Evaluating an ecosystem management approach for improving water quality on the Holnicote Estate, Exmoor.

Submitted by Miriam Glendell, to the University of Exeter as a thesis for the degree of Doctor of Philosophy by Research in Geography, July 2013.

I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

Abstract

The European Water Framework Directive 2000 established a new emphasis for the management of freshwaters by setting ecologically-based water quality targets that are to be achieved through holistic, catchment-scale, ecosystem management. However, significant knowledge gaps exist in the understanding of the cumulative effectiveness of multiple mitigation measures on a number of pollutants at a catchment scale. This research contributes to improved understanding of the effectiveness of an ecosystem management approach to deliver catchment-scale water quality improvements on the National Trust Holnicote Estate on Exmoor, UK.

This research is part of a larger multi-objective project funded by the UK Department for Environment, Food and Rural Affairs (Defra), to demonstrate the benefits of land use interventions for the management of flood risk. This thesis evaluates the effects of upland ditch blocking on physico-chemical and biological parameters of water quality in an upland Horner Water catchment one year after habitat restoration, and establishes a solid baseline for the monitoring of the effects of current and future land management changes in a lowland, intensively managed, agricultural Aller catchment.

The spatial variability of soil physical and chemical properties (bulk density, total carbon (TN), nitrogen (TN), C:N ratio, $\delta^{15}N$, total phosphorus (TP), inorganic phosphorus (IP), organic phosphorus (OP)) and water quality determinands (suspended sediment (SS), dissolved organic carbon (DOC), total particulate carbon (TPC), total oxidised nitrogen (TON) and dissolved reactive phosphorus (DRP)) in the two study catchments with contrasting land use has been characterised and linked to the prevailing land use. Agricultural land use resulted in extensive homogenisation of soil properties. The spatial dependence of all soil properties, except for bulk density and $\delta^{15}N$, was stronger in the agricultural than the semi-natural catchment (nugget:sill ratio 0.10-0.42 in the Aller and 0.15-0.94 in Horner Water), while bulk density, TP, inorganic phosphorus (IP), organic phosphorus (OP), C:N ratio, $\delta^{15}N$ and carbon storage showed a longer range of spatial auto-correlation in the agricultural catchment

(2,807-3,191 m in the Aller and 545-2,599 m Horner Water). The central tendency (mean, median) of all soil properties, except for IP and $\delta^{15}N$, also differed significantly between the two catchments ($P < 0.01$). The observed extensive alteration of soil physical and chemical properties in the agricultural catchment is likely to have long-term implications for the restoration of ecosystem functioning and water quality management.

The intensive land use seems to have resulted in an altered 'catchment metabolism', manifested in a proportionally greater total fluvial carbon (dissolved and particulate) export from the agricultural than the semi-natural catchment. The agricultural catchment supported significantly higher DOC concentrations ($P < 0.05$) and the quality of DOC differed markedly between the two study catchments. The prevalence of more humic, higher molecular weight compounds in the agricultural catchment and simpler, lower molecular weight compounds in the semi-natural catchment, indicated enhanced microbial turnover of fluvial DOC in the agricultural catchment as well as additional allochtonous terrestrial sources. During an eight month period for which a comparable continuous turbidity record was available, the estimated SS yields from the agricultural catchment (25.5-116.2 t km^2) were higher than from the semi-natural catchment (21.7-57.8 t km^2). Further, the agricultural catchment exported proportionally more TPC (0.51-2.59 kg mm^{-1}) than the semi-natural catchment (0.36-0.97 kg mm^{-1}) and a similar amount of DOC (0.26-0.52 kg mm^{-1} in the Aller and 0.24-0.32 kg mm^{-1} in Horner Water), when normalised by catchment area and total discharge, despite the lower total soil carbon pool, thus indicating an enhanced fluvial loss of sediment and carbon from the intensively managed catchment.

Whilst detection of catchment-scale effects of mitigation measures typically requires high resolution, resource-intensive, long term data sets, this research has found that simple approaches can be effective in bridging the gap between fine scale ecosystem functioning and catchment-scale processes. Here, the new macro-invertebrate index PSI (Proportion of Sediment-sensitive Invertebrates) has been shown to be more closely related to a physical measure of sedimentation (% fine bed sediment cover) ($P = 0.002$) than existing non-pressure specific macro-invertebrate metrics such as the Lotic Index for

Flow Evaluation (LIFE) and % *Ephemeroptera*, *Plecoptera* & *Trichoptera* abundance (% EPT) ($P = 0.014$). Further testing of PSI along a pronounced environmental gradient is recommended as PSI and % fine bed sediment cover have the potential to become a sensitive tool for the setting and monitoring of twin sedimentation targets.

Upland ditch management has not had any discernible effect on water quality in the semi-natural upland catchment one year after restoration, which may be due to the short-term post-restoration monitoring period but may also reflect benign effects of large-scale earth moving works on this high quality environment. The conceptual understanding of catchment processes developed in this thesis suggests that cumulatively, the recently completed mitigation works in the lowland agricultural catchment will likely result in reduced sediment and nutrient input into the aquatic environment. However, further research is needed to build on this detailed baseline characterisation and inform the understanding of the effectiveness of combined mitigation measures to reduce the flux of multiple contaminants at the catchment scale.

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Abbreviations

A	Aller
A7 – A13	Monitoring sites in Aller catchment
ANOVA	Analysis of Variance
BD	Soil bulk density
C	Carbon
C:N ratio	Carbon to nitrogen ratio
ECSFDI	England Catchment Sensitive Farming Delivery Initiative
DOC	Dissolved organic carbon
DRP	Dissolved reactive phosphorus
EU	Europen Union
EA	Environment Agency
Gt	Gigatonne = 10^{15} g
GLM	General linear model
H	Horner Water
H1 – H5	Monitoring sites in Horner Water catchment
HOST	Hydrology of Soil Types classification
IP	Inorganic phosphorus
LIFE	Lotic index for flow evaluation
min	Minute
ML	Megalitres = 10^6 litres
N	Nitrogen
NH_4^+-N	Ammonium
NNR	National Nature Reserve
NO_3^--N	Nitrate
NSRI	National Soil Research Institute
NTU	Nephelometric turbidity units
NVZ	Nitrate Vulnerable Zone
O:E	Environmental quality index (observed:expected ratio)
OECD	Organisation for Economic Cooperation and Development
OP	Organic phosphorus
P	Phosphorus
POC	Particulate organic carbon
PP	Particulate phosphorus
PSI	Proportion of sediment-sensitive invertebrates
Q	Discharge

SAC	Special Area of Conservation
SS	Total suspended sediment
SSSI	Site of Special Scientific Interest
t	Tonne
TOC	Total organic carbon
TON	Total oxidised nitrogen
TP	Total phosphorus
TPC	Total particulate carbon
WFD	European Union Water Framework Directive 2000
$\delta^{15}N$	Stable nitrogen isotope

Preface

"… people are integral parts of ecosystems and … a dynamic interaction exists between them and other parts of ecosystems, with the changing human condition driving, both directly and indirectly, changes in ecosystems and thereby causing changes in human well-being. At the same time, social, economic, and cultural factors unrelated to ecosystems alter the human condition, and many natural forces influence ecosystems… the actions people take that influence ecosystems result not just from concern about human well-being but also from considerations of the intrinsic value of species and ecosystems."

Millenium Ecosystem Assessment (2005, p. V.)

Chapter 1

INTRODUCTION

Both our wellbeing as individuals, and the material wealth of human society, depend critically upon the environment (UK NEA, 2011), yet increasing human population, rising expectations and changing diets are compromising the ability of Global ecosystems to sustain the needs of humans as well as those of other species (MEA, 2005). The rate of anthropogenic change to natural systems over the past 50 years is unparalleled in human history and it is estimated that approximately 60 % of ecosystem services are now being degraded or used unsustainably, including soils, fresh water and water purification (MEA, 2005). With the projected increase in human population, it is estimated that the global demand for food will rise by 70 % by 2050 (FAO, 2011). Satisfying this growing demand in a sustainable way in a changing climate is a major challenge for the governance of the world's natural resources.

The vast majority of global food production occurs under intensive agricultural regimes. As such, agriculture covers approximately 40 % of the land area of the Organisation for Economic Cooperation and Development (OECD) countries and thus has a significant effect on the environment. Whilst agricultural nutrient surpluses in OECD countries have declined and soil erosion has stabilised since the early 1990s, agriculture is still a significant source of diffuse water pollution (OECD, 2013). In the UK, agriculture covers approximately 70 % of the land area and agricultural intensification was a major driver of enhanced soil erosion, reduced soil quality, loss of biodiversity (UK NEA, 2011) and ecological impairment of water bodies (McGonigle et al., 2012) over the past 60 years.

In the UK, 30 % of ecosystem services are declining (UK NEA, 2011). While biodiversity underpins the functioning of all ecosystems (UK NEA, 2011), it continues to decline both nationally and globally (Lawton et al., 2010). Focussing biodiversity conservation efforts on management of small designated areas has not been successful in stemming the continued loss of species and habitats (Lawton et al., 2010) and a broader holistic approach to the management of multi-functional landscapes with the involvement of local stakeholders is called for to deliver the full range of ecosystem services (UK NEA, 2011).

Global awareness and development of a holistic ‘ecosystem management’ approach that combines the understanding of both natural and social factors to address environmental problems can be traced back to the Earth Summits 1992-2002 and the Convention on Biological Diversity 1992 (Hering et al., 2010). Water is a critical resource that underpins all ecosystem functions and social and economic activities (WWAP, 2012) and catchments provide a natural focus for the new integrated ‘ecosystem management’ approach to deliver the full range of ecosystem services. In Europe, EU environmental legislation has been a major driver behind the development of national environmental policies and environmental improvement (UK NEA, 2011). As an ambitious piece of environmental legislation, the EU Water Framework Directive (WFD) 2000 brought a new emphasis on holistic landscape-scale management of freshwater systems by including ecologically-based water quality outcomes, coupled with a requirement for the involvement of all stakeholders and the consideration of economic costs in the development of integrated solutions.

However, while intuitively correct and conceptually clear, the practical implementation of the WFD goals represents a great challenge (Page et al., 2012). The emphasis on ecologically relevant, basin-scale assessment of water quality poses a significant challenge to both the scientific community and the legislative bodies that enforce the WFD, in terms of translating detailed process-based understanding of single pollutants at often small scales to an integrated understanding of multiple pollutant responses to a combination of mitigation measures at a catchment scale (Haygarth et al., 2013). This up-scaling requires a multi-disciplinary approach, involving both natural and social scientists as well as the policy community (McGonigle et al., 2012, Neal and Heathwaite, 2005).

Catchments are complex systems, not easily conducive to the requirements of rigorous experimental design and replication (Haygarth et al., 2013), with many unknown and ‘un-knowable’ uncertainties (Harris and Heathwaite, 2012, Page et al., 2012). However, whilst acknowledging this uncertainty, policy demands practical ‘no-regret’ solutions to complex problems, often in a short time-scale (Jordan et al., 2012a, McGonigle et al., 2012). For example, whilst linking nutrient impact with ecological status in a quantitative manner is a huge challenge (Neal and Heathwaite, 2005), farmers and regulators need simple and easy metrics to monitor and assess the environmental impact of agriculture on soil and water quality (McGonigle et al., 2012).

Neal and Heathwaite (2005) identified many fundamental questions that need to be answered to secure sustainable management of freshwaters. These include:

- How do freshwater systems function on a catchment and basin scale?
- How do small-scale measures scale-up in large systems?
- How do we define ‘good ecological status’?
- What do we need to do to improve our detection, understanding and mitigation of diffuse pollution and its impact on ecosystem function?
- What are the impacts from anthropogenic activities on ecosystem health?

This thesis aims to address some of these questions. It takes a multi-pollutant approach to the evaluation of the cumulative effectiveness of mitigation measures to deliver water quality improvements. The research is undertaken at nested scales – the catchment and sub-catchment scale, across two contrasting catchments in the south-west of the UK.

Thesis structure

Chapter 2 provides a literature review of the current understanding of the effectiveness of an ecosystem management approach to deliver water quality objectives. The four results chapters 3-6 are structured as self-standing papers, two of which have been submitted to international journals; *Geoderma* (Chapter 3) and *Freshwater Biology* (Chapter 5) and the other two are in preparation for submission to *Science of the Total Environment* (Chapter 4) and *Journal of Environmental Management* (Chapter 6). Baseline land use, soils and water quality in the two contrasting study catchments are characterised in Chapter 3, which also examines the long-term effects of agricultural land use on the spatial variability of soil properties and the implications for potential legacy effects. Chapter 4 quantifies the fluvial loss of organic carbon from the two contrasting study catchments and raises the question about the implications of enhanced fluvial carbon loss for the ecological status of freshwaters and the global carbon cycle. Chapter 5 tests the sensitivity of a new macro-invertebrate index as a simple tool for the evaluation of sedimentation impacts in freshwater ecosystems, while Chapter 6 establishes a baseline understanding of the structure and function of the two catchments and discusses both the observed and potential implications of multiple mitigation measures on water quality at two nested scales within the two study catchments. Chapter 7 offers a synthesis of all research findings. Figures and Tables are numbered consecutively as mentioned in the text, including those presented in the Appendices.

Chapter 2

A REVIEW OF CURRENT ECOSYSTEM MANAGEMENT APPROACHES TO DELIVER WATER QUALITY OBJECTIVES

I. INTRODUCTION

Excessive nutrient loading of surface waters has been identified as a major cause of biodiversity loss and ecosystem degradation worldwide (MEA, 2005), including impacts on freshwater environments from increased inputs of sediment, phosphorus (P), nitrogen (N), faecal micro-organisms and dissolved organic carbon (DOC) into freshwater systems due to agricultural intensification over the past decades. While the role of increased P and N input into freshwater ecosystems in causing eutrophication is well documented (Powlson, 1998, Pierzynski et al., 2000, Jordan et al., 2005, Page et al., 2005, Haygarth et al., 2006, Leira et al., 2006, Silgram et al., 2006, Jarvie et al., 2012, Wall et al., 2012), the reliance of modern agriculture on finite resources of inorganic fertilisers is a major cause for concern (Haygarth et al., 2013). In a world of increasing human population, changing climate and diminishing natural resources, the issue of food security delivered through sustainable agricultural practices is ever more pressing (Dungait et al., 2012, Jarvie et al., 2012). Paradoxically, the damage inflicted on surface waters and soil health due to intensive agriculture may result in declining food productivity.

II. LEGISLATIVE BACKGROUND

The significant progress in reducing point source water pollution over the past decades (Hamilton, 2012) made the abatement of diffuse pollution from agriculture even more important (Oliver et al., 2007, Ockenden et al., 2012). Agriculture is responsible for approximately 55 % of non-point source pollution of eutrophic surface waters in the European Union (EU) (Buckley and Carney, 2013). In the UK agriculture covers about 70% of the land area and contributes around 55% of nitrates, 20% of P and 75% of sediment into the riverine environment (McGonigle et al., 2012).

A. EU Nitrates Directive

As one of the earliest pieces of EU legislation aimed at improving water quality (Buckley, 2012), the EU Nitrates Directive 91/676/EEC aims to reduce water pollution by N and P from agricultural sources and prevent such pollution occurring in the future. More than half of England has been identified at risk from increased nitrate loading from agricultural sources (Environment Agency, 2012). Nitrate Vulnerable Zones (NVZs) were first designated in 1996, covering 8% of England (Worrall et al., 2009) and were later extended in 2009 to cover 70 % of the land area (Cardenas et al., 2011). Within these areas, farmers are required to follow a programme of measures which include restricting the timing and application of fertilizers and manure, and keeping of accurate records. Reduction of stocking rates and grazing time were found to be the most cost-effective measures to reduce nitrate leaching across all farming systems, followed by measures that involve improvements in fertiliser and crop management (Cardenas et al., 2011). An assessment of the effectiveness of NVZs to deliver surface water improvements over a 12-15 year period has found that while 29 % of NVZs have improved, as compared to a control catchment outside NVZs, 31 % got worse (Worrall et al., 2009). Reviewing available evidence, Johnson et al. (2011) found that NVZs have not significantly reduced nitrate concentrations in surface waters in England and Wales, with some limited improvements observed in smaller livestock-dominated catchments with high manure inputs. While Worrall et al. (2009) concluded that reliance on the reduction of N inputs as a sole control measure may not be sufficient to secure desired water quality improvements, it may also be argued that long term ‘legacy effects’ may be responsible for the variable response between catchments and that policy expectations may have to be adjusted accordingly (Hamilton, 2012).

In Ireland, the Nitrates Directive has been implemented uniformly on a whole territory basis. Although this approach has been subject to criticism, as it does not allow tailoring of regulations to prevailing soil and hydrological conditions (Buckley, 2012), it does potentially allow for modification of farming practices over a larger geographical extent. Recent modelling of likely response times of a variety of Irish aquifers shows that improvements of groundwater nitrate concentrations can be expected within one to two decades from the start of implementation (Fenton et al., 2011).

A well documented extensive programme to combat diffuse water pollution by nitrogen has been implemented in Denmark since the late 1980s (Windolf et al., 2012). Following a reduction in N inputs, eight out of the 10 study catchments monitored between the period 1990-2009 have shown a significant reduction of the diffuse N loads, the majority in less than 5 years, with just two catchments showing a delay in response due to retention of nitrate in groundwater aquifers (Windolf et al., 2012). On the whole, the programme has been deemed successful, with a caveat that the reduction of nitrate loads in groundwater dominated catchments is likely to take longer and incur higher costs than in surface water dominated areas (Windolf et al., 2012).

B. EU Water Framework Directive

The EU Water Framework Directive (WFD) adopted in 2000 signalled a substantial change to water management in Europe (Martin-Ortega, 2012). The Directive aims to prevent further deterioration, promote sustainable water use and enhance the protection of the aquatic environment (Collins and McGonigle, 2008). It requires member states to restore watercourses to 'Good Ecological Condition' by 2015. Economic tools to determine the most 'cost-effective' measures and evaluate 'disproportionate' costs are key to the delivery of the Directives' objectives (Martin-Ortega, 2012), as is a new emphasis on catchment-wide management of water resources (Hutchins et al., 2009) and the involvement of all stakeholders.

However, the 'reference conditions' to which rivers should be restored are still a subject of debate, and further integrated interdisciplinary research is needed to clarify the links between geomorphology, hydromorphology and ecological responses in order to gain a better understanding of links between habitat form, biodiversity and ecosystem function (Newson and Large, 2006). While the exact direction and magnitude of the climate change impact on catchment hydrology is uncertain (Prudhomme et al., 2012), in Britain, it is likely to result in decreased summer flows (Prudhomme et al., 2012) and an increased incidence of extreme hydrological events (Whitehead et al., 2009). How these changes will affect the fluxes of macronutrients and their biogeochemical responses (Jarvie et al., 2012), as well as freshwater biota (Wilby et al., 2010), is still uncertain, making the definition of future optimum ecological condition and setting of relevant targets even more difficult (Whitehead et al., 2009).

Significant gaps in the understanding of quantitative links between the chemical parameters of water quality and their effects on freshwater ecology (Walling et al., 2007) give rise to questions over the relevance of water quality targets based on mean monthly pollutant concentrations, originally designed for the control of point source pollution (Mainstone et al., 2008). The temporal mismatch between the time of the highest risk of sediment and P delivery in autumn and winter and the ecologically active season further complicates the setting of relevant targets (Wall et al., 2011). Therefore, new approaches to target setting may be needed, as suggested by Bilotta and Brazier (2008) and explored in Chapter 5 of this Thesis.

Only 27 % of water bodies in England and Wales are currently in ‘good’ ecological status as defined by the EU Water Framework Directive (McGonigle et al., 2012) and the achievement of the WFD targets will require continued significant effort on the part of the Government, regulatory agencies, industry and the voluntary sector, along the full continuum from source, through pollutant mobilisation, to delivery and final impact on the aquatic environment (Haygarth et al., 2005a).

C. Adoption of mitigation measures

Adoption of diffuse water pollution mitigation measures by land managers at a sufficient scale is critical to the success of any National Action Plan. The policy levers available to policy-makers to encourage the uptake of mitigation measures range from baseline regulation, through voluntary initiatives to economic incentives such as agri-environment schemes and payment for ecosystem services (Fig. 2.1) (McGonigle et al., 2012).

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Fig. 2.1 Delivery mechanisms available to policy makers for measures to address diffuse water pollution from agriculture. Source: McGonigle, Harris et al. (2012)

The willingness of farmers to adopt voluntary measures depends on the degree to which they interfere with agricultural production, including the 'nuisance effect' and the cost involved (Buckley et al., 2012). Experimental approaches to support payment for ecosystem services trialled by the West-country Rivers Trust in the West of England (for example) found that whilst three quarters of farmers expressed an interest in the scheme, the long-term nature of the agreement to secure 'permanent' protection of water resources for 999 years was a major impediment (Smith et al., 2012). In an Irish study, the lack of scientific evidence to underpin the expected outcomes of land use changes was perceived as a major obstacle to the uptake of mitigation measures by some farmers (Buckley, 2012) and supports the continued need for targeted dissemination of available information (Buckley and Carney, 2013) and for better evidence (Bergfur et al., 2012).

A succession of national voluntary schemes that could help to deliver WFD objectives has been implemented in England and Wales over the past decade. While Kay (2009) found little scientific evidence of the effectiveness of mitigation measures available under the UK agri-environment schemes, the evaluation of the first five years of the England Catchment Sensitive Farming Delivery Initiative (ECSFDI) introduced in 2008 found that pollutant loadings were likely to have decreased by 5-10 % across the target areas to May 2010, although these predictions are uncertain due to the complex nature of catchment systems and the high cost of detailed monitoring programmes (CSF Evidence Team, 2011). However, so far, there is no sign of ecological improvement from within the Priority Catchments targeted by the ECSFDI (CSF Evidence Team, 2011). In 2009 River Basin Management Plans were drawn up for 11 River Basin Districts to deliver the WFD objective of 'Good Ecological Status' by 2015. These are currently being replaced with catchment-specific management plans for all 100 catchments in England and Wales, to be drawn up in wider cooperation with all stakeholders through a 'Catchment Based Approach' (CABA) initiative (Defra, 2012) to support the preparation of the 2nd cycle of River Basin Management Plans (Fig 2.2).

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Fig 2.2 Initial pilot programmes that informed the wider implementation of the 'Catchment Based Approach' across England, launched on 3rd June 2013, which aims to develop catchment-specific management plans to deliver the WFD objectives with the involvement of all stakeholders.

