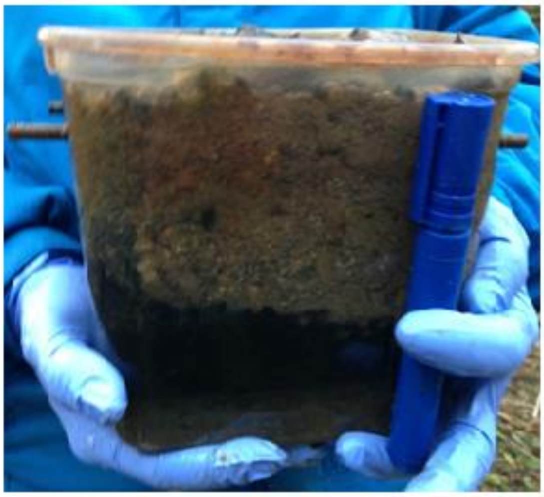
Appendix 3 Figure 7 Total phosphorus load (mg s^{-1}) and flow (m^3 s^{-1}) at the Newby Beck outlet, high resolution (30-min) data collected under the DTC for the period October 2014- July 2016.

Photo 1: 05/08/2015

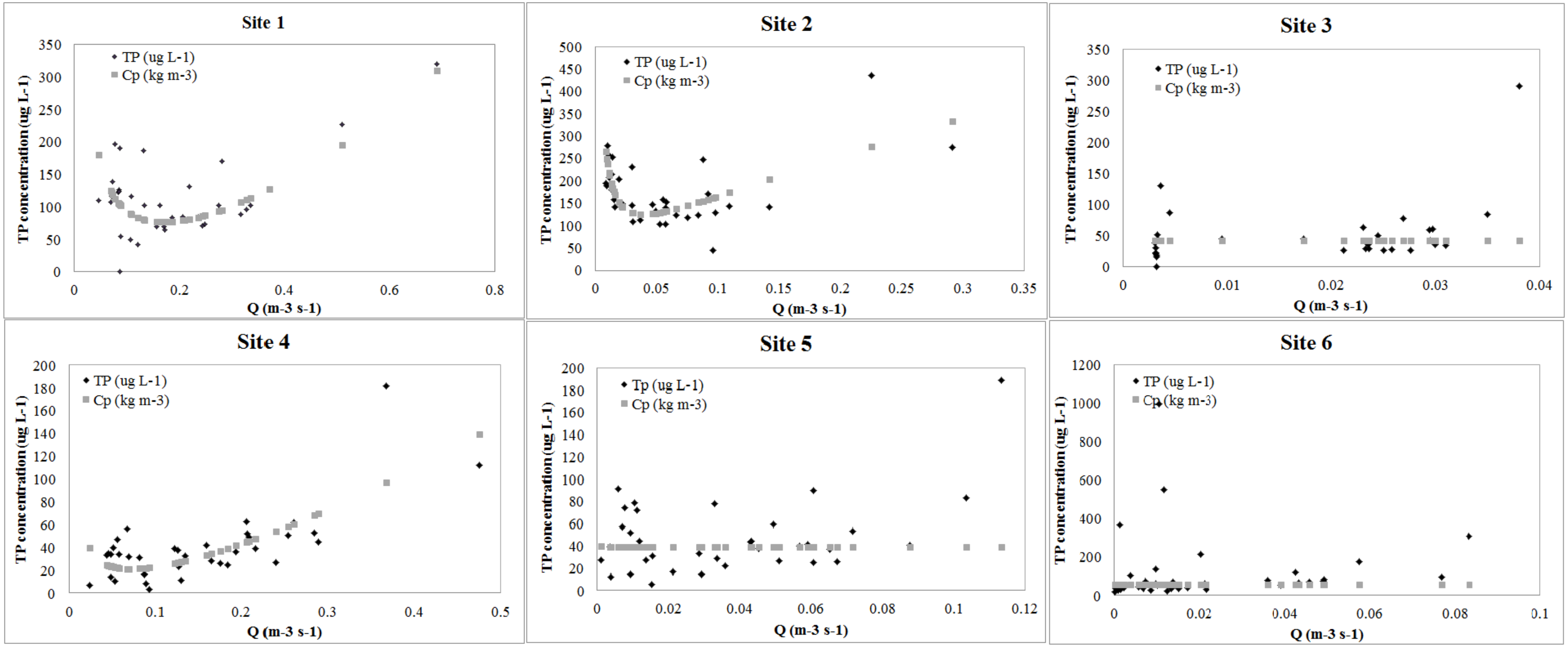
Photo 2: 11/09/2015

Photo 3: 11/09/2015

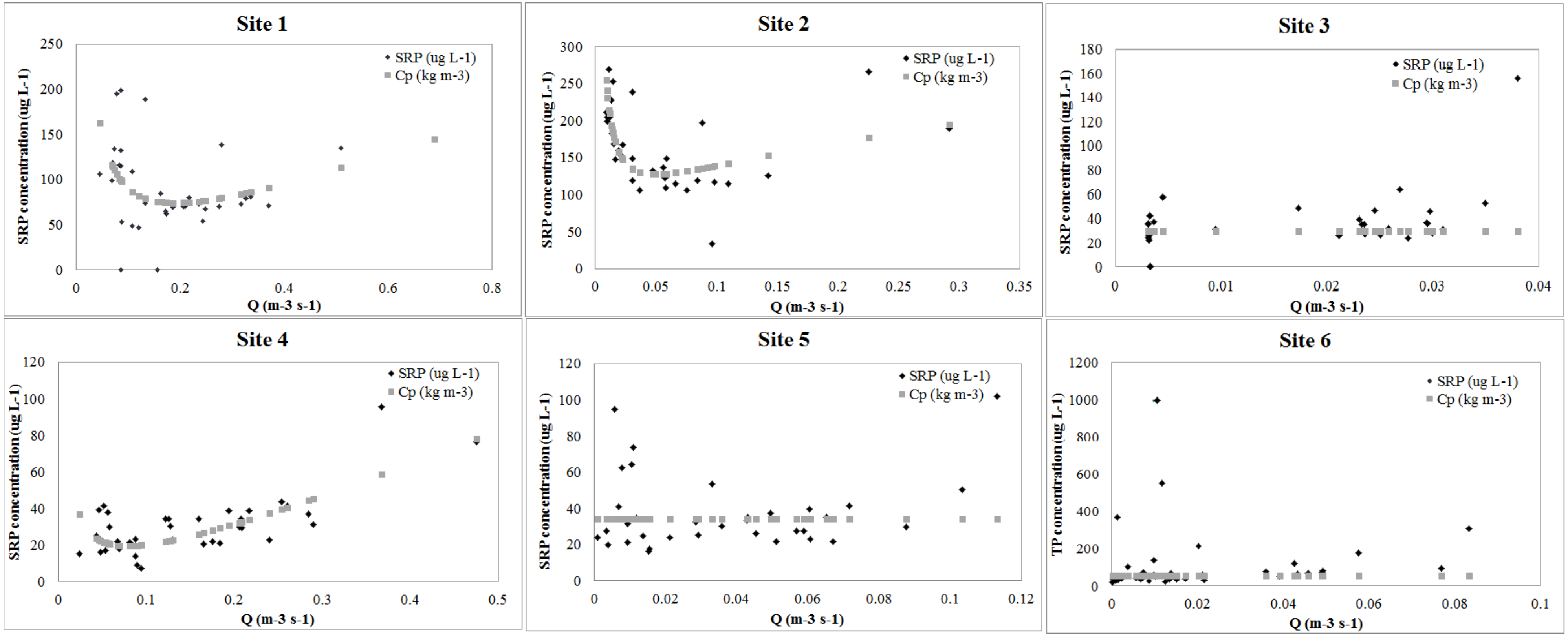