In New Zealand, where diffuse pollution mitigation relies on voluntary participation of farmers, a ‘toolbox’ approach allowing farmers to choose from a suite of mitigation options was seen as a positive way forward (Monaghan et al., 2009). Despite the fact that in New Zealand, diffuse water pollution from agriculture is perceived as the largest environmental issue, the control of diffuse water pollution to date has been largely based on voluntary agreements with farmers and the dairy industry (Monaghan et al., 2009, Howard-Williams et al., 2010). Although, according to industry sources, the ‘Dairying and Clean Stream Accord’ has achieved some notable improvements to farming practices (Howard-Williams et al., 2010), strengthening of the regulatory and institutional framework is still needed to secure the necessary improvements to water quality (MacDonald et al., 2004).

In the USA, the Clean Water Act 1987 enabled measures to address diffuse water pollution from agriculture, however implementation powers were delegated to individual states and have since mostly relied on non-regulatory approaches, which have secured only very slow progress in the remediation of impaired water bodies suffering from diffuse water pollution (Weitman, 2010). Whilst regulatory approaches may be seen as a better way of securing necessary environmental improvements, they may reduce farmer cooperation (Sharpley et al., 2009), which may in turn impede the implementation of best management practices at a minimal ‘threshold’ extent needed to improve stream ecosystems within a catchment (Yates et al., 2007).

Clearly, a combination of regulation and economic incentives is necessary for successful implementation of diffuse pollution mitigation measures at a national scale (McGonigle et al., 2012), coupled with scientifically robust monitoring (or modelling) of outcomes (Bergfur et al., 2012). Whilst some notable advances have been made in addressing diffuse water pollution in some areas, in most countries stronger regulation and further incentives are still needed to deliver the step-change required to deliver the current policy expectations.

D. Cost effective delivery

The Water Framework Directive is the first piece of EU environmental legislation that explicitly involves economic valuation in the delivery of its objectives (Balana et al., 2011), as it requires the EU member states to identify cost-effective measures to deliver Good Ecological Status. An evolution in the approach to the evaluation of the cost-effectiveness of mitigation measures over the past decade can be seen in the series of reports commissioned by Defra in England (Balana et al., 2011) that evolved from a “pollutant-centric” approach that focussed on individual pollutants, through a “measure-centric” approach that focussed on individual measures, to a combined approach of evaluating the effectiveness of multiple mitigation measures on a suite of pollutants (Cuttle et al., 2007).

While cost-effectiveness should be measured against a criterion that is most important in terms of ecological impact, this is hindered by the significant gaps that still exist in the understanding of linkages between the chemical and biological dynamics of aquatic systems (Hutchins et al., 2009). The cost effectiveness of adopted measures depends on the geographical location of where the improvements to water quality within a catchment will be assessed due to spatial variability in pollutant concentrations (Hutchins et al., 2009). The ranking of the cost effectiveness of mitigation measures is also affected by the selection of the chemical water quality criterion which is being evaluated (Hutchins et al., 2009) as well as a lack of quantitative evidence of the effectiveness of individual and combined mitigation measures at a catchment scale (Haygarth et al., 2009). Haygarth et al. (2009) found that while reducing actual agricultural inputs was the most cost effective way of reducing diffuse P pollution; the cost of ‘end-of-pipe’ solutions to prevent diffuse P transport, such as buffer strips and constructed wetlands, was also relatively modest in relation to the P reduction achieved.

Balana et al. (2011) reviewed several studies across the EU member states that evaluated the cost effectiveness of their delivery programmes. They found that most studies to date were limited by their scope, as they were based on the evaluation of model farms and thus did not reflect the full heterogeneity of the farming enterprises and usually focussed on a single mitigation measure or a single pollutant. Further, the cost analysis was typically based on the agricultural sector alone, without considering external and transactional costs, did not consider the co-benefits brought about by management changes and did not account for the uncertainty in the model prediction of either effects or costs. Hence, whilst a lot of progress has been made to date in the evaluation of the cost-effectiveness of diffuse water pollution mitigation measures, significant gaps still remain.

III. ENVIRONMENTAL IMPACT

A. Macronutrients

In natural ecosystems, C, P and N cycles are coupled through the cycling of soil organic matter (Dungait et al., 2012). However, in agricultural ecosystems, these cycles become de-coupled due to plentiful supply of soluble bio-available inorganic nutrients (Dungait et al., 2012). The excess additions of inorganic fertilisers have led to reduced nutrient use efficiency (Jarvie et al., 2012) and it is estimated that only approx. 30 % of P and 50 % of N applied to agricultural land is taken up by the crops, with the rest either retained in the soil or lost to the atmosphere and the aquatic environment (Dungait et al., 2012). Both P and N can be limiting nutrients in natural ecosystems. While N limitation generally increases downstream, P limitation is greatest in the headwaters (Whitehead and Crossman, 2012). However, in agricultural systems this balance has been altered, with consequences for drinking water quality, eutrophication and biodiversity (Whitehead and Crossman, 2012). Therefore, a better understanding of the links between macronutrient cycles in agricultural systems is needed to enable more efficient use of mineral fertilisers, better use of waste nutrients and exploitation of the accumulated nutrient reserves in the soil in order to deliver sustainable solutions to multiple challenges facing future agriculture (Dungait et al., 2012).

In natural systems, P is derived from the weathering of sedimentary deposits with a residence time of 100 My, while N is mainly sourced from biological N fixation and atmospheric deposition (Schlesinger, 1997). Anthropogenic activities have increased the global N cycle by 100 % and the P cycle by 400 % (Whitehead and Crossman, 2012), thus in altered ecosystems, P budgets are dominated by point source inputs and diffuse pollution from agriculture, while N is mostly sourced from agriculture and atmospheric deposition (Whitehead and Crossman, 2012).

Phosphorus is transported from soils to surface waters in two major forms: as dissolved (molybdate) reactive P (DRP) – readily available for algal uptake, and as particulate P (PP). Soil P saturation may increase relatively fast if the soil is poor in Al and Fe oxides (the major P-binding components in non-calcareous soils), resulting in increasing P losses to water bodies (Schlesinger, 1997). Phosphorus is most available to plants in a dissolved form at neutral pH of about 7, in acid soils P tends to be precipitated into an occluded form in Al and Fe oxides, whilst in base rich soils it tends to bind with Ca (Schlesinger, 1997). The presence of organic acids such as humic acids reduces the occlusion of P through preferential binding of Al and Fe cations (Schlesinger, 1997).

Nitrogen and carbon cycles are closely linked, from the cellular biochemistry to the global biogeochemical cycles (Schlesinger, 1997). Nitrogen is contained in proteins and is thus an essential constituent of living tissue. Nitrogen fixation, as well as denitrification requires a carbon substrate as a source of energy. Soil organic matter is the main store of N in the soil (Dungait et al., 2012) and C:N ratio is an important factor in determining the rate of decomposition of soil organic matter and hence the turnover rate of these nutrients (Schlesinger, 1997). Thus soil organic matter has a critical role in the turnover of nutrients and the regulation of soil physical, chemical and biological properties (Brady and Weil, 1999, Dungait et al., 2012).

Agricultural practices such as cropping and nutrient addition have increased the turnover and altered the composition of soil organic matter, with negative consequences for soil physical and chemical properties (Brady and Weil, 1999), nutrient retention (Kuzyakov et al., 2000, Bol et al., 2008) and carbon storage (Lal, 2002). Agriculture also alters the spatial heterogeneity of soil properties (Paz-Gonzalez et al., 2000). While the consequences of these alterations for biodiversity have been addressed (Ettema and Wardle, 2002, Gilliam and Dick, 2010), Chapter 3 examines these changes in relation to the estimation of soil carbon stocks and the implications for water quality.

The fluvial export of total organic carbon (TOC) (composed of dissolved (DOC) and particulate (POC) fractions) plays an important, yet often overlooked role in the loss of carbon from catchment systems (Evans et al., 2012). Increasing DOC concentrations over the past decades have been reported in rivers across Western Europe and North America (Evans et al., 2005). While the causes of these increased concentrations are still subject to debate (Whitehead and Crossman, 2012), their consequences for the ecological status of aquatic ecosystems are poorly understood (Evans et al., 2005, Stanley et al., 2011).

Until recently, research on the total export of organic carbon (dissolved and particulate) from agricultural catchments has been rare. While the results of studies of the impact of agricultural land use on fluvial dissolved organic carbon export to date are ambiguous, the ecological consequences of altered DOC dynamics are likely to be significant (Stanley et al., 2011). Therefore, Chapter 4 examines the controls on the total fluvial export of sediment, dissolved organic and particulate carbon in an agricultural and semi-natural catchment to elucidate the effect of agricultural land use on the fluvial carbon export at a catchment scale.

By comparison, research focused on the DOC dynamics in peatlands has been much greater, on account of their importance as significant stores of terrestrial carbon (Billett et al., 2012) and the high cost implications of increased DOC concentrations and water colour to the water treatment industry (Worrall et al., 2007). Increasing DOC concentrations have been reported in rivers in Western Europe and North America over the past decades (Evans et al., 2005). In the UK, the dissolved organic carbon concentrations have almost doubled relative to 1988-1993 means (Evans et al., 2005), likely to be caused by multiple factors, including recovery from acid deposition (Evans et al., 2005), response to increasing temperatures and/or rising CO_2 concentrations (Worrall and Burt, 2007), increasing frequency of severe droughts (Worrall et al., 2004), changes in hydrology and land-use change (Worrall et al., 2004). Draining of peatlands to improve agricultural production is thought to have contributed to the observed increased DOC concentrations (Worrall et al., 2007) and the conservation effort to remediate this via upland ditch blocking is ongoing (Grand-Clement et al., 2013).

B. Sediment

Since the onset of agriculture, human activities have accelerated soil erosion rates 10- to 100- fold above all estimated natural background levels (Montgomery, 2007a), resulting in an increased input of fine sediment and organic carbon into aquatic environments. Sedimentation is acknowledged as a major cause of river impairment and water quality problems worldwide (Wood et al., 2005b, Larsen et al., 2011, Bilotta et al., 2012). The impact of sedimentation on aquatic biota has been well documented (Wood and Armitage, 1997, Bilotta and Brazier, 2008, Kefford et al., 2010, Jones et al., 2012). The effects of sedimentation range from a reduction in overall invertebrate trait diversity (Larsen and Ormerod, 2010a), to increased drift (Larsen and Ormerod, 2010b), reduced invertebrate abundance (Larsen et al., 2011), density (Angradi, 1999, Lenat et al., 1981, Matthaei et al., 2006), biomass (Angradi, 1999), taxon richness (Matthaei et al., 2006) and changed community structure (Lenat et al., 1981, Wood and Armitage, 1999). In addition to direct ecological effects through reduced water transparency, smothering of substrate and blocking of substrate interstices (Ellis, 1936, Wood and Armitage, 1997), sediment is also responsible for the transport of a range of other contaminants such as pesticides (Owens et al., 2001, Warren et al., 2003), metals (Owens et al., 2001, Horowitz et al., 2012), pathogens (Tyrrel and Quinton, 2003), radionuclides (Owens et al., 2005), organic pollutants (Walling et al., 1997, Owens et al., 2007) and nutrients (Brazier et al., 2007, Hamilton, 2012).

While a range of water column and substrate sedimentation metrics have been proposed internationally as sedimentation targets (Collins et al., 2011), setting meaningful water quality thresholds has proven problematic due to limited quantitative understanding of the relationship between fine sediment delivery and the resultant ecological impacts (Walling et al., 2007, Larsen et al., 2011), as well as spatial variability in different types of surface waters.

It is widely recognised that the current guideline suspended sediment target of 25 mg L^{-1} informing the delivery of the EU Water Framework Directive (2000/60/EC) is not specific enough for the Directive's aim to restore watercourses to 'good ecological status' in a broad range of aquatic ecosystems found across Europe (Walling et al., 2007, Bilotta and Brazier, 2008, Cooper et al., 2008, Jones et al., 2012, Bilotta et al., 2012). As aquatic biota respond not only to the concentration of suspended sediment and other contaminants but also to duration (Newcombe and Macdonald, 1991), intensity and return period of incidents of exposure to sediment (UK TAG, 2008), as well as the sediment quality (Stutter et al., 2007), it has been proposed that more complex, site specific standards that consider timing and duration of sediment transfer events as well as their return period need to be developed (Bilotta and Brazier, 2008, Collins and Anthony, 2008, UK TAG, 2008). The development of modelling toolkits that couple sediment regimes with biological response for a range of biota has also been proposed (Collins et al., 2011). However, it can be argued that as many documented impacts of sedimentation on aquatic biota are related to sediment deposition on the river bed, a management target based on suspended sediment concentration, however complex, may not be meaningful to describe ecological status (Kefford et al., 2010, Jones et al., 2012).

Many ecosystems, including freshwaters, are vulnerable to a simultaneous impact of multiple-stressors (Ormerod et al., 2010, Matthaei et al., 2010), which can result in unexpected ecological effects due to complex interactions between multiple stressors and aquatic ecology (Townsend et al., 2008). The variety of interactions between sediment and other stressors, such as low flows (Matthaei et al., 2010) and nutrient enrichment (Townsend et al., 2008, Wagenhoff et al., 2011, Wagenhoff et al., 2012), further complicates the setting of water quality targets at different levels of these interacting pressures (Townsend et al., 2008). Therefore, several authors emphasise the need for the development of tools that would distinguish between multiple causes of river impairment at any one location (Matthaei et al., 2006, Townsend et al., 2008, Clews and Ormerod, 2009). Chapter 5 examines the utility of one of these new tools, a macro-invertebrate index PSI for setting of water quality sedimentation targets by examining the relationship between physical measures of sedimentation and the macro-invertebrate index.

C. Land use impacts and delivery pathways

Land use has a profound effect on the state of the aquatic environment. It affects sediment and nutrients along the full lengths of the source-mobilisation-delivery-impact continuum (Haygarth et al., 2005a) from the terrestrial to the aquatic environment. Even small increases in "high impact" land use such as arable cropping in sensitive watersheds may have significant effects on the ecological status of freshwater systems (Feld, 2013) and sediment yields (Yan et al., 2013). In a Scottish study, land-use in the immediate sub-catchment of a large watershed was found to be much more significant for water quality than the larger catchment area, while the proportion of intensive grassland within each sub-catchment was the best predictor of most ecological and chemical properties (Stutter et al., 2007). Similarly, in south-west England, Intensively managed grasslands, previously thought off as pollutant buffers, were shown to be more significant sources of P enrichment to surface waters than previously thought (Bilotta, 2008). Conversely, an increasing proportion of forest in the riparian zone appears to mitigate some of the negative effects of intensive land use (Feld, 2013, Yan et al., 2013).

Unsympathetic management practices such as excessive livestock densities and grazing of saturated land, may lead to the exposure of bare soil and soil compaction, which result in the alteration of soil physical properties and increased suspended sediment (SS) and P runoff (Bilotta et al., 2007). Intensive grass production tends to produce the highest losses of DRP whilst arable farming on erodible soils results in large losses of PP (Doody et al., 2012). Recent studies highlight the previously neglected contribution of intensively managed grasslands to sediment delivery and nutrient enrichment of watercourses. This is attributed to two previously overlooked but important factors in the processes of sediment delivery from intensively managed grasslands: a) an arbitrary threshold of 0.45 μm to distinguish between dissolved particles and suspended solids and b) P transport associated with fine colloidal material and the organic fraction of material contained within runoff (Brazier et al., 2007, Bilotta et al., 2008).

The diversity of potential pathways and their relative importance complicates the targeting of water quality mitigation measures at a catchment scale (Wall et al., 2012). As P is readily bound on the surface of soil particles, it is primarily transported through overland and shallow sub-surface flow. Conversely, the high solubility of nitrate means that it is mostly transported through the soil into groundwater and then to surface waters via sub-surface pathways (Wall et al., 2011, Hamilton, 2012). However, groundwater can also be a significant, and previously overlooked, source of DRP (Stutter et al., 2006, Holman et al., 2008), particularly in groundwater dominated catchments with high soil P saturation (Hamilton, 2012).

Comparison of the relative contribution of surface versus subsurface drain pathways found that drains act as preferential hydrological pathways for SS, P and DOC export (Russell et al., 2001, Evans et al., 2006, Deasy, 2007, Deasy et al., 2008, Dalzell et al., 2011). However, more recent work suggests that the presence of subsurface drainage may actually reduce the total export of SS and P from intensively managed grasslands due to reduced occurrence of infiltration excess overland flow (Bilotta et al., 2008). In arable situations, tramlines were shown to be a dominant pathway for surface runoff, enhancing sediment and P transport to the field edge (Silgram et al., 2006, Deasy et al., 2010) and potentially to water courses. Therefore, a conceptual understanding of the catchment hydrology and potential pathways, as discussed in Chapters 4 and 6, is necessary for the design and evaluation of effective pollution abatement strategies (Soulsby et al., 2002).

D. Critical Source Areas

The concept of Critical Source Areas (CSA), particularly in relation to P, has been studied since the mid 1990s (Sharpley et al., 2010). Unlike N losses, which tend to be geographically more widespread, occurring from a large catchment area, Critical Source Areas for P loss are typically spatially discrete (Sharpley et al., 2009), encompassing both enhanced soil nutrient sources and their hydrological connectivity to the receiving waters. In catchments where diffuse sources predominate, P transfers are generally positively related to discharge and catchment flashiness, demonstrating the preferential transport of

P from Critical Source Areas via surface and shallow sub-surface pathways (Jordan et al., 2012b). However, while the identification of areas with high soil P content is feasible, the characterisation of hydrological connectivity of transport processes remains elusive (Sharpley et al., 2010). Jordan et al. (2012b) have shown that a coupled understanding of both high risk source areas and the catchment hydrological connectivity is critical in the assessment of pollution risk. Page et al. (2005) explored the possibility of identifying likely Critical Source Areas (CSA) of phosphorus to inform catchment-wide mitigation strategies on the basis of topographic index based stratified soil P sampling, which represents the propensity of any point to become saturated and act as a source area for surface runoff. However, they found that soil P status showed a high spatial variability and was governed by multiple factors such as land use and field boundaries. The topographic index alone cannot therefore be used to estimate spatial patterns of soil P status and high soil P measurements do not necessarily indicate a CSA, hence more complex approaches that combine land use, soil nutrient status and a conceptual understanding of catchment hydrology are needed to get a better understanding of potential contributing areas of nutrients (Yates et al., 2013, Mellander et al., 2012).

Due to the complexity of Critical Source Area identification at a catchment scale, the linkages between their management and water quality benefits are still unknown (Sharpley et al., 2010). Jordan et al. (2012b) found that the effective reduction of P delivery to surface waters at a catchment scale will need to consider management of high source/risk areas in the context of the overall catchment hydrological response. In future, new technologies such as high resolution digital elevation models (DEM) derived from LIDAR measurements, may offer a promising tool for the characterisation of CSA at a catchment scale (Sharpley et al., 2010), although less topographic detail may be adequate to predict connectivity at a sub-catchment scale (Shore et al., 2013) and "soil type may be a useful proxy for connectivity in sub-catchments where these attributes are correlated" (Shore et al., 2013, p.12). A recently developed 'Sensitive Catchment Integrated Modelling and Analysis Platform' (SCIMAP) combines risk-based assessment of hydrological connectivity with likely diffuse pollution sources to identify the relative highest risk areas within a catchment, using only soil erodibility and the likelihoold that it will be delivered to the watercourse as the most basic processes sufficient to link risk with ecological impact (Reaney et al., 2011). However, Reaney et al. (2011) also show that *a priori* judgment of certain land uses as 'high risk' may not be ecologically most relevant and suggest a Bayesian approach of 'inverse modelling' to allow biological data to inform the understanding of the links between the ecological impact and ranking of pollution risk from different types of land uses (Reaney et al., 2011). The application of such an inverse modelling approach to chemical water quality data across 7,000 observation sites across England and Wales found that, while low impact land uses could be identified with more certainty, high impact land uses were not consistent between all study catchments and for different pollutants (N and P), suggesting that risk assessment and hence mitigation approaches will need to be catchment-specific (Milledge et al., 2013).

IV. APPROACHES TO CONTROL DIFFUSE WATER POLLUTION FROM AGRICULTURE

The complex processes of pollutant mobilisation, transport and delivery between the source area and the receiving water body, as well as the uncertainty associated with actual ecological impacts, complicate the evaluation of the effectiveness of measures to mitigate diffuse water pollution (Wall et al., 2012).

Over 80 mitigation measures to reduce diffuse water pollution from agriculture have been reviewed in the UK (Cuttle et al., 2007, Newell-Price et al., 2011) (Table 2.1), targeted at limiting agricultural inputs, reducing mobilisation and transport of pollutants from agricultural land and capture of pollutants before they enter waterbodies (Kay et al., 2009). No single measure will control all sources of pollution (Withers and Jarvis, 1998). As major sources of pollutants differ between catchments (Monaghan et al., 2008), mitigation measures will need to be matched to the prevailing physical conditions and farming systems (Buckley, 2012). The 'Mitigation Options for Phosphorus and Sediment' projects (MOPS1 and MOPS2) have shown that a combination of 'in-field' and 'edge-of-field' measures aimed at reducing both the mobilisation, transport and delivery of pollutants is likely to be most effective, providing a suite of measures along the full 'source-mobilization-transport-delivery' continuum (Deasy et al., 2010).

Construction of water meadows and wetlands to enhance denitrification were proposed as the most effective measures to control diffuse nitrate pollution (Kay et al., 2009) and an effective adaptation to likely increases in nitrate pollution due to climate change (Whitehead et al., 2006). Small scale field wetlands were shown to be effective at reducing diffuse pollution, including the removal of sediment, P and NO_3^--N (Blackwell and Pilgrim, 2011). MOPS2 data showed that small scale wetlands can be a cost-effective tool for the removal of sediment from impaired water courses, especially at sandy sites (Ockenden et al., 2012), while larger impoundments are also known to trap sediment well (Hamilton, 2012).

Method 1A – Convert arable land to unfertilised and ungrazed grass
Method 1B – Arable reversion to low fertiliser input extensive grazing
Method 2 – Convert arable/grassland to permanent woodlands
Method 3 – Convert land to biomass cropping (i.e. willow, poplar, miscanthus)
Method 4 – Establish cover crops in the autumn
Method 5 – Early harvesting and establishment of crops in the autumn
Method 6 – Cultivate land for crops in spring rather than autumn
Method 7 – Adopt reduced cultivation systems
Method 8 – Cultivate compacted tillage soils
Method 9 – Cultivate and drill across the slope
Method 10 – Leave autumn seedbeds rough
Method 11 – Manage over-winter tramlines
Method 12 – Maintain and enhance soil organic matter levels
Method 13 – Establish in-field grass buffer strips on tillage land
Method 14 – Establish riparian buffer strips
Method 15 – Loosen compacted soil layers in grassland fields
Method 16 – Allow field drainage systems to deteriorate
Method 17 – Maintain/improve field drainage systems
Method 18 – Ditch management
Method 19 – Make use of improved genetic resources in livestock
Method 20 – Use plants with improved nitrogen use efficiency
Method 21 – Fertiliser spreader calibration
Method 22 – Use a fertiliser recommendation system
Method 23 – Integrate fertiliser and manure nutrient supply
Method 24 – Reduce manufactured fertiliser application rates
Method 25 – Do not apply manufactured fertiliser to high-risk areas
Method 26 – Avoid spreading manufactured fertiliser to fields at high-risk times
Method 27 – Use manufactured fertiliser placement technologies
Method 28 – Use nitrification inhibitors
Method 29 – Replace urea fertiliser with another nitrogen form (e.g. ammonium nitrate)
Method 30 – Incorporate a urease inhibitor with urea fertiliser
Method 31 – Use clover in place of fertiliser nitrogen
Method 32 – Do not apply P fertiliser to high P index soils
Method 33 – Reduce dietary N and P intakes
Method 34 – Adopt phase feeding of livestock

Method 35 – Reduce the length of the grazing day/grazing season Method 36 – Extend the grazing season for cattle Method 37 – Reduce field stocking rates when soils are wet Method 38 – Move feeders at frequent intervals Method 39 – Construct water troughs with a firm but permeable base Method 40 – Low methane livestock feeds Method 41 – Reduce overall stocking rates on livestock farms Method 42 – Increase scraping frequency in dairy cow cubicle housing Method 43 – Additional targeted straw-bedding for cattle housing Method 44 – Washing down dairy cow collecting yards Method 46 – Frequent removal of slurry from beneath-slatted storage in pig housing Method 47 – Part-slatted floor design for pig housing Method 48 – Install air-scrubbers or biotrickling filters to mechanically ventilated pig housing Method 49 – Convert caged laying hen housing from deep-pit storage to belt manure removal Method 50 – More frequent manure removal from laying hen housing with belt clean systems Method 51 – In-house poultry manure drying Method 52 – Increase the capacity of farm slurry (manure) stores to improve timing of slurry applications Method 53 – Adopt batch storage of slurry Method 54 – Install covers on slurry stores Method 55 – Allow cattle slurry stores to develop a natural crust Method 56 – Anaerobic digestion of livestock manures Method 57 – Minimise the volume of dirty water (and slurry) produced Method 58 – Adopt (batch) storage of solid manures Method 59 – Compost solid manure Method 60 – Site solid manure field heaps away from watercourses/field drains Method 61 – Store solid manure heaps on an impermeable base and collect leachate Method 62 – Cover solid manure stores with sheeting Method 63 – Use liquid/solid manure separation techniques Method 64 – Use poultry litter additives Method 65 – Change from a slurry to solid manure handling system Method 66 – Change from a solid manure to slurry handling system Method 67 – Manure spreader calibration Method 68 – Do not apply manure to high-risk areas Method 69 – Do not spread slurry or poultry manure at high-risk times Method 70 – Use slurry band spreading application techniques Method 71 – Use slurry injection application techniques Method 72 – Do not spread FYM to fields at high-risk times Method 73 – Incorporate manure into the soil Method 74 – Transport manure to neighbouring farms Method 75 – Incinerate poultry litter for energy recovery Method 76 – Fence off rivers and streams from livestock Method 77 – Construct bridges for livestock crossing rivers/streams Method 78 – Re-site gateways away from high-risk areas Method 79 – Farm track management Method 80 – Establish new hedges Method 81 – Establish and maintain artificial wetlands Method 82 – Irrigate crops to achieve optimum yields Method 83 – Establish tree shelter belts around livestock housing and slurry storage facilities

Table 2.1 83 mitigation measures reviewed by Newell-Price et al. (2011) in 'An inventory of mitigation methods'.

The effectiveness of riparian buffer zones to control pollution varies with catchment geomorphology, hydrological pathways and the permeability of soils (Mellander et al., 2012). Where the riparian zone has been drained, the pollutants will bypass the buffer zone through sub-surface flow, thus making it ineffective (Mainstone and Parr, 2002, Oliver et al., 2007). In terms of nitrate removal, buffer zones are most effective in the absence of sub-surface drainage, on soils of medium hydrological conductivity at the hillslope-floodplain boundary (Burt, 2006), while P removal is most effective in catchments dominated by PP transport in overland flow (Mellander et al., 2012). In flat fields with permeable soils, the effectiveness of buffer strips for P removal will be highest in areas with high surface runoff and/or shallow sub-suface flow, provided accumulated P reserves in the buffer are periodically removed (Noij et al., 2013). Conversely, in the same situation, the effectiveness of the buffer strip for N removal will decrease, if flow is too shallow, due to reduced residence time (Noij et al., 2013). Buffer zones are more effective at trapping PP fractions associated with larger soil particles but are less able to intercept P associated with fine colloidal fractions and soil organic matter, as well as DRP, which are likely to be more bioavailable and thus more important for ecological water quality (Oliver et al., 2007, Owens et al., 2007). In terms of ecological status, riparian buffer zone length was found to be more closely linked to the health of freshwater macro-invertebrate communities than buffer zone width (Feld, 2013).

The effectiveness of buffers over the course of a year is also variable (Stevens and Quinton, 2009a). The efficiency of buffer strips as 'end-of-pipe' mitigation measures is lowest in winter when the delivery of nutrients to water bodies is highest, due to high local water tables, reduced infiltration rate, poor plant growth (Kay et al., 2009) and reduced temperatures affecting the rate of microbial processes (Stevens and Quinton, 2009a). However, the implications of this reduced efficiency during the period of least ecological activity are not clear and may be less significant in flowing waters due to shorter nutrient retention time.

Geomorphological restoration of river corridors over the past two decades has been undertaken in Europe and overseas, with a primary aim of increasing flood water storage and reducing flood risk in downstream areas (Scholz, 2007). However, creation of flood retention basins through re-connection of rivers to their floodplains has also been shown to result in water quality benefits, primarily through the deposition of suspended sediment and associated nutrients (Walling, 1999, Scholz, 2007, Kronvang et al., 2007). Floodplain sedimentation is associated with deposition of particulate phosphorus (Van der Lee et al., 2004), with highest removal rates in depressions due to reduced current velocity (Venterink et al., 2006), while denitrification is thought to be the most important mechanism for nitrate removal (Forshay and Stanley, 2005, Noe and Hupp, 2009). While quantitative estimates of the cumulative retention of nutrients and sediments in floodplains are scarce (Noe and Hupp, 2009), estimates of trapping efficiency for individual pollutants vary between 26-47 % for sediment (Walling and Owens, 2003, Kronvang et al., 2007), 3 - 37 % for N (Van der Lee et al., 2004, Forshay and Stanley, 2005, Noe and Hupp, 2009) and 4 - 59 % for P (Van der Lee et al., 2004, Kronvang et al., 2007, Noe and Hupp, 2009), with highest trapping efficiency associated with lower annual nutrient loads (Forshay and Stanley, 2005, Noe and Hupp, 2009). Highest rates of sediment and nutrient deposition were found in the riparian zone close to the river channel (Kronvang et al., 2007, Klaus et al., 2011), due to increased surface roughness associated with an abrupt reduction of flow velocity (Klaus et al., 2011), while high denitrification rates were recorded both in agricultural grasslands and ponds (Venterink et al., 2006). However, anaerobic floodplain inundation also carries a risk of enhanced P mobilisation from existing soil P reserves (Loeb et al., 2008). These results suggest that a combination of mitigation techniques involving source reduction and hydro-morphological restoration will be effective in reducing eutrophication impacts in large fluvial systems, albeit over long timescales, given the large spatial extent of required interventions (Houser and Richardson, 2010).

Until recently, the evidence for the effectiveness of upland ditch blocking to reduce DOC and SS concentrations and loads has been ambiguous (Wallage et al., 2006, Worrall et al., 2007, Armstrong et al., 2010). Although recent studies have found a positive impact of drain blocking on DOC concentrations (Armstrong et al., 2010, Turner et al., 2013) and fluxes (Worrall et al., 2007, Turner et al., 2013), the observed changes are not ubiquitous (Armstrong et al., 2010) and are most evident within the immediate sub-catchments around the blocked areas (Turner et al., 2013). Therefore, evidence of any hydrological and water quality impact of drain blocking at a larger catchment scale is still lacking (Ramchunder et al., 2009).

An assessment of the manifestation of some of these water quality mitigation approaches is undertaken in Chapter 6.

V. EVALUATING THE EFFECTIVENESS OF MITIGATION MEASURES AT A CATCHMENT SCALE

A. Monitoring strategies

Available methodologies for the assessment of the effectiveness of conservation practices span from plot and field experiments, through edge-of-field monitoring to watershed scale-studies, which are either based on the examination of observed time series before/after management interventions, or use paired watershed studies with a control/impact design (Tomer and Locke, 2010). While a combination of before/after and control/impact design is statistically most robust (Turner et al., 2013), it is often difficult to implement in practice at a catchment scale. Due to practical constraints with the implementation of statistically robust experimental design at a catchment scale, evaluation of landscape-scale mitigation measures often relies on modelling tools (Monaghan et al., 2008), which are themselves subject to uncertainties (Milledge et al., 2013). Modelling of water quality at catchment scales still remains a largely semi-empirical process, capable of predicting potential benefits that may accrue but not the precise location-specific outcomes (Tomer and Locke, 2010).

In Ireland, The Agricultural Catchments Programme, was set up to establish a baseline and evaluate the effectiveness of the EU legislation, including the Nitrates Directive and the WFD (Wall et al., 2011). The high spatial and temporal resolution of this monitoring platform allows new insights into the processes governing the response of pollutants to mitigation measures along the full source-mobilisation-delivery-impact continuum (Haygarth et al., 2005a) at a catchment scale (Wall et al., 2011, Melland et al., 2012, Jordan et al., 2012b). Within the programme, nutrient sources are audited at the farm scale, transport pathways are conceptualised and pollutant transport and delivery are studied at sub-catchment and catchment scales with high spatial and temporal resolution (Wall et al., 2011). A similar high resolution approach has been adopted in three experimental study catchments in England (Owen et al., 2012). Whilst extremely informative, such high resolution monitoring strategies are associated with high costs and man-power requirements and hence are unlikely to be available for widespread replication (Sharpley et al., 2009).

Although more affordable, reduced sampling frequency has serious implications for the accuracy of annual load estimates and hence the reliability of water quality monitoring schemes (Johnes, 2006, Cassidy and Jordan, 2011). In lowland catchments the level of uncertainty in total P load estimates increases with increasing catchment population density, reduced baseflow index and more extreme river regime (Johnes, 2006). In these situations, a daily sampling strategy for TP and DRP concentrations on the 35 highest flow days/year and weekly sampling during the remainder of the year may be a viable option for one sampling station at the basin outlet to constrain the level of sampling uncertainty. However, the sampling uncertainty relationships in upland, flashy, impermeable catchments are more poorly understood and even daily records may fail to capture the full range of P export behaviour in smaller catchments with flashy hydrographs (Johnes, 2006).

Infrequent sampling has been shown to lead to serious over- and under-estimation of nutrient loads, while all methods of load calculation have associated bias (Walling and Webb, 1985, Littlewood, 1992, Johnes, 2006). Recent research has found that P load calculations based on infrequent sampling led to an average 60 % under-estimation of the true load and that even daily sampling would fail to capture the true variability of P transfer in storm-flow (Cassidy and Jordan, 2011). Jordan et al. (2007) advocate the use of a continuous automated bank-side analyser, which collects samples at 10' minute intervals, aggregated to 1 hour intervals for comparison with flow and rainfall data, in order to synchronise measurements of both water discharge and contaminants to monitor the effects of mitigation measures on both diffuse and point source pollution sources in complex catchments. However, the high cost of such continuous sampling strategy may be a serious limitation to wider adoption (Jordan and Cassidy, 2011).

Flow-proportional passive samplers for determining P and N concentrations could potentially offer a compromise solution between the inaccurate load estimation associated with low-frequency monitoring and the high cost of continuous bank-side analysers; however rigorous testing has shown the currently commercially available designs to be seriously inaccurate (Jordan et al., 2013). Conversely, a sampling strategy of taking 24 systematic samples per week using the well established automatic water samplers may offer an accurate and feasible solution for the monitoring of total nutrient species and conservative solutes in routine monitoring programmes (Jordan and Cassidy, 2011). Harmel et al. (2007) also discuss methodologies for P monitoring in small watersheds of < 10 km^2, including logistic considerations such as resource constraints (man-power, number of samples and associated analysis costs and reliability of equipment). Base flow water quality sampling using at least monthly manual grab samples to establish point source, ground water and direct livestock stream nutrient inputs, complemented by high-resolution storm event sampling to characterise diffuse source pollution was proposed as the best cost-effective sampling strategy (Harmel and Haggard, 2007). Flow-integrated sampling, whereby a greater proportion of the samples are taken at higher flow and transport periods, improves the load estimates (Jordan and Cassidy, 2011) and should be based on a thorough understanding of catchment hydrology (Harmel and Haggard, 2007). Johnes (2006) also found that stratified sampling, with more frequent samples taken during the 10 % of the highest flow events, reduced the uncertainty in load estimation in flashy catchments. Further uncertainty is associated with the use of stage-discharge relationships to estimate the mass transport values of P (Harmel and Haggard, 2007) and SS (Bilotta et al., 2010), hence yield estimates based on ‘rating curve’ (discharge-concentration) approaches should ideally be based within an uncertainty framework (Bilotta et al., 2010, Scholefield et al., 2013).

B. Issues of Scale

Catchments are complex dynamic systems with potentially fractal behaviour and emergent properties (Kirchner et al., 2000), governed by processes ranging from small microbial to large hydrological scales (Harris and Heathwaite, 2005). Understanding this complexity requires a multi-disciplinary approach to study that encompasses both the theory-led, reductionist, hypothesis-testing approach traditionally applied in soil sciences, and an empirically-led observational, hypothesis-forming approach characteristic of ecological enquiry (Haygarth et al., 2005a).

Several authors emphasise the need for more detailed high resolution studies across a range of scales to discern a pattern in what may otherwise be perceived as simply ‘white noise’ in low resolution data (Harris and Heathwaite, 2005, Haygarth et al., 2005b). While replicated, plot-scale experiments have elucidated the mechanisms affecting pollutants along the source-mobilisation-transport-receptor continuum (McGonigle et al., 2012), evidence on how hydrological and biogeochemical processes will respond to land use interventions at a catchment scale is still lacking (Sharpley et al., 2009, McGonigle et al., 2012). Due to the complex nature of sediment and nutrient mobilisation, transport and delivery in catchments, extrapolation of findings from carefully controlled plot-scale experiments to farm and then catchment scale is difficult (McGonigle et al., 2012). A difference between observed trends at field and watershed scales may occur due to a disconnection between sources and sinks at the two scales (Sharpley et al., 2009). Further, the cumulative effect of multiple pollutants on aquatic ecosystems can have unexpected effects as compared to the effects of the same stressors acting in isolation (Townsend et al., 2008). Hence, there is a pressing need to investigate the cumulative effectiveness of various mitigation measures on multiple pollutants pre- and post- restoration at a catchment scale (Cherry et al., 2008, Haygarth et al., 2009, Haygarth et al., 2013) and in a range of river typologies to guide and inform catchment management strategies (Evans et al., 2006).

Monitoring at nested locations within a catchment aids the understanding of pollutant mobilisation and transport processes operating at a range of scales (Deasy, 2007), while the understanding of spatial heterogeneity of soil properties and land use elucidates potential pollutant sources, runoff pathways and hydrological connectivity (Peukert et al., 2012). Deasy (2007) examined the importance of different controls on diffuse P delivery to watercourses at a range of scales. Runoff was controlling sediment transfer, which in turn was closely related to P export at all scales. However, different processes were found to be important at different, within-farm, scales and the characteristics of P transfer did not increase or decrease consistently with scale, attributed to anthropogenic alterations of land use. Nevertheless, it was still possible to generalise findings from hillslope observations to the catchment scale, using empirical relationships, possibly due to the relatively small extent of nested observation scales. Thus, despite potential difficulties with experimental replication (Haygarth et al., 2013) and generalisation of results between catchments with differing physical and biological characteristics (Johnes et al., 2007), nested catchment scale studies provide both qualitative and quantitative evidence that may be more informative for practical catchment management than small scale replicated experiments alone (Haygarth et al., 2005a, Deasy, 2007).

C. Time lags

The expectations for the delivery of anticipated environmental improvements within current policy timescales need to be tempered with the realities of environmental and social response lags (Sharpley et al., 2009). The potentially substantial time lag in observed responses to mitigation actions (Cherry et al., 2008, Collins and McGonigle, 2008) have been ascribed to the accumulated nutrient reserves in soils and aquatic sediments (Ekholm et al., 2005, Kay et al., 2009), accumulation of dissolved nutrients in aquifers (Mainstone and Parr, 2002, Hutchins et al., 2009) and prolonged flushing time of accumulated sediments from fluvial systems (Hamilton, 2012). Ecological resilience to chemical manipulations in some impacted systems also presents a significant challenge in the short-term (Johnes et al., 2007, Harris and Heathwaite, 2012).

Recently, significant progress has been made in estimating the response time of different pollutants to catchment-scale mitigation measures. While some ecosystems are likely to respond to N reduction measures in the medium 7-20 year time scale (Fenton et al., 2011), others have shown little or no response even after 20 years of nutrient reductions (Windolf et al., 2012), depending on the catchment hydrogeology and prevailing hydrological pathways. In catchments with a significant groundwater input, the effects of land use change on reduced N loads in rivers may take decades to manifest (Hutchins et al., 2009). Recent modelling predicted a decline of accumulated P reserves in soil to optimum agronomic levels within 2-20 years (Schulte et al., 2010, Wall et al., 2013). These time lags mean that an extended period of monitoring is necessary to evaluate the impact of a suite of mitigation measures on water quality at a catchment scale (Wall et al., 2011). The shorter the monitoring programme, the more frequent measurements are required to detect a significant change (Sharpley et al., 2009). Comparison with a control catchment (Worrall et al., 2009), where available, together with a before-after experimental design would increase statistical power and the likelihood of a signal detection. However, ultimately, the long timescale required for an ecosystem-wide response to become manifest in many catchments, may have to be accepted by the scientific and policy community (Hamilton, 2012).

D. Pollution swapping

Pollution swapping, whereby a measure introduced to control one pollutant results in an increase in another pollutant, is a widely accepted concept and is receiving increasing attention (Collins and McGonigle, 2008, Stevens and Quinton, 2009b). Stevens and Quinton (2009a) recently reviewed diffuse pollution mitigation options in arable systems, concluding that no single mitigation measure will reduce all pollutants, in fact a single management strategy may not provide complete protection of receiving waters even just from one type of pollutant such as pathogens (Oliver et al., 2007). Therefore, it is necessary to take a holistic approach to mitigation (Collins and McGonigle, 2008), both in terms of a suite of mitigation measures needed to be deployed at an appropriate scale, and in terms of the resulting chemical balances that might be achieved. Ultimately, it may have to be accepted that negative tradeoffs between mitigation interventions are inevitable and location-specific cost-benefit analysis (Balana et al., 2011) may be required to reconcile the competing outcomes.

VI. THESIS OBJECTIVES AND STRUCTURE

In recent years, significant investment into research infrastructure has been directed at addressing the existing knowledge gaps in the understanding of the effectiveness of ecosystem management approaches to deliver water quality improvements at catchment scales. These include the Irish Teagasc Agricultural Catchments Programme (Wall et al., 2011, Teagasc, 2013) and the Demonstration Test Catchments research platform in England (McGonigle et al., 2012, Owen et al., 2012, DTC, 2013) which will provide an opportunity to examine the processes controlling the mitigation of diffuse water pollution at a number of scales through a high resolution nested monitoring strategy within real-world social and economic constraints of working farm enterprises. A new Biotechnology and Biological Sciences Research Council (BBSRC) farm-scale research platform at Rothamsted Research, North Wyke, will examine the impact of different grassland management regimes at a field and sub-catchment scale, using a sub-hourly high resolution monitoring strategy within three hydrologically isolated units (Peukert et al., 2012). This national research facility will allow a rigorous comparison of the viability and environmental impact of conventional, reduced input and innovative new farming approaches to inform the development of future sustainable grassland farming system (Rothamsted Research, 2013).

Aligned with these principles, and as part of a national Defra-funded, catchment-scale, multi-objective flood management demonstration project, this thesis aims to contribute to the emerging understanding of the effectiveness of multiple ecosystem management measures to deliver water quality improvements at a catchment scale. This research complements existing hydrological monitoring commissioned by the National Trust, with biological, physical and chemical water quality monitoring. In addition, it delivers a comprehensive characterisation of the status of soils and land management across two catchment scales, in order to elucidate the controls and sources of pollutants found in-stream.

The two research catchments Aller and Horner Water are located in south-west England on the north-east edge of Exmoor National Park. South-west England is predominantly rural in nature and covers approx. 24,000 km^2 (Findlay, 1984). It includes the counties of Gloucestershire, Bristol, Wiltshire, Dorset, Somerset, Devon and Cornwall and comprises two National Parks (Exmoor and Dartmoor) and a number of other protected landscapes (Areas of Outstanding Natural Beauty). The geology of south-west England represents almost the whole geological time scale found in Britain, from primary igneous and metamorphic rocks to more recent sediments (Findlay, 1984). Devon and Cornwall Peninsula is formed of an old massif of Palaeozoic rocks made of Devonian and Carboniferous sediments, folded from the south at the end of Carboniferous period. The sediments that metamorphosed under pressure now form the southward dipping sandstones and slates of the Exmoor upland (Findlay, 1984). The lowlands are formed of more recent Mesozoic and Tertiary strata and Quaternary deposits. The underlying geology shapes the landscape, with the highest ground in the west (up to 621 m a.s.l. on Dartmoor and 521 m a.s.l. on Exmoor) coinciding with the hard rocks of older formations (Met Office, 2011).