Photo 4: Trap installed in July 2015



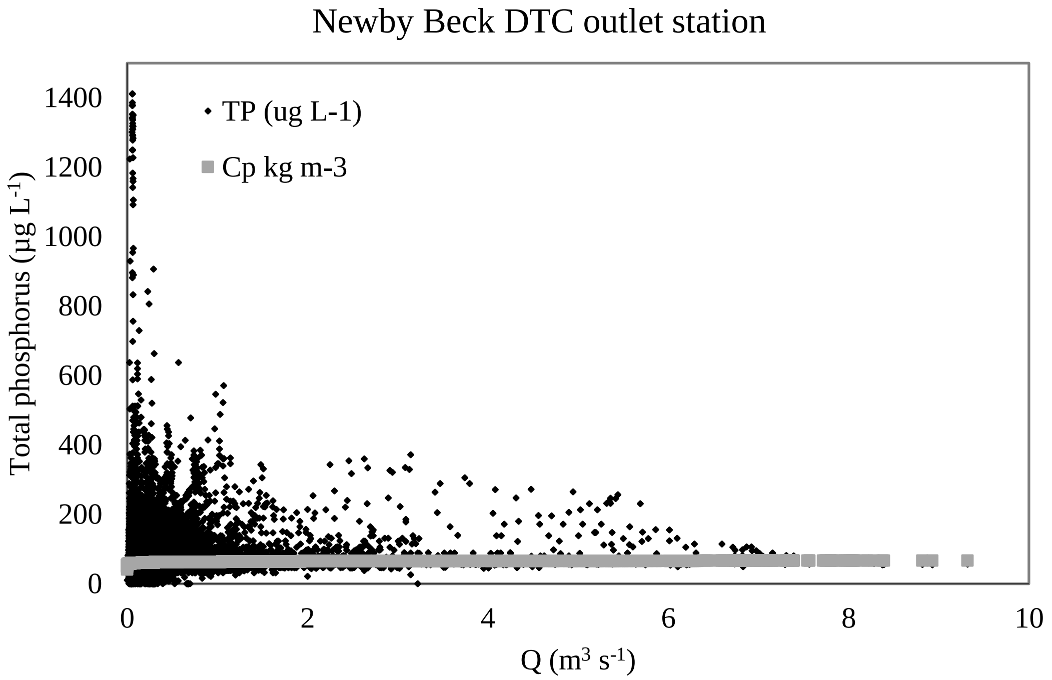
Photos to support observations of in-stream pollution events at site 6.



Appendix 3 Figure 8 The relationship between total phosphorus concentration (TP ug L-1) and flow (Q m-3 s-1) for study sites in Newby Beck+. Black diamonds are raw data; grey squares are combined TP concentrations from point and diffuse sources, using load apportionment modelling.



Appendix 3 Figure 9 The relationship between soluble reactive phosphorus concentration (SRP µg L-1) and flow (Q m-3 s-1) for study sites in Newby Beck+. Black diamonds are raw data; grey squares are combined SRP concentrations from point and diffuse sources, using load apportionment modelling.