The mild and wet maritime climate of the south-west peninsula is influenced by the surrounding sea (Met Office, 2011). The 9ºC range between the mean monthly temperature of the warmest and coldest months is narrower than in most of the UK and the mean annual rainfall is higher than in the east of the country, ranging between 644-2,584 mm yr^{-1}, being influenced by altitude, aspect and the proximity to the sea (Findlay, 1984, Met Office, 2011). Agriculture accounts for up over 70 % of rural land use within the region, with the rest covered by semi-natural vegetation such as woodland, moorland and coastal habitats (Findlay, 1984). The high average rainfall facilitates grass growth and dairy farming is well established within the region, particularly in lower lying areas (Findlay, 1984). On higher ground, sheep and beef rearing is prevalent.

The two contrasting research catchments represent a geological, climatic and land use gradient typical of south-west England, from semi-natural vegetation on the high ground in Horner Water to intensive agricultural land use near sea level in the Aller vale. The close proximity of these two study catchments allows to compare the effects of contrasting land use and to evaluate a range of land use mitigation measures on water quality. A detailed characterisation of the geology, soils, climate and land use in the two study catchments is provided in Chapter 3.

Specifically, the following questions are addressed in this thesis:

Chapter 3

- How does the spatial variability of key soil properties vary between the two contrasting study catchments and what are the implications for water quality and mitigation of poor water quality?

Chapter 4

- What are the current rates of fluvial carbon export in terms of dissolved organic and particulate carbon from the two catchments and how do they relate to soils, prevailing land use and habitat mitigation?

Chapter 5

- Can the new pressure-specific invertebrate index PSI act as a tool for determining ecologically relevant water quality sedimentation targets?

Chapter 6

- How does upland ditch restoration impact on the chemical and biological indicators of water quality in three headwater tributaries of Horner Water?
- Are the proposed mitigation measures in the lowland Aller catchment likely to deliver water quality improvements at a catchment scale?

Chapter 7

- Summarises the key findings across the four results chapters and addresses the overall question: How effective can an ecosystem management approach to deliver water quality objectives be?

Additional figures and tables that would normally accompany a journal manuscript as supplementary information are presented in the Appendix. Where they are referred to in the text, the page number is given in parentheses.

Chapter 3

QUANTIFYING THE SPATIAL VARIABILITY OF SOIL PHYSICAL AND CHEMICAL PROPERTIES IN RELATION TO MITIGATION OF DIFFUSE WATER POLLUTION

I. ABSTRACT

Understanding spatial variability of soil properties in relation to land use impacts is essential for targeting and evaluating the effectiveness of measures taken to address the impact of diffuse water pollution from agriculture. However, despite the growing emphasis on integrated catchment-scale implementation of land use mitigation measures, baseline, landscape-scale evaluation of the spatial variability of key soil nutrients is scarce. This study employs a high resolution geostatistical approach to characterise the spatial variability of soil bulk density, total soil carbon (TC), nitrogen (TN), phosphorus (TP) and $\delta^{15}N$ in two study catchments with contrasting land use (agricultural Aller and semi-natural Horner Water) that are subject to targeted management interventions to reduce flood risk and improve water quality. The spatial dependence of all soil properties, except for bulk density and $\delta^{15}N$, was stronger in the agricultural than the semi-natural catchment (nugget:sill ratio 0.10-0.42 in the Aller and 0.15-0.94 in Horner Water). Further, bulk density, TP, inorganic phosphorus (IP), organic phosphorus (OP), C:N ratio, $\delta^{15}N$ and carbon storage showed a longer range of spatial auto-correlation in the agricultural catchment (2,807-3,191 m in the Aller and 545-2,599 m Horner Water). The central tendency (mean, median) of all soil properties, except for IP and $\delta^{15}N$, also differed significantly between the two catchments ($P < 0.01$). The correlations between different soil properties helped to elucidate the mechanisms that may be responsible for the observed differences, while the kriged surfaces of soil variables identified likely critical source areas for targeting of land management interventions to improve water quality. An improved understanding of the implications of the links between the observed homogenisation of soil properties in the agricultural catchment and the ecological status of associated freshwaters is needed. A comparison with

the nationally available NSRI soil survey dataset shows that both the detailed geostatistical approach and the national dataset produce comparable estimates of soil C (NSRI mean C stock 146 t, geostatistical survey 132-168 t) and TP stocks (NSRI TP stock 0.5-2.4 t, geostatistical survey 1.13-1.48 t) in the top 5 cm of soil profile in two study catchments. However, the national dataset underestimates the spatial variability of (i) soil bulk density and C content in clay soils under semi-natural land use and (ii) loamy soils under arable crops, while it overestimates the spatial variability of (iii) C content in peat under permanent pasture. As the restoration of soil spatial heterogeneity may take several decades, a high resolution geostatistical approach should be included in the future design of catchment-scale monitoring schemes to inform catchment management strategies and elucidate the time frame over which landscape scale improvements in soil properties and corresponding ecosystem services can be achieved.

II. INTRODUCTION

Characterising the spatial variability of soil properties is essential for the understanding of the effects of land management on soil function and associated ecosystem services including those involving water quality, carbon sequestration and biodiversity (Cambardella et al., 1994, Ettema and Wardle, 2002, Goovaerts, 1998, Stutter et al., 2009). In addition, understanding the heterogeneity of the soil resource is necessary for an effective design of experimental sampling (Oliver and Webster, 1991) and evaluation of the effectiveness of diffuse pollution mitigation measures to protect receiving surface waters (Rivero et al., 2007, Peukert et al., 2012). However, few studies describe spatial variability of multiple soil properties and their inter-relationships at a landscape scale (Paz-Gonzalez et al., 2000, Bruland et al., 2006, Rivero et al., 2007, Stutter et al., 2009, Liu et al., 2012), despite the growing need to assess the catchment scale effectiveness of soil management measures designed to mitigate diffuse water pollution from agriculture. Herein, it is argued that understanding the variability of soil properties at a landscape scale will inform the prioritisation of areas for restoration and management (Bruland et al., 2006) and as such is a useful tool to aid soil use and management decision-making.

As soil is a continuum, its spatial properties have to be auto-correlated at a certain scale (Oliver and Webster, 1991) and hence any quantitative analysis of soil properties has to take into account the spatial coordinates of the observations (Goovaerts, 1998). Geostatistics allows the quantification of the degree of spatial auto-correlation between environmental properties and uses it for prediction of values at unmeasured locations (Oliver and Webster, 1991, Webster and Oliver, 2001), enabling the quantification of the scales of spatial variability (Stutter et al., 2009) and facilitating a better understanding of the mechanisms and processes that control spatial patterns (Goovaerts, 1998).

Nutrient content, distribution and supply have a profound influence on the functioning of ecosystems (Fraterrigo et al., 2005). The role of increased P and N loading in causing eutrophication of freshwaters is widely accepted (Pierzynski et al., 2000, Wang et al., 2009), while alterations to the terrestrial-aquatic linkages in DOC dynamics are likely to have multiple effects due to its wide-ranging role in the functioning of aquatic ecosystems (Stanley et al., 2011). Intensive land use has persistent effects on soil properties, including bulk density (Fraterrigo et al., 2005) and soil organic matter (Bradford et al., 2008). Tillage and addition of inorganic P and N accelerate the decomposition of organic matter (Bradford et al., 2008, Brady and Weil, 1999, Zhang et al., 2012), resulting in the alteration of soil physical, chemical and biological properties (Brady and Weil, 1999, Senbayram et al., 2008). However, land management has long-term effects on the spatial heterogeneity of soil resources that may not be detectable when averaged values are compared between sites and soil types (Fraterrigo et al., 2005). Whilst agricultural land use has been shown to reduce the spatial variability of soil properties through cultivation, fertilizer application and grazing (Paz-Gonzalez et al., 2000, Gilliam and Dick, 2010, Li et al., 2010), the natural spatial distribution of physical and chemical soil properties in temperate upland moorland soils other than histosols is less understood (Stutter et al., 2009).

Further research is needed to quantify alterations in soil spatial variability resulting from changes in land use (Li et al., 2010) in order to aid accurate estimation of nutrient budgets and cycling rates (Fraterrigo et al., 2005, Stutter et al., 2009) and to aid in the identification of possible 'critical source areas' of pollution to aquatic ecosystems.

With these findings in mind, this study takes a high resolution, catchment-scale and geostatistical approach to characterise the baseline spatial distribution of the macronutrients; C, N and P to identify possible sources of nutrient pollution and support evaluation of diffuse water pollution mitigation schemes. In addition, soil bulk density is quantified as it has a profound influence on soil hydrological properties (Batey and McKenzie, 2006, Price et al., 2010), while the C:N ratio and $\delta^{15}N$ enrichment ratio elucidate the rates of soil organic matter turnover (Brady and Weil, 1999, Kuzyakov et al., 2000). The research focuses on two neighbouring catchments with contrasting land use that are subject to targeted land management interventions in order to alleviate flood risk and reduce diffuse water pollution. The upland catchment is dominated by semi-natural moorland and woodland habitats, while the lowland catchment has more intensive agricultural management. It is hypothesised that the spatial variability and the central tendencies (median, mean) of soil properties in the two study catchments with contrasting land use will differ, and that a high resolution geostatistical approach is needed to provide a sound baseline for monitoring of the effects of land-use changes and the assessment of nutrient stocks.

Specifically, this Chapter aims to:

1. Characterise and compare the catchment-scale spatial variability and central tendencies of soil properties, including bulk density, total C (TC), total N (TN), total P (TP) and the stable N isotope ratio ($\delta^{15}N$) between two contrasting study catchments;
2. Elucidate possible mechanisms controlling the observed spatial variation;
3. Provide a baseline for monitoring the effectiveness of land management interventions to mitigate diffuse water pollution from agriculture at a catchment scale;
4. Compare the characterisation of spatial variability and nutrient stocks (C and P) using the detailed geostatistical approach and mean values from a national dataset.

III. Methods

A. Study site

The two study catchments Aller and Horner Water are located in south-west England on the north-east edge of Exmoor National Park (51^{o}11'52N 3^{o}34'41W) (Fig. 3.1). The Aller catchment covers 17.6 km^2 with an altitude range of 4-425 m above sea level. Horner Water catchment covers 22 km^2 with an altitude range 20-516 m above sea level.

The 30-year average annual rainfall for the period 1961-1990 for Horner Water catchment is 1,489 mm and for the Aller it is 1,056 mm (Spackman, 1993). The average annual temperature for the two catchments is 11-12°C (MetOffice, 2011).

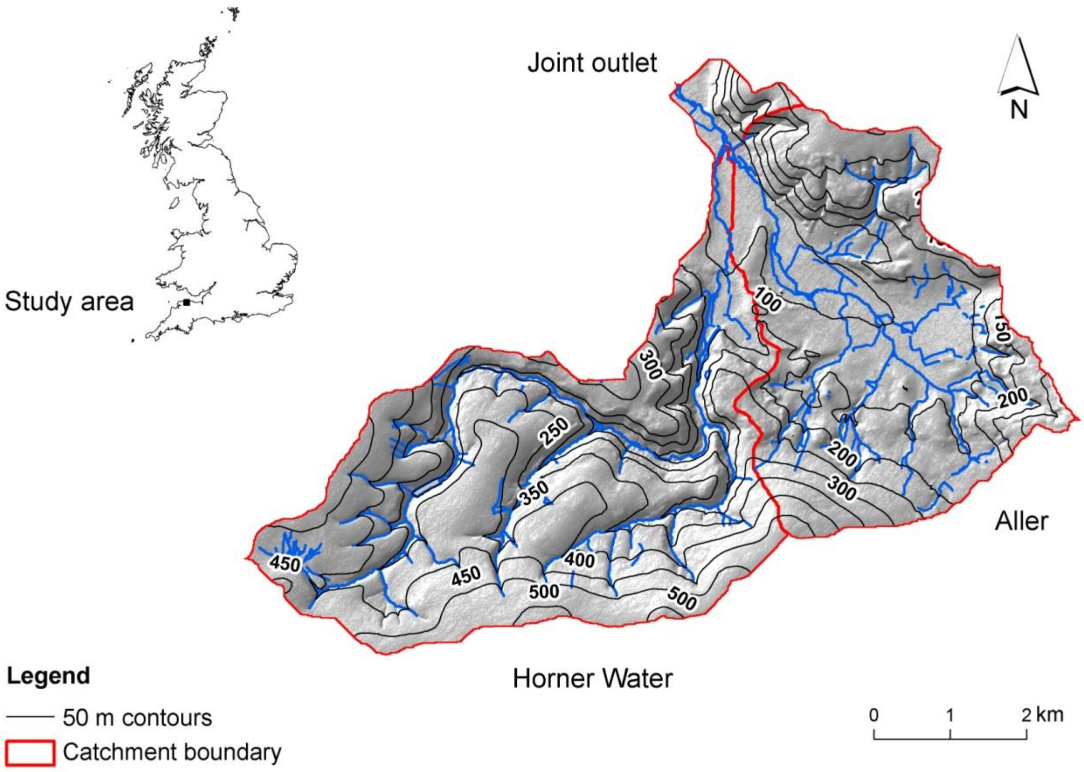

Fig. 3.1 The study site showing the Aller and Horner Water catchments and the joint catchment outlet.

The solid geology of both catchments is Devonian red sandstone of the Hangman Grits Formation on the higher ground with Triassic mudstone and breccia at lower altitude in the Aller catchment (Fig. 3.2, p. 202). The superficial geology of Aller Vale is mostly dominated by Quaternary river terrace deposits, alluvium, silt, sand and gravel (BGS 1:50,000 bedrock and superficial geology maps).

In both study catchments, the soils are predominantly loamy brown earths and podzols. In addition, clayey calcareous and argillic pelosols are present in the lowest lying area of the Aller catchment, while peaty-topped loamy stagnopodzols and stagnohumic gley soils are found on the highest ground of Horner Water catchment (National Soil Map 1:250,000) (Fig. 3.3, p. 202). Fig. 3.4 (p. 203) shows the dominant Hydrology of Soil Types (HOST) classes (Boorman et al., 1995) within the two study catchments. Both study catchments predominantly support permeable soils, with the exception of HOST type 21 over clay soils in the Aller catchment, with a propensity for short seasonal saturation and generation of overland flow. Similarly, HOST types 15 & 26 in the upper reaches of the Horner Water catchment represent peaty soils with a propensity for saturation excess overland flow.

Land use in the Aller catchment is dominated by livestock rearing, primarily sheep, with a smaller number of cattle and ponies. The upper tributaries originate in unimproved heathland and permanent, semi-improved grassland (Fig. 3.5, p. 203). Most of the pastures are improved, with the exception of the steepest ground. Livestock are fed on home-grown hay or silage from short-rotation leys, on roots and imported concentrates. Arable land is rotated between short-term grass leys, winter wheat/spring barley, roots and peas. Maize is only grown at the eastern end of the catchment. No slurry is applied and soil fertility is maintained by farm-yard manure applications and inorganic NPK fertilisers, typically applied in the spring before the start of the growing season.

The Horner Water catchment is designated as a Site of Special Scientific Interest (SSSI) and a Special Area of Conservation (SAC) under the European Union Habitats Directive 1992 92/43/EC (JNCC, 2006) for its Western Sessile Oak Wood and Atlantic Heath interest (Fig. 3.6, p. 204). Semi-natural vegetation predominates and agricultural land use is mostly extensive livestock grazing, with limited arable farming on the flat plateaux in the upper reaches of the main tributary in the west of the catchment.

Environment Agency monthly water quality data for the years 2000-2010 (Table 3.1) show concentrations below the current drinking water quality standard for total oxidised N (TON) of 50 mg L^{-1} (Leeson et al., 2003) but above levels of 0.5-1 mg N L^{-1} (2.21 – 4.43 mg L^{-1} as TON) associated with eutrophication in rivers (Hilton, 2006, Pierzynski et al., 2000). Long-term mean monthly orthophosphate levels in both rivers are below the current good ecological status standard of 40 µg L^{-1} for Horner Water and 120 µg L^{-1} for Aller (UK TAG, 2012). The suspended sediment concentrations in both rivers are below the Freshwater Fish Directive Guideline Standard for suspended solids of annual mean of 25 mg L^{-1} (UK TAG, 2008).

Under the EU Water Framework Directive, the Environment Agency has classified the Ecological Status of the River Aller as ‘moderate’, on account of its macrophyte status, whilst Horner Water has been classified as ‘good’ (P. Grigorey, pers. comm. 22nd July 2013).

EA Monthly Water Quality sampling 2000-2010	SS (mg L^{-1})	DRP (mg L^{-1})	TON (mg L^{-1})	pH	TON in groundwater* (mg L^{-1})
Aller	20.08	0.05	11.73	7.98	2.68
	(3 - 1,290)	(0.01)	(1.95)	(0.26)	(0.90)
Horner Water	11.67	0.03	5.09	7.77	-
	(3 - 726)	(0.01)	(3.23)	(0.30)	-

Table 3.1 Mean monthly values and standard deviation (in brackets) for key water quality variables in Rivers Aller and Horner Water, EA 2000-2010. SS data were not normally distributed, therefore minimum and maximum values are given instead of standard deviation. SS – suspended solids, DRP – reactive soluble P, TON – total oxidised N. * Groundwater data is available from a private borehole in the upper reaches of the Aller catchment between 2003-2009, measured twice per year.

B. Field sampling and laboratory analysis

A combined strategy of stratified spatially distributed soil sampling was applied to allow for the requirements of both classical statistics and geostatistics. The soils described are the lead series of the soil associations found in the two catchments according to the National Soil Map (Soil Survey of England and Wales, 1983); in this study, soils have been grouped into three broad texture categories of clay, loam and peat (having a peaty topsoil) (Findlay et al., 1984) (Table 3.2). Four land use categories were defined: arable and grass ley, permanent pasture, moorland and woodland. In each catchment, twelve random sampling points were identified within each soil type and land use combination, using ArcGIS 9.3.1. (ESRI, Redlands, CA, USA), with a minimum distance of 50 m between individual samples. A total of 205 soil samples were collected in July and September 2010 in the Aller and Horner Water catchments, giving an overall sampling density of 5.18 samples km^{-2}. Sampling density in the Aller catchment was 6.31 samples km^{-2} and in the Horner Water catchment 4.27 samples km^{-2}, which compares favourably with published studies that quantify spatial variability of soil properties at a landscape scale. For example, Bruland et al. (2006) used average sampling density 0.16 samples km^{-2} and Rivero et al. (2007) 0.27 samples km^{-2}. The greater sampling density in the Aller catchment was due to a greater diversity of soil-land use combination categories. Samples were taken to 5 cm depth to characterise the 'active' surface soil properties subject to overland flow, using plastic rings with a 10 cm diameter (volume of 408.56 cm^3). Random points were located in the field using Garmin GPS device with 10 m accuracy. Allocation to land use categories was checked in the field and corrected, if necessary, to ensure that each point was appropriately located in terms of local, contemporary land use. The distribution of sampling points is shown in Fig.3.7.

Soil category	Soil series	Soil group (Avery, 1980)	FAO (1993)	USDA (1999)
Clay	Evesham	4.1 Calcareous pelosols	Calcic cambisols	Haplaquepts
	Worcester	4.3 Argillic pelosols	Orthic luvisols	Hapludalfs
Loam	Crediton, Milford, Newnham, Rivington, Wigton Moor	5.4 Brown earths	Dystric cambisols	Dystrochrepts
	Larkbarrow	6.3 Podzols	Placic podzols	Orthods
Peat	Lydcott	6.5 Stagnopodzols	Placic podzols	Aquods
	Wilcocks	7.2 Stagnohumic gley soils	Humic gleysols	Humaquepts

Table 3.2 The allocation of soil series in the study to sampling categories.

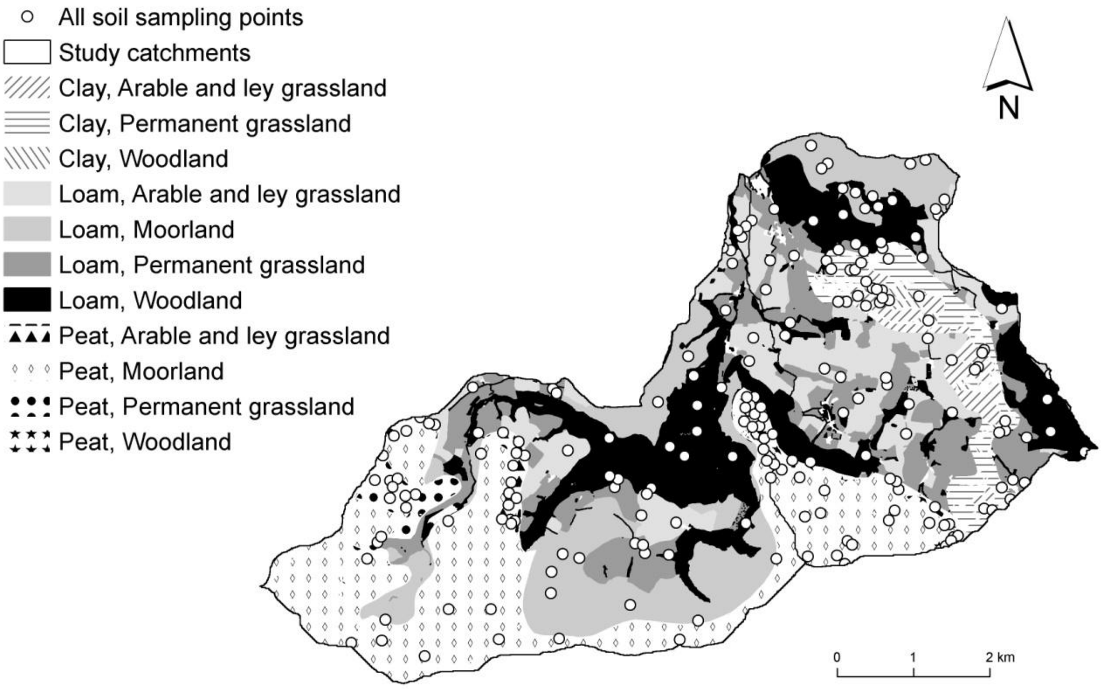

Fig. 3.7 Distribution of random soil sampling points stratified by soil type and land use.

The samples were weighed, oven dried at 45°C until constant weight and re-weighed in the laboratory to determine wet and dry weight. They were then passed through a 2 mm sieve to remove stones and vegetative matter before being milled and analysed for TC, TN and TP.

Bulk density was calculated as:

$$BD = s/v \qquad \text{Eq. 3.1}$$

where BD is the bulk density of the soil (g cm^{-3}), *s* is the mass of dry soil (g) and *v* is the volume of the sampling tin (cm^3).

For TC, TN and $\delta^{15}N$ analysis the soil was finely ground and then analysed on an elemental analyser (NA2000, Carlo Erba Instruments, Milan, Italy) linked to a SerCon 20-22 isotope ratio mass spectrometer (SerCon Ltd., Crewe, UK) at Rothamsted Research – North Wyke. Total phosphorus (TP) content was determined using sulphuric acid extraction method by Saunders and Williams (1955), which also allows calculation of the organic (OP) and inorganic (IP) phosphorus fraction. In both analyses, reference standards were used for analytical quality control purposes.

C. Statistical analysis

Geostatistical analysis was conducted to elucidate the spatial patterns of soil variability within the two study catchments. Omni-directional experimental semivariograms that quantify the dissimilarity γ(**h**) between observations as a function of the separation distance **h** were computed in ArcGIS 9.3.1 (ESRI, Redlands, CA, USA) as half the average squared difference between the components of every data pair:

$$\hat{\gamma}\,(\mathbf{h}) = ½\, \boldsymbol{N}(\mathbf{h}) \sum_{(\alpha=1)}^{N\,(\mathbf{h})} [z(\mathbf{u}_\alpha - z(\mathbf{u}_\alpha + \mathbf{h})]^2 \qquad \text{Eq. 3.2}$$

where $N(\mathbf{h})$ is the number of data pairs for a given distance and $z(\mathbf{u}_\alpha)$ denotes a set of soil variable values (Goovaerts, 1998).

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Fig. 3.8 Generalised semivariogram and key features. Source: Anderson and Kuhn (2008)

Sill variance is the maximum value that the variogram reaches after the initial increase (Fig. 3.8). It depicts the total variance of the process. The range is the distance at which the variogram reaches the sill and beyond which the process is no longer spatially dependent. The nugget is the variance at lag distance 0 and represents a combination of measurement error and variation over distances less than the shortest sampling interval (Webster and Oliver, 2001).

High nugget variance indicates a high, unquantified, fine-scale variability as well as measurement error, while high sill values indicate that soil properties are more heterogeneous (Bruland et al., 2006). The ratio of nugget to sill variance can be used as a measure of the strength of spatial correlation, whereby a ratio of < 0.25 depicts strong, 0.25-0.75 medium and > 0.75 weak degree of spatial auto-correlation (Cambardella et al., 1994).

Semivariogram sensitivity to different parameters and properties (eg. lag size, number of lags, trend and anisotropy) was tested and the optimal set of parameters was chosen based on the physical knowledge of the area and the plausibility of the model output (Goovaerts, 1998). To enable fair comparison between the two study catchments, the lag size was standardised at 200 m or the average distance between sampling points across the two study catchments (Webster and Oliver, 2001). The number of lags was chosen so as to give a semivariogram extent of approximately half the distance between the furthest sampling points within the study area. Point measurements of soil variables were extrapolated to un-measured locations by fitting generalised least-squares regression algorithms to the experimental semivariogram (Oliver and Webster, 1991) in ArcGIS 9.3.1. The best fitting model was selected on the basis of cross-validation as outlined by Webster and Oliver (2001) whereby the mean error should be 0, mean square error should be small and mean squared deviation ratio should be as close to 1 as possible. Spatial variability was visualised using simple kriging with declustering as sampling points were not evenly distributed. Prior to geostatistical analysis, all data were standardized using normal score transformation to allow comparison of model parameters between variables with different units (Peukert et al., 2012).

Exploratory data analysis using the Kolmogorov-Smirnov test showed that most soil properties were not normally distributed, with the exception of TP, OP and IP, the latter following log transformation. Therefore with the exception of P, data for all variables was analysed using non-parametric statistics, as normality could not be achieved through any transformation. Differences in soil properties between the two catchments, soil types and land uses were examined using the Mann-Whitney U test and Kruskal-Wallis H test. For all three P variables, t-test and one-way Anova were applied. Spearman rank correlation was used to examine the relationship between different soil properties. All statistical analyses were carried out in IBM SPSS v.19 (IBM Armonk, New York, USA) and MS Excel 2007 (Microsoft Corporation, Redmond, USA).

Calculation of 95 % confidence limits for the ratio of two standard deviations (calculated as square root of the nugget:sill ratio) (Davies, 1967) was used to compare the variability of soil properties between the two study catchments. The same test was used to compare the variability of bulk density, soil C and TP between this dataset and the UK National Soil Research Institute (NSRI) data (NSRI, 2012). The NSRI dataset provides a single value for bulk density and soil organic carbon content for each combination of soil series and arable, grass ley, permanent grassland and "other" land uses, respectively. As the NSRI data does not provide any values of soil bulk density and organic C for the two peaty soil series (Lydcott and Wilcocks) in arable land use, the available values for permanent grassland for these soil series were used. Conversely, the NSRI data set provides a single mean, minimum and maximum value of TP content for each soil series, irrespective of land use. Minimum and maximum estimates of soil C and TP stocks from the geostatistical survey were calculated as $minStock=\sum minStorage*a$ and $maxStock=\sum maxStorage*a$, where *minStock* and *maxStock* are sums of the lowest and highest estimates of C and P stocks in all classes presented on the krigged surface maps (in t and kg, respectively); *minStorage* and *maxStorage* are minimum and maximum estimates in g cm^{-2} within each class and *a* is the area of each class in cm^2.

Soil C stock from the NSRI dataset was calculated in tonnes as:

$$Cstock = \sum_{(n=1)}^{34}(C*BD*d*a/1{,}000{,}000) \qquad \text{Eq. 3.3}$$

where C is % carbon, BD is bulk density in g cm^{-3}, *d* is soil depth of 5 cm, *a* is the area in cm^2 and *n* is the number of available NSRI values for different soil series/land use combinations. TP stock from the NSRI dataset was calculated in kg as:

$$TPstock = \sum_{(n=1)}^{10}(TP*BD*d*a/1{,}000{,}000) \qquad \text{Eq. 3.4}$$

where TP is soil P content in mg kg^{-1}, BD is bulk density in g cm^{-3}, *d* is soil depth of 5 cm, *a* is the area in cm^2 and *n* is the number of soil series. Three separate estimates of TP stocks were made using the mean, minimum and maximum TP values available in the NSRI data set for each soil series.

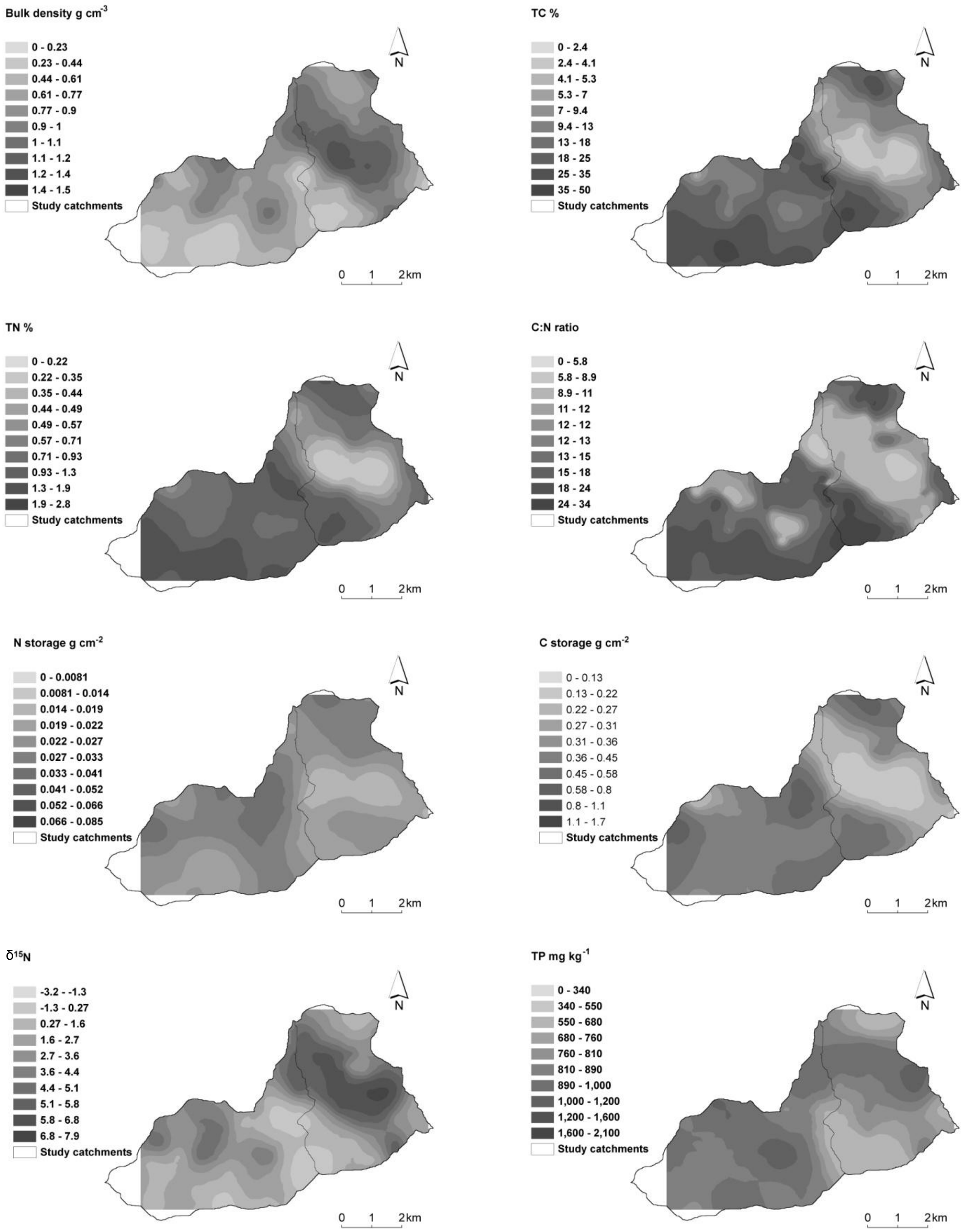
IV. RESULTS

A. Characterisation of soil properties in the two contrasting study catchments

The spatial interpolation of soil properties in the two study catchments is visualised in Fig. 3.9. Table 3.3 summarises the parameters of the fitted theoretical semivariograms within the two study catchments (Figs. 3.10-3.12, pp. 206-210). The results show a stronger degree of spatial dependence of soil properties in the Aller than in the Horner Water catchment, with all soil properties, except for bulk density and $\delta^{15}N$ having a significantly lower nugget:sill ratio (Table 3.3). Bulk density, TP, IP, OP, C:N ratio, $\delta^{15}N$ and carbon storage showed a longer range of spatial auto-correlation in the Aller catchment than in Horner Water. The exponential model provided the best estimate of spatial variability for six variables in the Aller catchment but only one variable (IP) in the Horner Water catchment.

In the Aller catchment, the theoretical semivariograms for seven out of the 10 variables do not reach a sill within the extent of the empirical semi-variogram, however they still show strong spatial dependence. In the Horner Water catchment, the semi-variograms for all variables show shorter ranges than in the Aller catchment, with the exception of TN, TC and N storage, which do not reach a sill within the extent of the empirical semivariogram (Table 3.3).

Median soil bulk density, TC, TN, C:N ratio, C storage, N storage, TP and OP differed significantly between the two study catchments. Median soil IP content and $\delta^{15}N$ did not differ significantly between the two study catchments (Table 3.4).


Bulk density g cm-3
0 - 0.23
0.23 - 0.44
0.44 - 0.61
0.61 - 0.77
0.77 - 0.9
0.9 - 1
1 - 1.1
1.1 - 1.2
1.2 - 1.4
1.4 - 1.5
Study catchments
TC %
0 - 2.4
2.4 - 4.1
4.1 - 5.3
5.3 - 7
7 - 9.4
9.4 - 13
13 - 18
18 - 25
25 - 35
35 - 50
Study catchments
TN %
0 - 0.22
0.22 - 0.35
0.35 - 0.44
0.44 - 0.49
0.49 - 0.57
0.57 - 0.71
0.71 - 0.93
0.93 - 1.3
1.3 - 1.9
1.9 - 2.8
Study catchments
C:N ratio
0 - 5.8
5.8 - 8.9
8.9 - 11
11 - 12
12 - 12
12 - 13
13 - 15
15 - 18
18 - 24
24 - 34
Study catchments
N storage g cm-2
0 - 0.0081
0.0081 - 0.014
0.014 - 0.019
0.019 - 0.022
0.022 - 0.027
0.027 - 0.033
0.033 - 0.041
0.041 - 0.052
0.052 - 0.066
0.066 - 0.085
Study catchments
C storage g cm-2
0 - 0.13
0.13 - 0.22
0.22 - 0.27
0.27 - 0.31
0.31 - 0.36
0.36 - 0.45
0.45 - 0.58
0.58 - 0.8
0.8 - 1.1
1.1 - 1.7
Study catchments
δ15N
-3.2 - -1.3
-1.3 - 0.27
0.27 - 1.6
1.6 - 2.7
2.7 - 3.6
3.6 - 4.4
4.4 - 5.1
5.1 - 5.8
5.8 - 6.8
6.8 - 7.9
Study catchments
TP mg kg-1
0 - 340
340 - 550
550 - 680
680 - 760
760 - 810
810 - 890
890 - 1,000
1,000 - 1,200
1,200 - 1,600
1,600 - 2,100
Study catchments
N
0 1 2 km

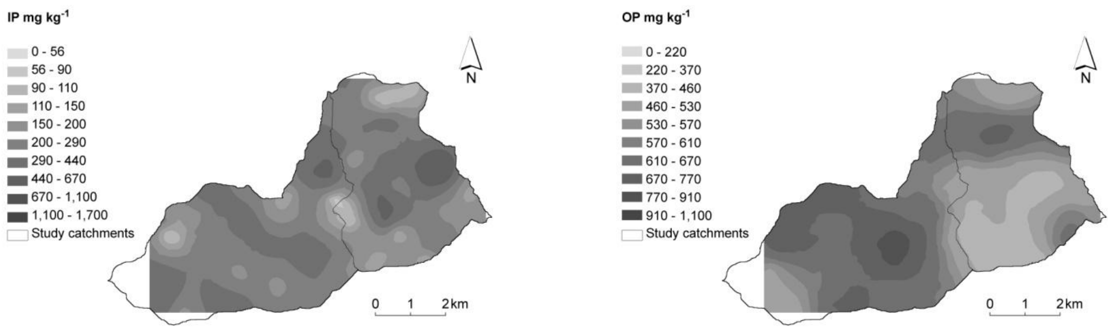


Fig. 3.9 Kriged surfaces for soil properties broadly reflect the land use and soil types in the two study catchments. TC – total carbon, TN – total nitrogen, TP – total phosphorus, OP – organic phosphorus, IP – inorganic phosphorus, $\delta^{15}N$ – stable N isotope.

Soil parameter	nugget	range	sill	nugget:sill	dependence	model	lag
Aller							
Bulk density	0.31	2806.96	1.08	0.29	medium	spher	200x16
TN	0.26	3190.61	1.11	**0.24**	strong	exp	
TC	0.22	2891.27	1.19	**0.19**	strong	spher	
C:N ratio	0.12	3190.61	1.29	**0.10**	strong	spher	
TP	0.21	3190.61	1.18	**0.18**	strong	exp	
IP	0.50	2940.90	1.19	**0.42**	medium	spher	
OP	0.32	3190.61	1.17	**0.28**	medium	exp	
$\delta^{15}N$	0.15	3190.61	1.31	0.11	strong	exp	
C storage	0.26	3190.61	1.09	**0.24**	strong	exp	
N storage	0.40	3190.61	1.03	**0.39**	medium	exp	
Horner							
Bulk density	0.36	1173.47	0.98	0.37	medium	spher	200x16
TN	0.59	3190.61	0.97	**0.61**	medium	spher	
TC	0.52	3190.61	0.98	**0.53**	medium	spher	
C:N ratio	0.73	2599.01	1.03	**0.71**	medium	spher	
TP	1.02	2071.27	1.08	**0.94**	weak	spher	
IP	0.75	545.33	1.14	**0.66**	medium	exp	
OP	0.91	2080.29	1.08	**0.84**	weak	spher	
$\delta^{15}N$	0.15	1216.07	0.96	0.15	strong	spher	
C storage	0.49	1041.44	1.02	**0.47**	medium	spher	
N storage	0.90	3190.61	1.14	**0.79**	weak	spher	

Table 3.3 Summary of geostatistical analysis in the two study catchments. Properties with significantly different nugget:sill ratios are highlighted in bold ($P < 0.05$). TC – total carbon, TN – total nitrogen, TP – total phosphorus, IP – inorganic phosphorus, OP – organic phosphorus, $\delta^{15}N$ – stable N isotope. Units: bulk density g cm^{-3}, C %, N %, total P mg kg^{-1}, IP mg kg^{-1}, OP mg kg^{-1}, $\delta^{15}N$ ‰, C storage g cm^{-2}, N storage g cm^{-2}.

	Aller					Horner					
	Mean	SD	CV %	Median	N	Mean	SD	CV %	Median	N	P <
Bulk density ($g\ cm^{-3}$)	0.87	0.37	42.94	0.97	110	0.71	0.37	51.23	0.81	94	0.002
TC (%)	13.91	14.83	106.63	6.06	111	19.05	16.04	84.22	11.73	94	0.001
TN (%)	0.80	0.60	74.85	0.56	111	1.05	0.63	59.36	0.88	94	0.001
C:N ratio	14.21	6.44	45.29	11.58	111	15.70	5.75	36.59	14.51	94	0.009
$\delta^{15}N$ (‰)	3.35	2.61	77.86	3.01	111	2.83	2.74	96.83	3.45	93	ns
TP ($mg\ kg^{-1}$)	764.36	317.35	41.52	763.35	111	911.49	308.22	33.81	872.26	94	0.001
IP ($mg\ kg^{-1}$)	235.65	231.22	98.12	161.36	111	245.74	188.81	76.84	190.58	94	ns
OP ($mg\ kg^{-1}$)	528.95	185.55	35.08	511.46	111	665.81	201.30	30.23	657.01	94	0.001
C storage ($g\ cm^{-2}$)	0.36	0.25	68.89	0.30	110	0.44	0.19	42.85	0.43	93	0.001
N storage ($g\ cm^{-2}$)	0.02	0.01	46.26	0.02	110	0.03	0.01	36.87	0.03	93	0.004

Table 3.4 Summary statistics and significant differences in the measured soil properties between the two study catchments, Mann-Whitney U test and t-test for TP, IP and OP variables. TC – total carbon, TN – total nitrogen, TP – total phosphorus, IP – inorganic phosphorus, OP – organic phosphorus, $\delta^{15}N$ – stable N isotope.

B. Possible mechanisms controlling the observed spatial variation

In both catchments, bulk density was strongly, negatively correlated with TC, TN, C:N ratio and C storage and strongly positively correlated with $\delta^{15}N$ (Table 3.5), which was also apparent from the mapped patterns of soil properties (Fig. 3.9).

Spatial distribution of TP, OP and IP in the study area followed a different pattern to the above variables. In the Aller catchment, TP and IP were weakly to moderately positively correlated with soil bulk density and negatively correlated with soil TC and C storage. Inorganic P was negatively correlated with N. Total P was strongly positively correlated with IP and OP but the latter two variables are only weakly positively correlated to each other. Carbon storage was strongly negatively correlated with $\delta^{15}N$. Bulk density was weakly negatively correlated with N storage (Table 3.5). In contrast, in the Horner Water catchment bulk density and N storage were moderately positively correlated. Nitrogen storage was also weakly negatively correlated with C:N ratio and weakly positively correlated with TP (Table 3.5).

All soil properties differed significantly between the 12 combinations of soil type and land use treatments ($P < 0.001$) (Table 3.6). Mean TC, TN and C:N ratio increased in the order arable < pasture < woodland < moorland while the pattern for soil bulk density was reversed. For TP the pattern was more complex but arable land use and permanent pasture contained the highest TP levels on all soil types.

	Bulk density ($g\ cm^{-3}$)	TC (%)	TN (%)	C:N ratio	TP ($mg\ kg^{-1}$)	IP ($mg\ kg^{-1}$)	OP ($mg\ kg^{-1}$)	$\delta^{15}N$ ‰	C storage ($g\ cm^{-2}$)
Aller									
TC %	-.888**								
TN %	-.862**	.966**							
C:N ratio	-.773**	.868**	.746**						
TP	.206*	-.254**		-.532**					
IP	.312**	-.345**	-.253**	-.503**	.779**				
OP				-.287**	.756**	.284**			
$\delta^{15}N$	.665**	-.747**	-.655**	-.860**	.557**	.534**	.280**		
C storage	-.683**	.912**	.885**	.796**	-.265**	-.324**		-.664**	
N storage	-.195*	.447**	.538**				.322**		.670**
Horner									
TC %	-.844**								
TN %	-.799**	.959**							
C:N ratio	-.813**	.888**	.752**						
TP				-.393**					
IP				-.234*	.752**				
OP				-.380**	.836**	.329**			
$\delta^{15}N$	.644**	-.687**	-.629**	-.638**	.294**		.256*		
C storage	-.313**	.714**	.719**	.568**				-.373**	
N storage	.380**			-.255*	.237*		.386**		.624**

Table 3.5 Spearman correlation coefficients for measured soil properties. Only significant relationships are shown. ** $P < 0.01$, * $P < 0.05$. TC – total carbon, TN – total nitrogen, TP – total phosphorus, IP – inorganic phosphorus, OP – organic phosphorus, $\delta^{15}N$ – stable N isotope.