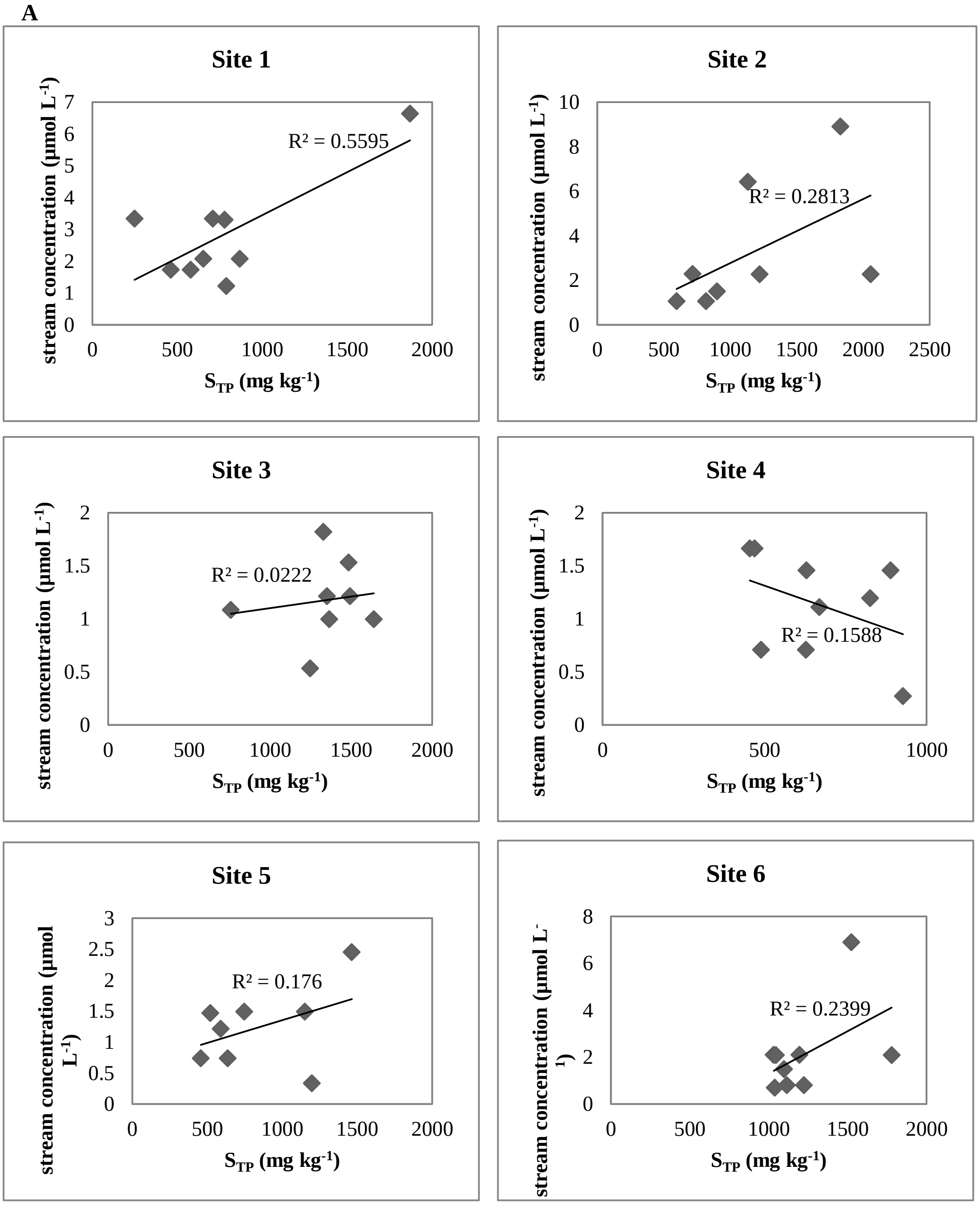
Appendix 3 Figure 10 Phosphorus load apportionment model for total phosphorus (TP µg L^{-1}) and flow (Q m^3 s^{-1}) high-resolution Newby Beck DTC outlet station data.