Soil type	Land use		Bulk density (g cm^{-3})	TC (%)	TN (%)	C:N ratio	δ^{15}N (‰)	TP (mg kg^{-1})	IP (mg kg^{-1})	OP (mg kg^{-1})	C storage (g cm^{-2})	N storage (g cm^{-2})
Clay	Arable	Mean	1.24	2.04	0.24	8.49	7.17	978.04	484.69	493.34	0.12	0.015
		CV %	8	29	24	11	9	22	52	41	24	19
		N	8	8	8	8	8	8	8	8	8	8
	Pasture	Mean	1.06	4.84	0.50	9.67	5.37	981.36	334.18	647.18	0.25	0.026
		CV %	14	29	29	8	30	35	112	24	24	26
		N	17	17	17	17	17	17	17	17	17	17
	Woodland	Mean	0.85	11.20	0.83	12.58	3.16	935.15	249.91	685.24	0.39	0.031
		CV %	29	76	52	20	61	19	59	13	34	34
		N	10	10	10	10	10	10	10	10	10	10
Loam	Arable	Mean	1.18	3.37	0.37	9.18	5.81	957.93	364.62	593.31	0.19	0.021
		CV %	14	38	38	6	13	32	49	35	30	29
		N	21	21	21	21	21	21	21	21	21	21
	Pasture	Mean	1.04	5.58	0.55	9.91	4.29	989.09	257.73	731.36	0.28	0.028
		CV %	16	37	31	11	37	24	61	23	34	28
		N	23	23	23	23	23	23	23	23	23	23
	Moorland	Mean	0.58	26.09	1.29	18.77	1.82	683.62	159.11	524.98	0.52	0.029
		CV %	61	60	47	29	114	36	81	30	41	40
		N	24	24	24	24	25	24	24	24	24	24
	Woodland	Mean	0.68	20.35	1.16	16.68	1.00	786.07	214.87	571.20	0.51	0.032
		CV %	44	67	53	34	152	42	85	33	42	37
		N	24	25	25	25	25	25	25	25	24	24
Peat	Arable	Mean	0.99	8.72	0.62	12.76	5.11	957.17	264.76	692.40	0.42	0.030
		CV %	15	109	70	22	30	35	71	26	95	60
		N	12	13	13	13	13	14	14	14	12	12
	Pasture	Mean	0.93	11.74	0.85	13.53	4.78	852.78	143.36	709.42	0.50	0.037
		CV %	21	45	35	16	26	41	161	30	32	24
		N	15	15	15	15	14	14	14	14	15	15
	Moorland	Mean	0.32	35.08	1.52	23.35	0.89	750.39	248.27	502.12	0.49	0.021
		CV %	42	38	42	19	225	48	80	47	35	32
		N	24	24	24	24	23	24	24	24	24	24
	Woodland	Mean	0.52	26.33	1.24	19.11	0.38	575.71	110.04	466.47	0.44	0.024
		CV %	73	68	57	30	428	39	74	42	55	55
		N	26	25	25	25	25	25	25	25	25	25

Table 3.6 Summary statistics of the measured soil properties in different land use treatments on different soil types.

C. Baseline for the monitoring of the effectiveness of land management interventions to mitigate diffuse water pollution

The kriged surfaces of soil variables showed a meaningful pattern in line with the physical knowledge of the study area (Fig. 3.9). Prediction of soil properties to un-sampled locations estimated the highest bulk density and $\delta^{15}N$ values for the most intensively managed agricultural land in the lower lying Aller catchment as well as the upper reaches of the Horner Water, while highest soil TC, TN, C:N ratio and C storage were predicted for open moorland, and to a lesser extent woodland outside farm boundaries. The spatial distribution of IP also identified hotspots of highest soil P concentrations in areas with most intensive land use.

D. Comparison of spatial variability and key nutrient stocks (C and P) using the detailed geostatistical approach and the NSRI dataset

A comparison of mean values and variability of bulk density, soil C and TP with the National Soil Research Institute (NSRI) dataset for the same soil types and land uses shows a significantly higher variability of bulk density and soil C on clay in semi-natural land use and bulk density on loam in arable land use using the geostatistical approach, while the variability of soil C on peat in permanent pasture estimated from the NSRI data is greater (Table 3.7).

			Holnicote case study			NSRI		
Soil type	Land use		Bulk density (g cm^{-3})	C (%)	TP (mg kg^{-1})	Bulk density (g cm^{-3})	C (%)	TP (mg kg^{-1})
Clay	Arable	Mean	1.24	2.04	978.04	1.2	3.18	756.59
Evesham Worcester		Std. Deviation	0.1	0.6	213.86	0.05	0.79	197.58
		N	8	8	8	4	4	2
	PP	Mean	1.06	4.84	981.36	1.06	4.15	
		Std. Deviation	0.15	1.42	345.05	0.04	0.78	
		N	17	17	17	2	2	
	OT	Mean	0.85	11.2	935.15	1.08	3.75	
		Std. Deviation	**0.25**	**8.54**	179.75	**0.01**	**0.35**	
		N	10	10	10	2	2	
Loam	Arable	Mean	1.18	3.37	957.93	1.26	2.79	738.4
Crediton Larkbarrow Milford Newnham Rivington Wigton Moor		Std. Deviation	**0.17**	1.29	309.68	**0.05**	0.77	281.18
		N	21	21	21	10	10	6
	PP	Mean	1.04	5.58	989.09	1.04	5.28	
		Std. Deviation	0.16	2.09	235.03	0.1	2.9	
		N	23	23	23	6	6	
	OT	Mean	0.63	23.16	735.89	1	7.8	
		Std. Deviation	0.33	14.85	292.88	0.2	9.42	
		N	48	49	49	6	6	
Peat	Arable	Mean	0.99	8.72	957.17			
Lydcott Wilcocks		Std. Deviation	0.15	9.53	331.12			
		N	12	13	14			
	PP	Mean	0.93	11.74	852.78	0.76	16.1	
		Std. Deviation	0.2	**5.28**	350.35	0.23	**12.3**	
		N	15	15	14	2	2	
	OT	Mean	0.43	30.62	661.27	0.33	32.15	774.46
		Std. Deviation	0.3	16.39	308.35	0.01	6.86	214.66
		N	50	49	49	2	2	2

Table 3.7 Comparison of the variability of selected soil properties recorded in this study with the NSRI data. NSRI dataset presents one average value for each combination of soil type and land use treatment, where available, except for TP where values are independent of land use. Significantly different standard deviations, and hence variability, are highlighted ($P < 0.05$).

The mapped mean values of key soil properties available from the NSRI dataset show a more uniform spatial distribution with abrupt class boundaries, as compared to those derived from the detailed geostatistical approach (Fig. 3.13).

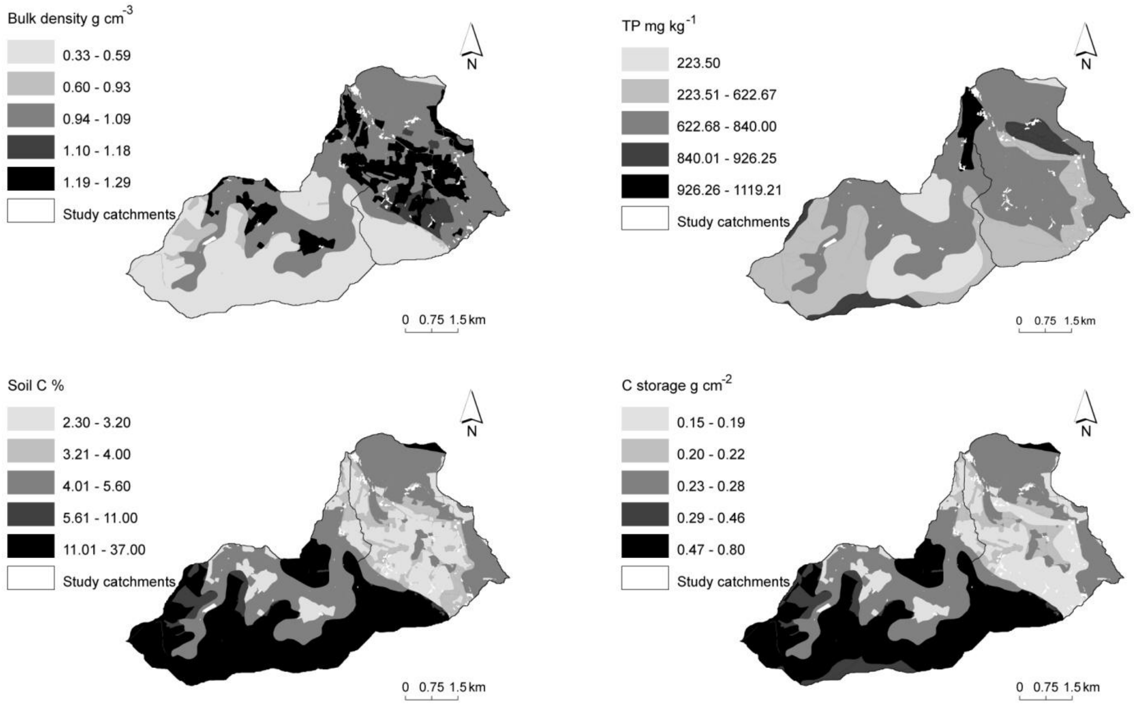


Fig. 3.13 Mapped mean values of soil properties in soil series under different land uses available from the NSRI dataset show a more uniform spatial distribution of soil properties at a catchment scale, with abrupt class boundaries. The white gaps represent built-up areas and a reservoir.

The calculation of C and TP stocks in the top 5 cm of the soil profile shows comparable values using both the high resolution geostatistical approach, and the average values for individual soil series (Table 3.8).

	C stock (t)			P stock (kg)		
	mean	min	max	mean	min	max
NSRI	146.51	-	-	1.12	0.50	2.40
Geostatistical survey	-	132.35	168.01	-	1.13	1.48

Table 3.8 Comparison of the estimated C and TP stocks in the top 5 cm of the soil profile within the study area, using the mean NSRI values for individual soil series and the high resolution geostatistical survey approach.

V. DISCUSSION

A. Characterisation of soil properties between the two contrasting study catchments

The stronger degree of spatial dependence and longer range of spatial auto-correlation in the Aller catchment indicates a homogenisation of the spatial variability of soil properties, perhaps due to intensive agricultural land use (Paz-Gonzalez et al., 2000, Li et al., 2010). This spatial homogenisation effect is supported by the observation that seven out of the ten soil properties in the Aller catchment did not reach a sill within the extent of the experimental semivariogram, indicating that variance continued to increase without a limit at this plot scale (Marriott et al., 1997).

Conversely, the significantly higher nugget:sill ratios in the Horner Water catchment, did indicate a higher degree of small-scale variation below the soil sampling resolution used in this study. Similar results have been found by other researchers in semi-natural habitats, particularly in forest soils (Li et al., 2010, Worsham et al., 2010). Furthermore, in this catchment, only three soil properties (TN, TC and N storage) did not reach a limit of spatial auto-correlation. These long-range auto-correlations may be related to landscape-scale controls, such as climate or large continuous extent of semi-natural habitat, that span several soil types (Rivero et al., 2007, Stutter et al., 2009). Conversely, the shorter range of spatial dependence of TC in the Aller compared to Horner Water catchment may indicate a greater patchiness of soil TC distribution, possibly due to regular organic manure applications. Li et al. (2010) also found that land use affected both the spatial variability and central tendency of soil TC, TN and C:N ratio, however, similar to this study, it also did not affect the spatial variability of bulk density, but only its central tendency.

The exponential model provided the best estimate of spatial variability for six variables in the Aller catchment and only one variable (IP) in Horner Water catchment, indicating a difference in the underlying processes controlling spatial structure. Webster and Oliver (2001) describe the spherical function as one representing the spatial variation of features that appear as patches of large and small values, with the range of the model representing the average diameter of the patches, while the exponential model is deemed to describe processes where differences in soil type are the main source of soil variation and the extent of the structures is random (Webster and Oliver, 2001). The greater prevalence of such random processes in the Aller catchment may be due to the observed homogenisation of spatial variability of soil properties and the effects of land use in this catchment.

B. Possible mechanisms controlling the observed spatial variation

Three soil properties – the bulk density, IP and δ^{15}N, readily describe the degree of anthropogenic influence on soils in a catchment (Brady and Weil, 1999, Fraterrigo et al., 2005, Bol et al., 2008). The greater prevalence of peaty and forest soils with high organic matter content and low bulk density explains the significantly lower soil bulk density and higher TC, TN, C:N ratio, OP, C and N storage in the Horner Water catchment. However, the lack of significant difference in IP concentration and δ^{15}N values between the two study catchments is notable and suggests that, where applied, the rates of fertiliser input and its effect on increased organic matter turnover are similar between the two catchments.

Organic matter has a dominant influence on many soil physical, chemical and biological properties, however tillage exposes sub-soil organic matter and aids overall C mineralisation (Brady and Weil, 1999). Subsequently, soil with reduced organic matter content following such disturbances is less effective in promoting soil structural stability (Brady and Weil, 1999, Kechavarzi et al., 2010), resulting in increased soil bulk density; along with the effects of trampling by grazing animals and compaction by farm traffic. The addition of inorganic and organic fertilisers accelerates the decomposition of organic matter (Senbayram et al., 2008), including that of the more stable soil organic matter fraction (Bradford et al., 2008). This positive ‘priming effect’ has been defined as “strong short-term changes in the turnover of soil organic matter caused by comparatively moderate treatments of the soil” (Kuzyakov et al., 2000, p. 1485). As the losses of inorganic N tend to increase with the rates of fertiliser application, soil processes continue to discriminate against the heavier δ^{15}N isotopes because of N process fractionation (Senbayram et al., 2008), leading to soil $\delta^{15}N$ enrichment as a result of the greater 'leakiness' of the system (Bol et al., 2008). Overall, the outcome of this soil N process fractionation may explain the observed soil $\delta^{15}N$ enrichment on most intensively managed arable land. However, it must also be noted that $\delta^{15}N$ enrichment can also result from long-term application of manure. Manure as a N source material tends to be enriched in $\delta^{15}N$ compared to most soils (Riga et al., 1971, Senbayram et al., 2008). A combination of both process and source $\delta^{15}N$ fractionation are likely to be responsible for the differences in soil $\delta^{15}N$ enrichment observed in the Aller and Horner Water catchments.

Reduced C:N ratios observed in the agricultural Aller catchment further favours higher organic matter turnover (Brady and Weil, 1999). A study by Mooshammer et al. (2012) found that N mineralization and nitrification increased with decreasing C:N ratio. In low C:N environments a higher proportion of available N is in the form of inorganic cations ammonium (NH_4^+-N) and nitrate (NO_3^--N) (Pierzynski et al., 2000). This results in a greater pool of NO_3^--N that is potentially available for leaching to the aquatic environment (Pierzynski et al., 2000), thus reducing N storage and increasing 'leakiness' from soil to water. Long-term fertilizer addition increases N mineralization rates with a corresponding increase of NO_3^--N production, with mineral fertilizer applications in particular promoting the mineralization of recalcitrant organic N (Zhang et al., 2012). These processes contribute to the overall reduction of N storage in the Aller catchment and an increased pool of NO_3^--N that is available for leaching into the aquatic environment, reflected in higher average monthly TON concentrations in this catchment (Table 3.1). The low C:P ratio observed also favours mineralisation of P from organic to inorganic forms resulting in a surplus of IP as compared to plant requirements (Pierzynski et al., 2000). This mechanism offers a plausible explanation for the positive correlation between TP, IP and bulk density and negative correlation with soil TC and C storage as well as the negative correlation between C storage and $\delta^{15}N$ in the Aller catchment.

Conversely, the higher C:N ratio in the Horner Water catchment suggests slower decomposition of organic matter due to N limitation and confirms the more recalcitrant nature of soil organic matter in peaty and forested environments (Brady and Weil, 1999). Such environments/ecosystems also promote the conversion of inorganic N to organic forms (Pierzynski et al., 2000). The resulting greater prevalence of organic N forms may explain the positive correlation between soil bulk density and N storage in this catchment, as organic N is not so readily lost from the soil and storage therefore increases with increasing bulk density.

C. Baseline data to monitor the effectiveness of land management interventions to mitigate diffuse water pollution from agriculture at a catchment scale

Land use has been shown to have a long-lasting, multi-decadal effect on the spatial variability of soil properties (Fraterrigo et al., 2005). Undisturbed ecosystems are typically spatially heterogeneous (Gilliam and Dick, 2010), with this heterogeneity influencing the “patchiness of populations of soil organisms and the ecosystem processes that they carry out” (Ettema and Wardle, 2002, p. 182), such as nutrient cycling and decomposition (Li et al., 2010). Fromm (1993) found that at a farm scale, management practice and cultivation had more influence on the spatial distribution of soil biota than soil types. Thus, landscape-scale spatial homogenisation of soil properties, and by implication of the soil ecosystem, is likely to have long-term implications for ecosystem functioning (Ettema and Wardle, 2002, Li et al., 2010). Gilliam and Dick (2010) found that in pasture soil factors such as available N, organic matter, soil moisture, pH, calcium and magnesium, were more closely linked to plant variables than they were in an old abandoned field, indicating that soil physical and chemical properties exert a stronger control in altered ecosystems (Ettema and Wardle, 2002). While linkages between the spatial heterogeneity of soil physical and chemical properties and terrestrial above- and below-ground biodiversity have been explored (Ettema and Wardle, 2002, Gilliam and Dick, 2010), the implications of the altered spatial heterogeneity and associated soil processes for the ecological status of aquatic environments are unclear. Meanwhile, chronosequence analysis has shown that restoration of soil spatial heterogeneity (Boerner et al., 1998, Li et al., 2010) and soil physical and chemical properties (Matlack, 2009) spans decades, in contrast to the short-term expectations for the outcomes of measures to mitigate diffuse water pollution from agriculture at a landscape scale. Hence this study lends support to the calls for realistic expectations for the outcomes of ecosystem management in terms of the timescales over which improvements to ecological status of terrestrial ecosystems and associated watercourses can be detected and for an improved understanding of complex terrestrial/freshwater linkages at a range of scales (Harris and Heathwaite, 2012).

D. Comparison of spatial variability and key nutrient stocks (C and P) using the detailed geostatistical approach and the NSRI dataset

The results suggest that the national dataset under-represented the true variability of: (i) soil bulk density and C content in clay soils under semi-natural land use and (ii) bulk density in loamy soils under arable crops. Conversely, the national dataset over-estimated the variability of C content in peat under permanent pasture. The national dataset clearly provided a more uniform visualisation of the spatial variability of bulk density, C and TP, less directly linked to land management impacts, than the detailed geostatistical approach. However, despite these differences, the calculation of C and TP stocks in the top 5 cm of the soil profile did generally show comparable values using the data from the high resolution survey approach or the average values for individual soil series from the national dataset. These results seem to contradict other studies, which identified a need for a higher resolution of soil sampling in semi-natural habitats because of their greater spatial variability of soil properties (Paz-Gonzalez et al., 2000, Li et al., 2010, Worsham et al., 2010), in order to characterise soil C stocks accurately; at least for the top 5 cm of the soil profile that is most susceptible to erosion. However, such agreement does not necessarily negate the need for high resolution soil sampling (as was undertaken in the present study), as such studies are required to identify those locally impacted areas that are most likely to act as sources of surface runoff and diffuse water pollution. Therefore, while at these two catchment scales, end-users could confidently rely upon national-scale soils data to broadly describe the nutrient stocks across the catchment, it was not possible to map the detailed spatial distribution of key soil properties adequately in these catchments without a high resolution sampling strategy. Hence, for practical management purposes, such as the understanding of the contributing source areas of macronutrients, detailed geostatistically-based sampling strategy is a useful research tool.

VI. CONCLUSIONS

Geostatistical analysis allowed detailed visualisation and quantification of the spatial variability of soil properties in two study catchments at a landscape scale and provided a baseline for the comparison and evaluation of the effectiveness of ecosystem management in mitigating diffuse pollution from agriculture. Intensive land use in the agricultural catchment resulted in greater homogenisation and reduced variability of soil properties at a landscape scale, indicating large scale alterations of the ‘natural’ variability inherent in these ecosystems. This finding may have significant implications for the scale of land-use changes that may be required to restore ecosystem functioning to a more natural state and effect desired changes to the ecological status of both terrestrial habitats, but also the receiving surface waters. While the national dataset shows that it can be relied upon for a broad quantification of nutrient stocks in the two study catchments, for practical management purposes, a detailed geostatistical approach is required. Geostatistical analysis should therefore be included in the future design of catchment scale research and monitoring schemes to quantify the long-term effects of mitigation programmes and elucidate the time frame over which landscape scale improvements in soil properties and corresponding ecosystem processes can be achieved.

Chapter 4

QUANTIFYING FLUVIAL EXPORT OF SEDIMENT AND ORGANIC CARBON IN TWO CONTRASTING SOUTH-WEST CATCHMENTS: IMPLICATIONS FOR WATER QUALITY AND LAND MANAGEMENT

I. ABSTRACT

The fluvial export of organic carbon (particulate and dissolved) plays an important role in the transfer of organic carbon from terrestrial to aquatic ecosystems, with implications for the ecological status of water courses and the understanding of the global carbon cycle. Many factors, such as topography, hydrological regime and vegetation are known to influence the fluvial export of dissolved organic carbon (DOC) from catchments. However, most work to date has focused on DOC losses from either forested or peaty catchments, with only limited studies examining the controls and rates of total fluvial carbon fluxes from agricultural catchments, particularly during storm events.

This research quantified the fluxes of total suspended sediment (SS), DOC and total particulate carbon (TPC) and examines the different controls on these fluxes in two adjacent catchments with contrasting agricultural and semi-natural land-use. Results showed that the agricultural catchment exports significantly higher median peak event SS concentrations on a storm-by-storm basis than the semi-natural catchment (312 vs. 130 mg L^{-1}, $P = 0.029$), although these exports are short-lived, as the catchment is hydrologically very responsive. The semi-natural catchment displayed more attenuated hydrological behaviour, with longer response times (median lag from start of event to peak discharge of 885 vs. 615 minutes, $P = 0.045$), higher % TPC content (21 % vs. 14 %) and higher DOC instantaneous fluxes (10.42 g s^{-1} vs. 4.14 g s^{-1}). Peak discharge exerted a greater control over peak SS, TPC and DOC concentrations in the agricultural than the semi-natural catchment. During small and medium size events, peak discharge explained a significant amount of SS and TPC variability in the

agricultural catchment (R^2 = 0.94 and 0.86, resp., $P < 0.001$), while it was not significantly related to these variables in the semi-natural Horner Water. Peak discharge was only significantly related to peak event DOC concentrations in the agricultural, but not in the semi-natural catchment, during small, medium and extreme rainfall events (R^2 = 0.44, $P < 0.05$). Baseflow DOC concentrations in the agricultural catchment were significantly higher ($P < 0.05$) and the quality of DOC differed markedly between the two study catchments, with more humic, higher molecular weight compounds prevailing in the agricultural catchment and simpler, lower molecular weight compounds prevailing in the semi-natural catchment. The greater prevalence of higher molecular weight compounds in the agricultural catchment may indicate enhanced microbial turnover of fluvial DOC and preferential mineralisation of simpler compounds as well as additional allochtonous terrestrial sources.

During an eight month period for which a comparable continuous turbidity record was available, the estimated SS yields from the agricultural catchment (25.5-116.2 t km^2) were higher than from the semi-natural catchment (21.7-57.8 t km^2). Further, despite the lower total soil carbon pool and lower water yield, the agricultural catchment exported proportionally more TPC (0.51-2.59 kg mm^{-1}) than the semi-natural catchment (0.36-0.97 kg mm^{-1}) and both catchments exported a similar amount of DOC (0.26-0.52 kg mm^{-1} in the Aller and 0.24-0.32 kg mm^{-1} in Horner Water), when normalised by the area and total discharge. In addition, the agricultural catchment supported a lower DOC:TPC ratio (0.15-1.01) than the semi-natural catchment (0.25-10.02), indicating an enhanced TPC input.

These results indicate that intensive agriculture may enhance the fluvial SS and TPC export and alter both the quantity and quality of DOC entering the fluvial environment, when compared with semi-natural land use. Thus, it is argued that enhancing semi-natural vegetation within intensive agricultural catchments could increase their resilience to more extreme hydrological events, anticipated as a result of climate change, and reduce the losses of sediment and carbon from these intensively managed areas.

II. INTRODUCTION

Human activities are currently estimated to be responsible for annual global carbon emissions of around 10 Gt, of which around 1.5 Gt may be a result of land use change (Trumper et al., 2009). The terrestrial biosphere contains about three-times as much stored carbon in the soil and vegetation as the atmospheric carbon pool, thus a small change in the terrestrial carbon pool may have significant implications for atmospheric CO_2 concentrations (Schuman et al., 2001). The stability of natural carbon pools under changing climate is of major concern (Whitehead et al., 2006) and ecosystem carbon management must play a critical part in the global climate change mitigation effort.

The fluvial export of total organic carbon (TOC), composed of dissolved (DOC) and particulate (POC) fractions, plays an important, yet often overlooked role in the loss of carbon from catchment systems. Each year streams and rivers transform or store nearly 2 Gt of terrestrial organic carbon, a large fraction of the global annual terrestrial net ecosystem production (NEP) (Battin et al., 2008). Whilst the total riverine organic carbon flux from UK rivers has been estimated to be a fairly modest amount when compared to Britain's national fossil fuel emissions (less than 1% in total in 1993), it is similar in magnitude to the estimates of carbon sequestration by wetlands and afforestation (Hope et al., 1997b).

DOC is thought to be the major component of fluvial TOC in most aquatic systems (Hope et al., 1997a, Dawson et al., 2002, Stanley et al., 2011). It is an important intermediate stage in the global carbon cycle and the global flux of terrestrial DOC (0.25 Gt C y^{-1}) represents the largest transfer of reduced carbon from the land to the ocean, with POC being estimated at 0.18 Gt C y^{-1} (Battin et al., 2008). Critically, DOC is the 'chemical backbone' of aquatic ecosystems (Stanley et al., 2011), influencing the light regime, energy and nutrient supply, pH and metal toxicity in the aquatic environment (Hope et al., 1994, Wallage et al., 2006, Whitehead et al., 2006). Human activities are undoubtedly altering DOC dynamics, but there are still significant gaps in our understanding of the net effects (Stanley et al., 2011), due to many counteracting soil processes and environmental factors (Chantigny, 2003). Increasing DOC concentrations over the past decades have been reported in rivers across Western Europe and North America (Evans et al., 2005), however the ecological consequences of these increasing concentrations are not clear (Evans et al., 2005, Stanley et al., 2011) and are rarely assessed on a catchment scale.

Since the onset of agriculture, human activities have accelerated soil erosion rates 10- to 100- fold above all estimated natural background levels (Montgomery, 2007a), resulting in an increased input of fine sediment and organic carbon into aquatic environments. Whilst significant amounts of particulate organic carbon are delivered to surface waters and re-deposited in the landscape through soil erosion, the ultimate fate of this carbon remains poorly understood (Lal et al., 2004a, Lal et al., 2004b, Van Oost et al., 2004, Quinton et al., 2010). National estimates of soil carbon losses by water erosion suggest that rivers are either a small source of C or can act as sinks by deposition of alluvium (Quinton et al., 2006).

Management activities that affect the degree of disturbance and rates of soil erosion are likely to cause an increase in the fluvial export of POC (Hope et al., 1997a, Dawson and Smith, 2007). However, an improved understanding of the fate of eroded carbon in the landscape and the effect of soil erosion on the potential to fix carbon in soil is needed (Quinton et al., 2006, Quinton et al., 2010), in order to assess the capacity of soils to act as a carbon sink at a landscape scale.

Many factors, including soils, topography, hydrological regime and vegetation are known to influence the fluvial export of carbon from catchments (Hope et al., 1997b). In temperate ecosystems, most of the terrestrial organic carbon is stored in the soil pool (Milne and Brown, 1997, Aitkenhead et al., 1999, Hope et al., 1997a, Hope et al., 1997b, Dawson and Smith, 2007), which has been found to be a good predictor of DOC in stream water, particularly in smaller catchments (Hope et al., 1997a, Aitkenhead et al., 1999). Agriculture alters the quality of dissolved organic matter in soils (Chantigny, 2003, Graeber et al., 2012), with a corresponding impact on the qualitative composition of fluvial DOC (Stanley et al., 2011). However, to date most work has focused on fluvial DOC losses from either forested or peaty upland watersheds (Hope et al., 1997a, Dawson et al., 2002) with only limited studies examining the controls and rates of combined total carbon (dissolved organic and particulate) fluxes from agricultural catchments (Hope et al., 1994, Dawson and Smith, 2007, Vidon et al., 2008, Stanley et al., 2011). So far, the direction and magnitude of agricultural impact on fluvial DOC dynamics in agricultural catchments is equivocal (Stanley et al., 2011), demonstrating the great challenge in understanding the effects of anthropogenic impact on DOC dynamics at catchment scales (Hernes et al., 2008).

This study tested the hypothesis that quality and quantity of the total sediment and fluvial carbon export will differ between the two neighbouring study catchments with contrasting land use. We hypothesised that 1) the agricultural Aller catchment will support increased concentrations, fluxes and yields of SS sediment, due to more intensive land use and higher soil bulk density and 2) the concentrations, fluxes and yields of TPC and DOC will be greater from the semi-natural Horner Water catchment, due to the prevalence of more carbon-rich soils and a greater total soil carbon pool.

Specifically, this study aims to contribute to the understanding of total organic carbon dynamics in agricultural and semi-natural watersheds by:

1. Comparing event-based hydrological characteristics of two adjacent study catchments with contrasting intensive agriculture and semi-natural land-uses;

2. Examining the controlling factors on total fluvial carbon fluxes in both catchments;

3. Examining the qualitative differences in DOC composition between the two study catchments;

4. Quantifying the fluvial fluxes of total suspended sediment, total dissolved and total particulate carbon in the two study catchments;

5. Providing a database with which the implications of sediment and carbon loss can be assessed in terms of water quality and land management.

III. MATERIALS AND METHODS

A. Study sites

Two adjacent, yet contrasting, study catchments, the Aller and Horner were chosen as they represent a hydromorphological and land use gradient, typical of south west England (Findlay et al., 1984), from a high altitude semi-natural moorland and woodland in a steep-sided valley, to a low lying intensively managed agricultural catchment. Climate, geology, soils and land use characteristics of the two study catchments are described in Chapter 3, Part A.

B. Field sampling

Rainfall data from Environment Agency weather stations (one in each catchment) were used in all analyses. The location of the rainfall and water quality monitoring sites considered in this Chapter is shown in Fig. 4.1.

DOC was sampled each month in baseflow or near-baseflow conditions at the two catchment outlets between 25th February 2010 and 26th November 2012. The samples were filtered in the field through 0.45 μm glass microfiber filters into acid-washed and furnaced (at 450°C for 4 hours) glass bottles with PTFE lids and acidified with 1M HCL to pH≈2.

At the Aller catchment outlet (A7) stage was recorded in 15-min intervals using an ISCO 4230 flow meter (Teledyne Isco, Lincoln, USA) and was converted to discharge using stage-discharge rating equation, presented in Table 6.1 and Fig. 6.5. Further details of how the rating equations were derived are provided in Chapter 6 as the same method was applied across all monitoring sites with a continuous discharge record within the two study catchments. Horner Water catchment outlet monitoring point (H5) is located at the Environment Agency hydrometric station No.51002 Horner Water at West Luccombe (Marsh and Hannaford, 2008), that provided the discharge data for this study.

Time-integrated storm samples were collected using ISCO 3700 samplers (Teledyne Isco, Lincoln, USA) programmed to sample on discrete, high-resolution time-steps of 30 (Aller) and 60 (Horner Water) minutes respectively, based on analysis of the catchment hydrological response. The samples were collected as soon as possible after each rainfall event (defined below), usually within 24 hours, and immediately transferred to a refrigerator on return to the laboratory where they were analysed for dissolved organic carbon (DOC), total suspended sediment (SS) and total particulate carbon (TPC).

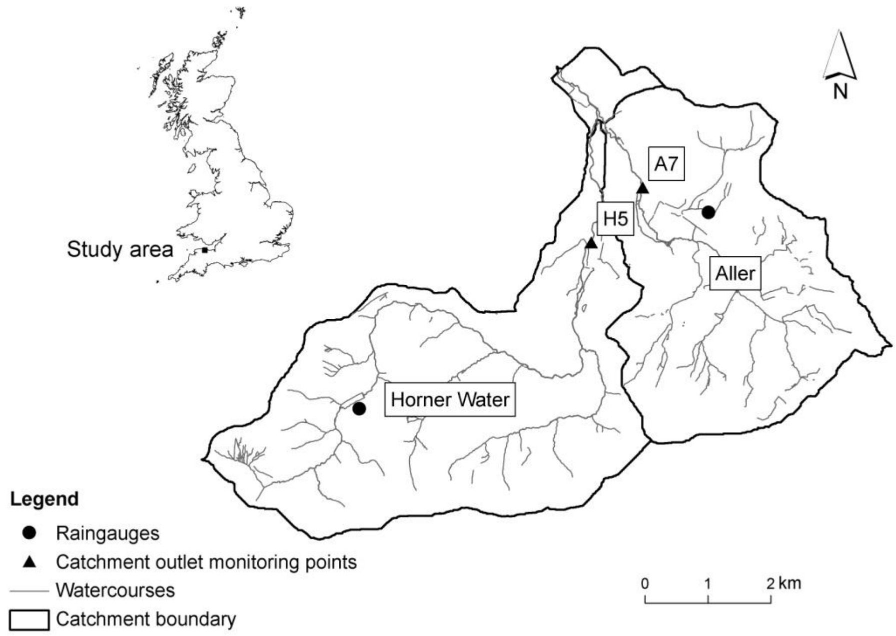


Fig. 4.1 The study site showing the Aller (A7) and Horner Water (H5) catchment outlet monitoring points and Environment Agency rain gauging stations.

A continuous turbidity record was collected at the Aller catchment outlet during the period between July 2011 and January 2013 using a self-cleaning Analite 195/4/30-G 400 NTU turbidity probe (McVan Instruments, Mulgrave, Australia). At H5, a self-cleaning turbidity sensor, the Greenspan TS3000 (Greenspan Analytical, Milperra, Australia, 1,000 NTU) was deployed between January 2012 and January 2013.

C. Laboratory analysis

The storm samples were analysed for DOC using a UV spectrometer for chemical free substance analysis ProPS CW (Trios Gmbh, Rastede, Germany) with adjustable 10 mm path length at a spectral range of 190-360 nm as this is a quick and cost effective method for analysing a large number of samples

(Peacock et al., 2013, Sandford et al., 2010). DOC was analysed as soon as possible after sample collection and always within 7 days of each event as storage tests identified a mean loss of 0.38 mg L^{-1} of DOC per day (N=16, SD=0.07) across the range of concentrations (Fig. 4.2, p. 211). The samples were not filtered as the spectrometer is designed to work as a ‘proxy method’ for *in-situ* field measurements of DOC without filtration.

Baseflow DOC samples were refrigerated immediately on return to the laboratory and were chemically analysed on a Skalar Formacs^{HT} CA14 TOC Analyser (Skalar, Breda, The Netherlands) with limits of detection of 0.08 mg L^{-1}, as the baseflow DOC concentrations were consistently below the limits of detection of the Trios probe (≥3.57 mg L^{-1}).

Trios measurements showed a statistically significant overestimation of values when compared with chemical analysis (t-test, $P < 0.001$, N = 30, Fig. 4.3, p. 211). Therefore, to make the two datasets comparable, Trios values were recalculated for each catchment using a linear regression of Trios vs. chemical DOC concentration in unfiltered stormflow samples from a single rainfall event that represented the full range of DOC concentrations recorded during the period of study (Aller $R^2 = 0.95$, N = 13, $P < 0.001$; Horner Water $R^2 = 0.94$, N= 7, $P < 0.001$, Fig. 4.4, p. 212).

Unfiltered samples measured on the Trios probe were shown to have higher concentrations than filtered ones, however as this difference was not statistically significant (t-test, $P < 0.355$, N=24, Fig. 4.5, p. 212), it was not pursued further in the interpretation of data.

To calculate the total suspended sediment concentration, each water sample was allowed to settle for at least 3 days. The supernatant was then decanted into a measuring cylinder without disturbing the sediment. The remaining sample was agitated, measured in a measuring cylinder and then dried for 48 hours in desiccated pre-weighed ceramic evaporation dishes at 80°C. The sediment concentration was calculated as:

$$c(SS) = 1{,}000{,}000 * (m_2 - m_1)/(v_1 + v_2) \qquad \text{Eq. 4.1}$$

where:

c(SS) – suspended sediment concentration mg L^{-1}

m_1 – mass of empty ceramic dish in g

m_2 – mass of ceramic dish with dried sediment in g

v_1 – volume of supernatant in ml

v_2 – volume of evaporated water sample with suspended sediment in ml

Suspended sediment total carbon content (here-after referred to as total particulate carbon TPC) was quantified using an elemental analyser (NA2000, Carlo Erba Instruments, Milan, Italy). As far as possible, all storm flow samples were analysed individually and were only pooled when the sample mass was too small to allow analysis of TPC.

DOC qualitative analysis was carried out on samples from one storm event that occurred simultaneously in both study catchments (22nd November 2012), using Unicam UV/VIS Spectrometer UV4-100 (Thermo Fisher Scientific, UK). Samples were filtered through 0.45 µm glass fibre filter and spectral absorption (A) was measured at 254 nm, 365 nm, 465 nm and 665 nm. The following ratios were calculated:

- $SUVA_{254}$ is specific absorbance at 254 nm divided by DOC concentration and is positively correlated with increasing molecular weight. $SUVA_{254} > 4$ indicates hydrophobic aromatic dissolved organic matter (DOM) composition, whilst $SUVA_{254} < 3$ indicates less aromatic hydrophilic compounds (Weishaar et al., 2003, Piirsoo et al., 2012).
- E2:E3 as a ratio of A_{254} and A_{365} and indicates a proportion of fulvic (lower molecular weight, less aromatic, more susceptible to microbial decomposition) and humic acids (higher molecular weight, more aromatic, more resistant to degradation) (Brady and Weil, 1999) in DOM, thus higher E2:E3 indicates lower molecular weight and lower aromaticity because of stronger light absorption by high molecular weight molecules at the longer wave-length (Helms et al., 2008, Piirsoo et al., 2012).
- E4:E6 as a ratio of A_{465} and A_{665} as another proxy for the measurement of the proportion of fulvic:humic acids in DOC (Grayson and Holden, 2012). Higher E4:E6 ratios have been found in the upper layers of

upland peat, indicating higher microbial activity, while lower ratios were found in deeper peat layers (Wallage et al., 2006).

D. Data analysis

Thirty five hydrological events (18 for Aller and 17 for Horner Water) recorded between 21st August 2010 and 3rd January 2012 were used for analysis of runoff, SS and carbon transfers. A rules-based method, based on Deasy (2007), was used to define a hydrological event as follows:

1. The event started when runoff began to increase after the start of the triggering rainfall.
2. If baseflow fluctuated, the event started when runoff reached its lowest value after the start of the triggering rainfall.
3. If runoff increased from the start of the rainfall, the event started with the start of the rainfall.
4. The event ended when runoff returned to its initial pre-event level.
5. If runoff did not return to its initial value, the hydrological event ended when flow reached its lowest value before the next increase in response to triggering rainfall.
6. The hydrological event would be considered to be bi-modal or multimodal, if the rainfall trigger did not have a break of at least 3 hours.

The precipitation, runoff and water quality characteristics calculated for each event are presented in Table 4.1.

Rainfall	Total rainfall (mm) Peak rainfall intensity (mm hr^{-1})
Runoff	Total Q (m^3) Peak event Q ($m^3 s^{-1}$) Event duration (min) Lag from event start to peak Q (min) Lag from peak of rainfall intensity to peak Q (min)
Water quality	Peak SS, DOC and TPC concentration mg/l Peak suspended sediment % carbon content (% TPC) Peak SS, DOC and TPC instantaneous flux (mg s^{-1})

Table 4.1 Rainfall, runoff and water quality characteristics calculated for each rainfall event.

Linear interpolation was used between time-step measurements of water quality parameters that were greater than the resolution of the hydrological data. As flow-integrated sampling usually only covered a proportion of the full event duration, the full event yields and loads were not calculated. The proportion of the total event sampled for water quality was calculated as P = Qm/Q where Qm is the total discharge during the monitored period and Q is the total event discharge. The difference between the proportions of events sampled in the two study catchments was tested using Mann-Whitney U test and was found not to be statistically significant, indicating that event sampling intensity was comparable between the two study catchments.

Non-parametric Mann-Whitney U test was used to compare storm flow hydrological and water quality event characteristics between the two study catchments. Student t-test was used to compare the baseflow DOC concentrations between the two study catchments. To examine the hydrological controls on organic and particulate carbon export within each catchment, best-fit, stepwise-multiple linear regression models were constructed using only significantly correlated (Spearman Rho $P < 0.05$) variables. A minimum number of independent variables was used and variables were screened for co-linearity. Non-normally distributed variables were $Log_{10}(x+1)$ transformed. The same analysis was repeated with and without extreme hydrological events to understand the differences in the hydrological controls operating normally and during infrequent high magnitude events. All analyses were carried out in MS Excel 2007 and SPSS version 19. The rating curve equations were calculated and visualised in 'R' version 2.15.3 (2013-03-30, The R Foundation for Statistical Computing).

SS, TPC and DOC yields were calculated using two methods to give an indication of uncertainty associated with yield estimation, as no method is without a bias (Walling and Webb, 1985, Bilotta et al., 2010). Firstly, total yields of SS in the two study catchments were calculated for an eight month period, using turbidity data collected simultaneously at the two catchment outlets between 26th January 2012 and 22nd September 2012. A full year of turbidity data could not be used for yield calculation as during the autumn data quality deteriorated due to abundant debris and leaves, which frequently obscured the turbidity sensor in the semi-natural catchment. NTU turbidity measurements were calibrated against observed SS concentrations and rating equations were calculated (Fig. 4.6, p. 213, Table 4.2, p. 214). Secondly, extrapolation methods for total load estimation (Littlewood, 1992) were used to provide additional yield estimates and a measure of the uncertainty in the yield calculation for the same study period, using rating curves between SS concentration, DOC instantaneous load and discharge (Fig. 4.6, p. 213, Table 4.2, p. 214). TPC yield was calculated as a product of SS yield estimates based on both NTU and discharge rating curve calculations and average % TPC in each catchment. Additionally, DOC yield was calculated using the Walling and Webb Method 5 (Walling and Webb, 1985):

$$F = K * Q_r * \left(\sum_{i=1}^{n} C_i * Q_i\right) / \left(\sum_{i=1}^{n} Q_i\right) \qquad \text{Eq. 4.2}$$

where:

F – is the total solute load (g)

K – time period over which the load occurred (in seconds)

Q_r –mean discharge from a continuous record (m^3)

Q_i – instantaneous discharge ($m^3\ s^{-1}$)

C_i –instantaneous concentration ($mg\ L^{-1}$)

n – number of samples.

This method is deemed to provide the least biased estimates of load from infrequent data, where a continuous discharge record is available (Littlewood, 1992, Walling and Webb, 1985, Clark et al., 2007).

Differences between the two study catchments were examined using both actual yields ($t\ km^{-2}$), and yields normalised by both catchment area and total discharge ($kg\ mm^{-1}$) for this period to offer a fair comparison between two catchments with different area (km^2) and water yield ($ML\ km^{-2}$). The minimum and maximum DOC:TPC ratio was calculated as a ratio of the minimum estimated DOC yield to the maximum estimated TPC yield and *vice versa*.

IV. RESULTS

A. Differences in event-based hydrological characteristics between the two study catchments

Hydrological characteristics for the 35 hydrological events examined are presented in Table 4.3 (p. 216) and summary statistics for hydrological variables in the two study catchments are presented in Table 4.4. The two catchments showed significant differences in their hydrological response to rainfall events in five hydrological characteristics: total event rainfall was significantly higher in the Horner Water catchment than in the Aller ($P < 0.032$, Fig. 4.7a).

Horner Water catchment exhibited a significantly slower hydrograph response than the Aller, with a significantly longer lag between the start and the peak of hydrological event ($P < 0.045$, Fig. 4.7b).

The rainfall-runoff coefficient, which represents the ratio between total event rainfall and total runoff, was significantly higher in the Horner Water catchment ($P < 0.035$, Fig. 4.7c) than in the Aller.

Peak event discharge and total event discharge were both significantly higher in the Horner Water catchment ($P < 0.001$ and $P < 0.001$, Fig.4.7d-e).