Sediments

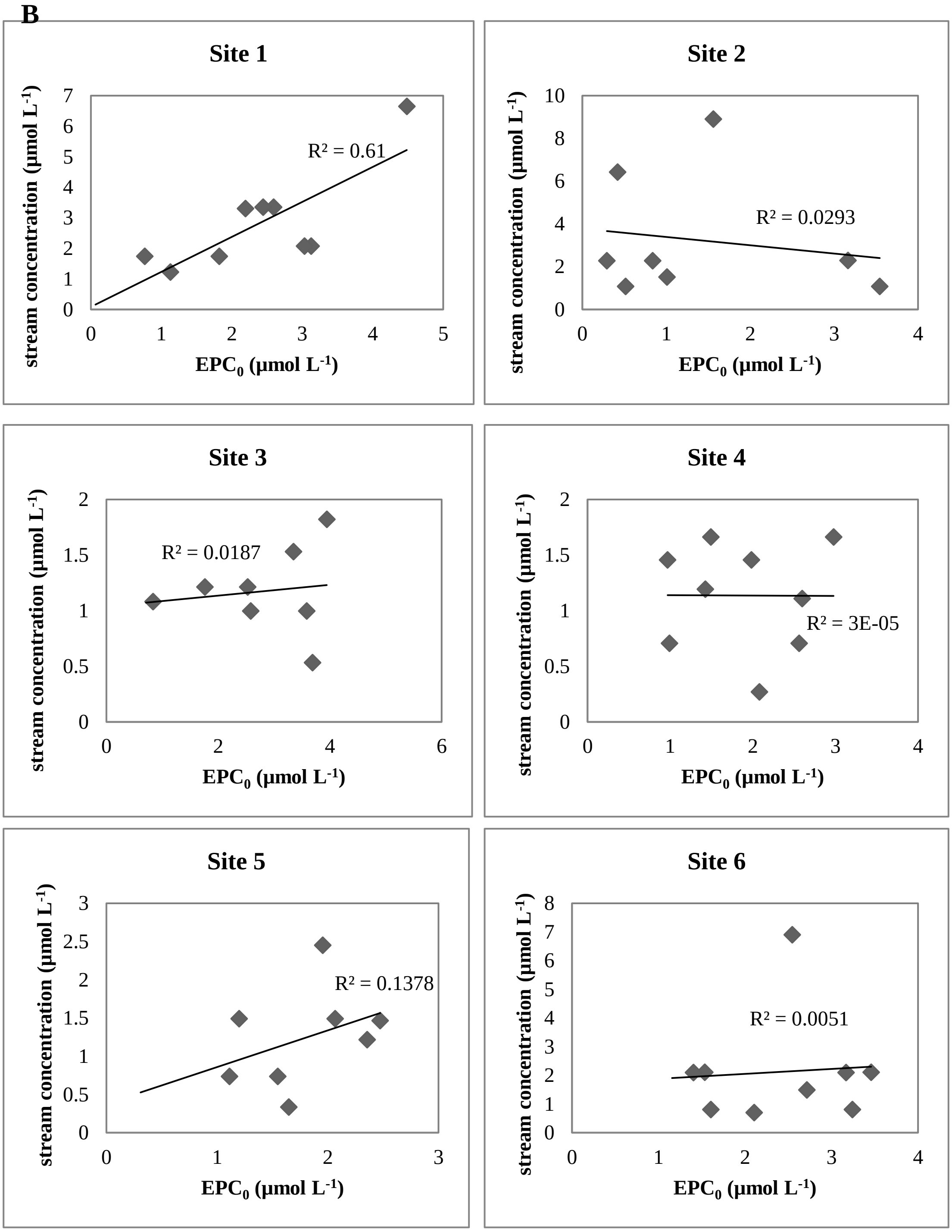
Appendix 3 Table 3 Suspended solids (mg L^{-1}) for each site (1-6) in Newby Beck+ and surface sampling period February- May 2016.

	Feb 2016	**Mar 2016**	**Apr 2016**	**May 2016**
site	Suspended Solids (µmol L^{-1})			
1	78.87	29.06	83.94	55.05
2	51.66	-	81.51	87.17
3	41.97	43.59	86.94	89.43
4	45.20	30.67	78.87	51.66
5	56.50	85.56	86.52	74.74
6	147.08	166.27	70.57	25.05

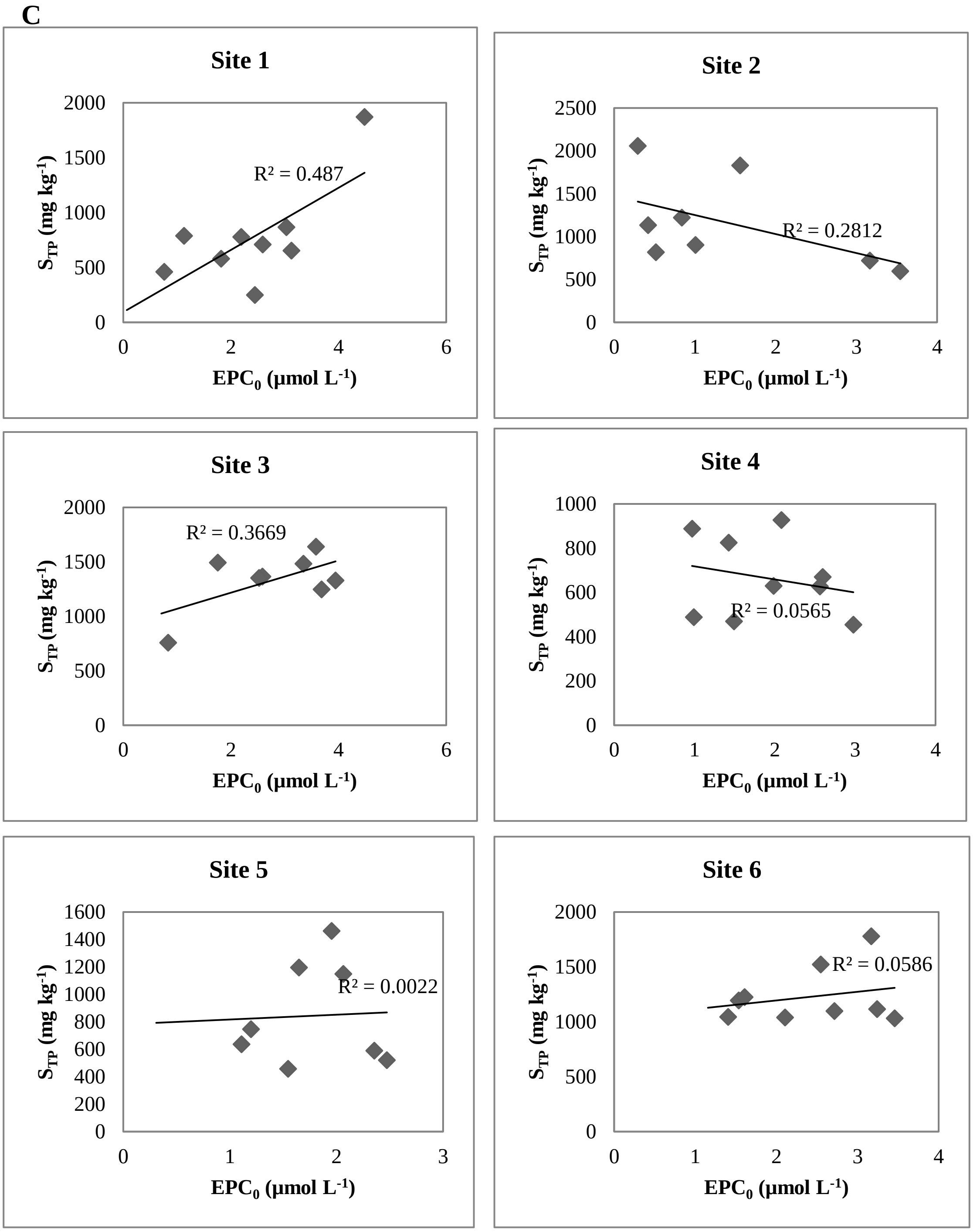
The following graphs explore the correlation between A) sediment total phosphorus (S_{TP} mg kg^{-1}) and stream concentration (µmol L^{-1}); B) equilibrium phosphorus concentration (EPC_0 µmol L^{-1}) and stream concentration (µmol L^{-1}); and C) sediment total phosphorus (S_{TP} mg kg^{-1}) and equilibrium phosphorus concentration (EPC_0 µmol L^{-1})for both surface and trap sediment samples.



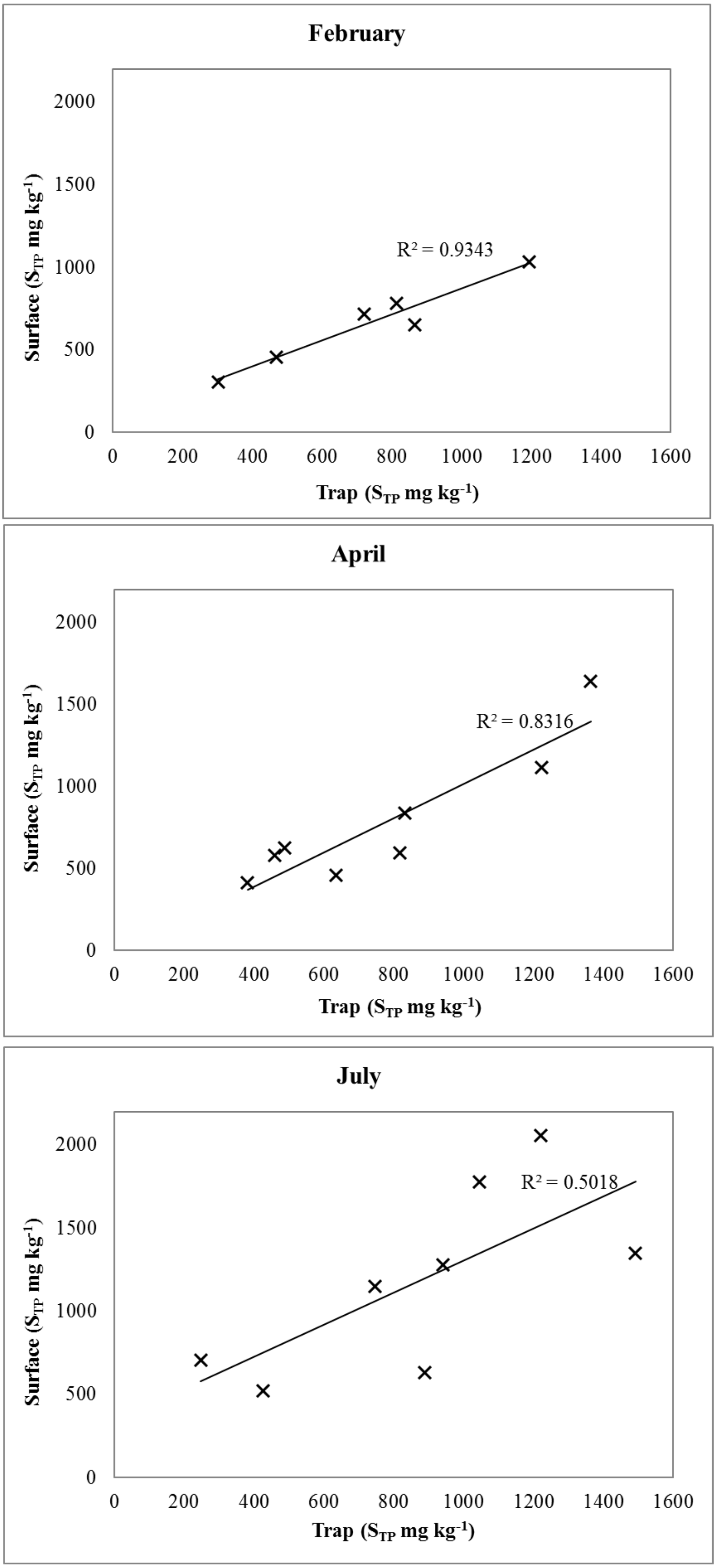
Appendix 3 Figure 11 Sediment total phosphorus (S_{TP} mg kg^{-1}) and stream concentration (µmol L^{-1}). Linear regression R^2 values reported.



Appendix 3 Figure 12 Equilibrium phosphorus concentration (EPC₀ µmol L^{-1}) and stream concentration (µmol L^{-1}). Linear regression R^2 values reported.



Appendix 3 Figure 13 Sediment total phosphorus (S_{TP} mg kg^{-1}) and equilibrium phosphorus concentration (EPC$_0$ µmol L^{-1}) for both surface and trap sediment samples. Linear regression R^2 values reported.



Appendix 3 Figure 14 Trap and surface sediment total phosphorus (S_{TP} mg kg^{-1}) for sampling months February, April and July 2016. Linear regression R^2 values reported.