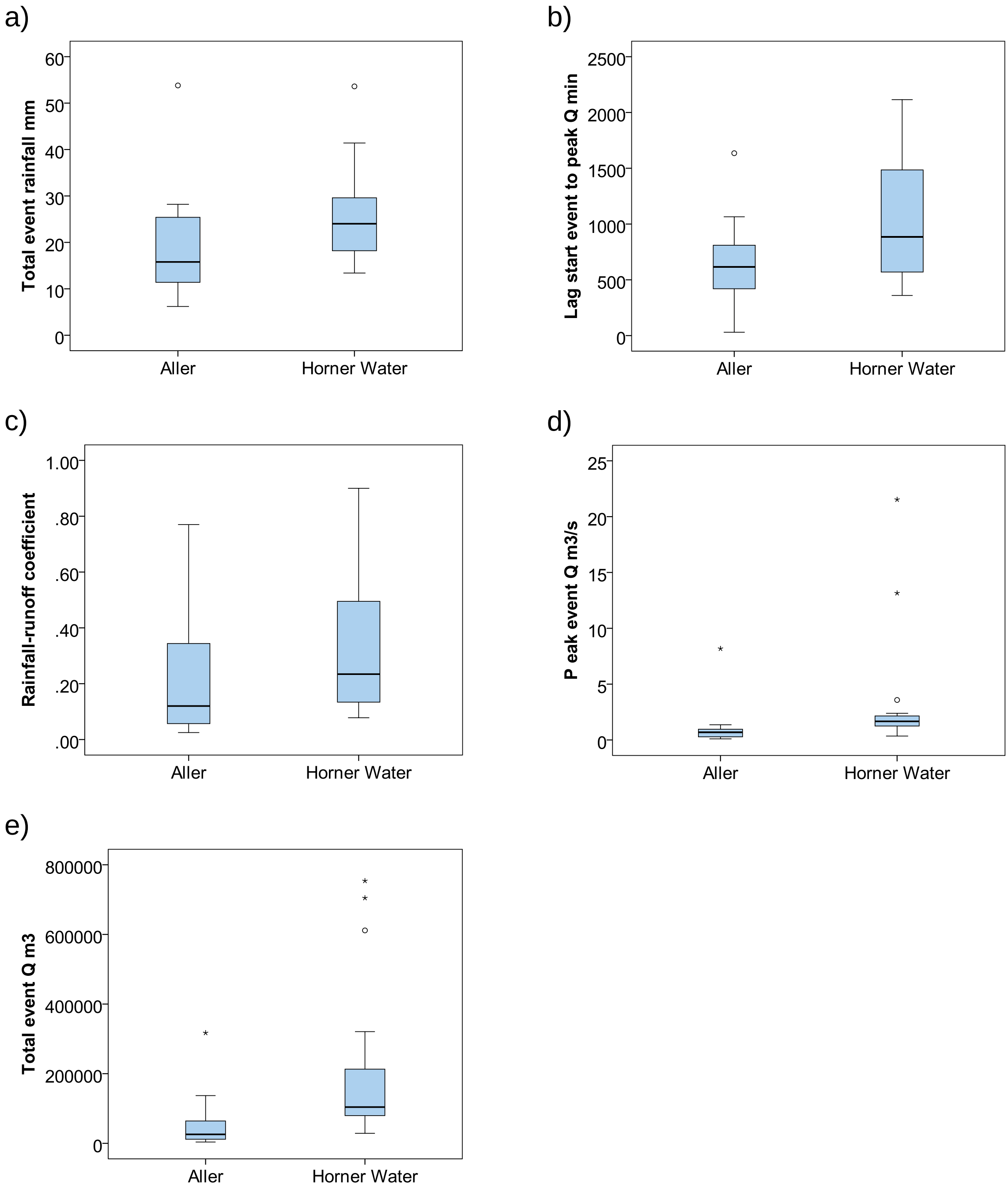


Fig. 4.7 Statistically significant differences in hydrological event characteristics between the two study catchments, calculated from 35 hydrological events captured at the two catchment outlets (Aller N=18, Horner N=17) between 21st August 2010 and 3rd January 2012. a) Total event rainfall b) time lag from start of event to peak discharge c) rainfall-runoff coefficient d) peak event discharge e) total event discharge discharge.

Catchment		Total rainfall (mm)	Peak rainfall intensity (mm hr^{-1})	Total monitored event Q (m^3)	Peak Q (m^3 s^{-1})	Event duration (min)	Lag start event to peak Q (min)	Lag peak rainfall intensity to peak Q (min)	Rainfall/runoff coefficient
Aller	Median	15.80	7.20	8280.30	0.69	2250.00	615.00	187.50	0.12
	Minimum	6.20	1.60	1164.59	0.10	930.00	30.00	105.00	0.03
	Maximum	53.80	26.40	185845.60	8.18	6480.00	1635.00	840.00	0.77
	N	18	18	18	18	18	18	18	18
Horner Water	Median	24.00	8.00	44799.30	1.66	2640.00	885.00	270.00	0.23
	Minimum	13.40	3.20	13347.90	0.35	1470.00	360.00	75.00	0.08
	Maximum	53.60	19.20	571388.40	21.53	4500.00	2115.00	1485.00	0.90
	N	17	17	17	17	17	17	17	17

Table 4.4 Summary statistics of hydrological characteristics of 35 hydrological events examined in the Aller and Horner Water catchments between 21st August 2010 and 3rd January 2012. Q – discharge, min – minutes.

B. Differences in event-based SS, TPC and DOC characteristics in the two study catchments

Water quality characteristics for the 35 hydrological events examined in this chapter are presented in Table 4.5 (p. 218) and summary statistics for the two study catchments are presented in Table 4.6. Summary statistics for DOC baseflow measurements are presented in Chapter 6, Table 6.4 (p. 227) along with baseflow data from all monitoring sites across the two study catchments. The following results explore relationships between event-based water quality characteristics and the hydrological variables that are thought to control those characteristics.

The two catchments showed a significantly different response in event-based sediment and carbon transfers. The Aller catchment showed a significantly higher peak event suspended sediment concentration than the Horner ($P < 0.029$, Fig. 4.8a) whilst the suspended sediment % TPC content was significantly higher in the Horner Water than the Aller ($P < 0.001$, Fig. 4.8c). Horner Water supports higher peak instantaneous DOC fluxes ($P < 0.03$, Fig. 4.8b).

The remaining sediment and carbon parameters, including DOC and TPC concentration and SS and TPC fluxes were not significantly different between the two study catchments. However, there was a significant difference in baseflow DOC concentrations between the two study catchments ($P < 0.05$, Fig. 4.8d).

Catchment		Peak SS conc. (mg L^{-1})	Peak SS flux (g s^{-1})	Peak DOC conc. (mg L^{-1})	Peak DOC flux (g s^{-1})	Peak TPC (%)	Peak TPC conc. (mg L^{-1})	Peak TPC flux (g s^{-1})
Aller	Median	312.49	148.68	5.26	4.14	13.82	30.87	17.65
	Minimum	57.84	5.0	3.98	1.44	7.97	7.39	0.64
	Maximum	1183.67	5273.67	14.03	84.62	17.63	153.80	323.18
	N	18	18	10	10	18	18	18
Horner Water	Median	129.57	195.16	6.19	10.42	20.80	20.86	39.47
	Minimum	16.09	9.11	4.67	6.02	14.07	2.60	1.40
	Maximum	1642.54	27588.06	7.59	132.53	30.76	199.49	2451.39
	N	17	17	11	11	17	17	17

Table 4.6 Summary statistics of water quality variables measured during 35 hydrological events in the two study catchments between 21st August 2010 and 3rd January 2012. SS – suspended sediment, DOC – dissolved organic carbon, TPC – total particulate carbon. Flux refers to instantaneous flux.

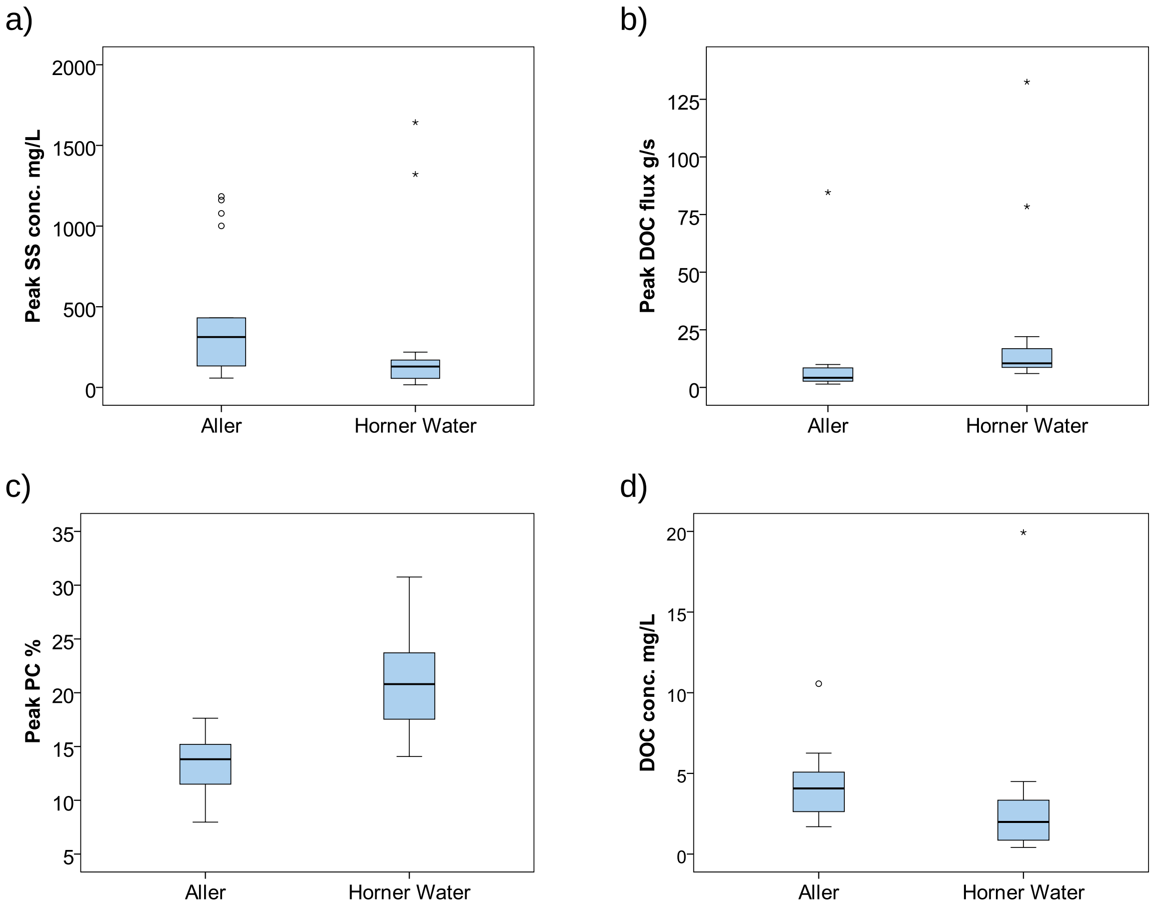


Fig. 4.8 Statistically significant differences in a) peak event suspended sediment concentration (SS) b) peak event dissolved organic carbon (DOC) instantaneous flux c) peak event total particulate carbon (TPC) content and d) baseflow DOC concentrations between the two study catchments. Event characteristics were calculated from 35 hydrological events captured at the two catchment outlets between 21st August 2010 and 3rd January 2012 (Aller N=18, Horner N=17), while baseflow concentrations include 34 monthly samples taken between 25th February 2010 and 26th November 2012.

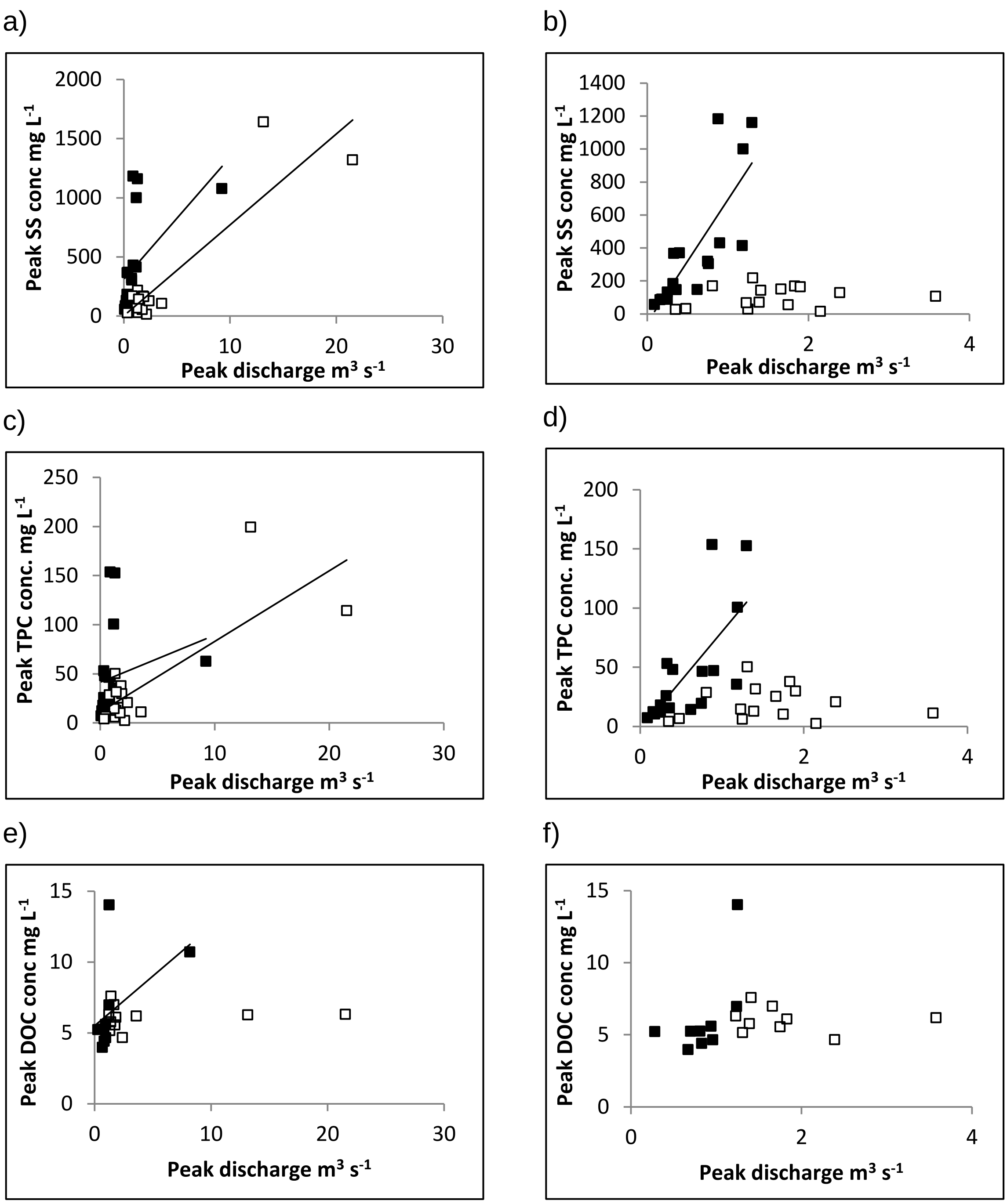


Fig. 4.9 Relationship between peak event discharge (Q) and peak event suspended sediment (SS), dissolved organic carbon (DOC) and total particulate carbon (TPC) concentrations in the presence and absence of extreme hydrological events: a) Peak event SS concentration vs. peak event Q with extreme events b) Peak event SS concentration vs. peak event Q without extreme events c) Peak event TPC concentration vs. peak event Q with extreme events d) Peak TPC concentration vs. peak discharge without extreme events e) Peak event DOC concentration vs. peak event Q with extreme events f) Peak event DOC concentration vs. peak event Q without extreme events. ■ – Aller, □ – Horner Water. Only statistically significant lines of best fit are shown.

Scatter-plots of peak event discharge against dependant variables are presented in Fig. 4.9 to illustrate the influence of extreme events on the response of sediment and carbon transfers. Only statistically significant lines of best fit are shown. Parameters of stepwise multiple regression models of the significantly different sediment and carbon characteristics are presented in Tables 4.7 and 4.8 (p. 220, 222).

Peak discharge and the lag between peak rainfall intensity and peak event discharge describe a significant amount of variability in peak event SS and TPC concentration in the Horner Water catchment (R^2 = 0.736 and 0.644, respectively, $P < 0.001$). However, these functional relationships are only significant when extreme events are included in the analysis. In the absence of extreme hydrological events, no hydrological variables can explain a significant amount of variability in peak SS and TPC concentrations (Table 4.8, p. 222).

Peak event discharge and the lag between peak rainfall intensity and peak discharge also describe a significant amount of variability in peak instantaneous fluxes of SS and TPC (R^2 = 0.902 and 0.881, respectively, $P < 0.0001$) in the Horner Water catchment. However, this relationship becomes weaker in the absence of extreme hydrological events (R^2 = 0.653, $P < 0.001$ and 0.614, $P < 0.001$, respectively).

In the Horner Water catchment, the % TPC content is negatively related to the runoff coefficient, which increases throughout the hydrological season, however this relationship is weak (R^2 = 0.292, $P < 0.025$) and becomes insignificant when extreme hydrological events are excluded.

In the Aller catchment, event duration and peak discharge describe a significant amount of variability in the peak SS and TPC concentrations both in the presence (R^2 = 0.840 and 0.875, respectively, $P < 0.001$), and in the absence of extreme hydrological events (R^2 = 0.938 and 0.865, $P < 0.001$), respectively. Event duration and peak discharge also describe a significant amount of variation in the maximum instantaneous flux of SS and TPC both in the presence (R^2 = 0.932 and 0.932, respectively, $P < 0.001$), and in the absence of extreme hydrological events (R^2 = 0 .976 and 0.957, respectively, $P < 0.001$).

The % TPC content in the Aller catchment is negatively related to the runoff coefficient and positively related to peak rainfall intensity both in the presence (R^2 = 0.864, P < 0.001), and absence (R^2 = 0.620, P < 0.001) of extreme hydrological events.

Event-based hydrological variables do not describe the variability in DOC concentrations in the Horner Water catchment well, whilst in the Aller catchment peak event discharge describes 35 % of the variability (R^2 = 0.435, P < 0.038).

Peak discharge is strongly related to DOC peak instantaneous fluxes in both Horner Water and Aller catchments (R^2 = 0.972 and 0.969, respectively, P < 0.001), although this relationship becomes weaker when extreme events are excluded from the analysis (R^2 = 0.804, P < 0.001 and 0.818, P < 0.001, respectively).

C. Comparison of DOC composition between the two study catchments

The results in this section examine the qualitative differences in DOC composition in order to elucidate the potential sources, hydrological pathways and processes controlling DOC fluxes in the two study catchments. Fig. 4.10 shows UV absorbance ratios for samples from one simultaneous hydrological event in the two study catchments. All three UV absorbance ratios indicate a higher proportion of more aromatic humic compounds with a higher molecular weight in the Aller than Horner Water catchment.

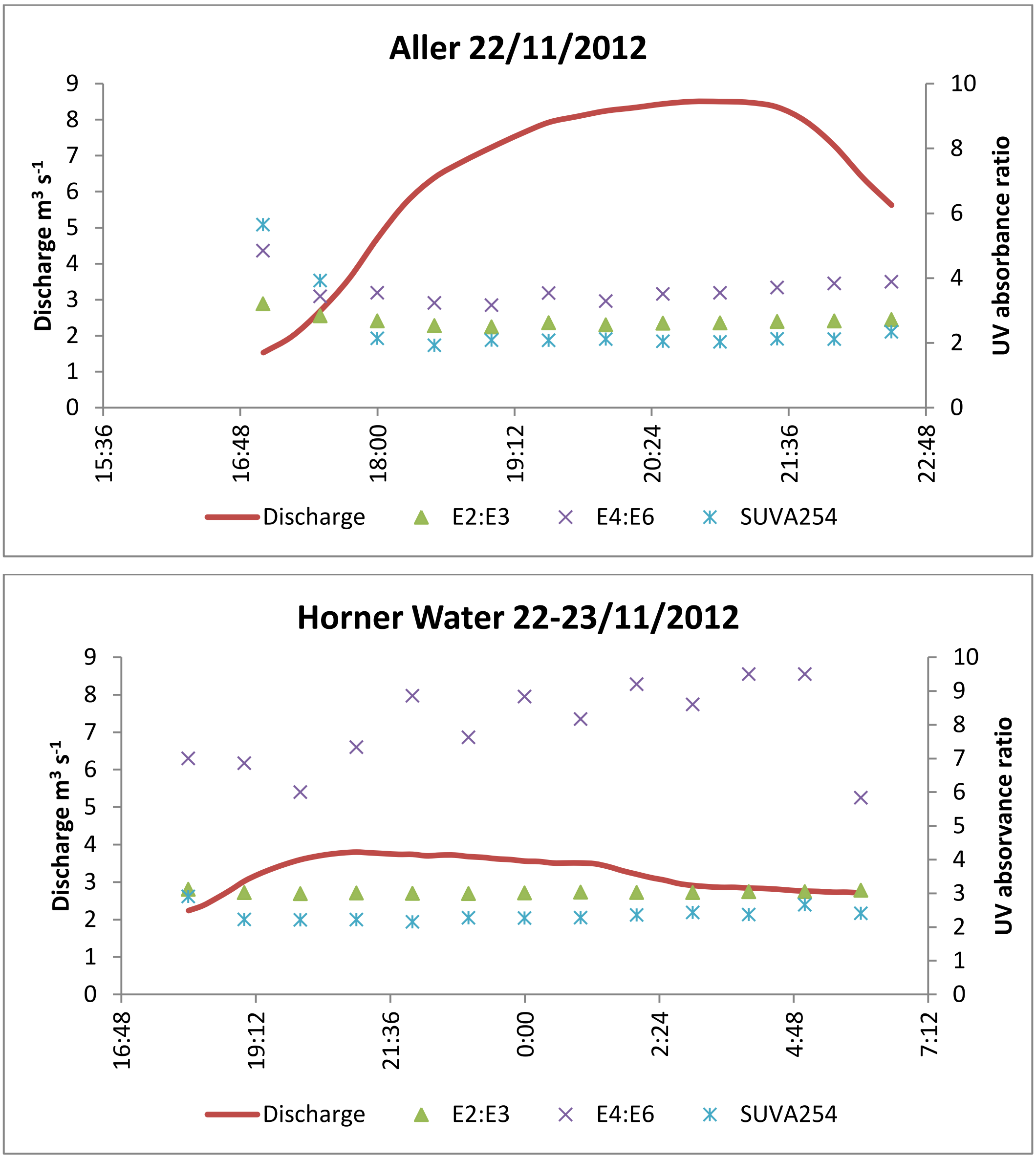


Fig. 4.10 UV absorbance (A) ratios for samples from one storm event recorded simultaneously in the two study catchments on 22nd November 2012. $SUVA_{254}$ is specific absorbance (a ratio of A at 234 nm to DOC concentration) and is positively correlated with increasing molecular weight. E2:E3 (a ratio of A at 254 and 365 nm) and E4:E6 (a ratio of A at 465 and 665 nm) indicate a proportion of fulvic to humic acids in the sample, a higher ratio indicating lower molecular weight and lower aromaticity.

D. Annual fluvial export of SS, DOC and TPC based on continuous turbidity and discharge record

This section examines the total fluvial export of SS, DOC and TPC for the period between the 26th January 2012 and 22nd September 2012 for which a continuous simultaneous turbidity record was available in both study catchments. Two estimates of SS, DOC and TPC yield are provided to give an indication of uncertainty associated with determinand yield estimates. Differences between the two study catchments are examined using both actual yields (t km^{-2}), and yields normalised by the total discharge for this period (kg mm^{-1}).

The total discharge in the Horner Water catchment for the period between the 26th January 2012 and 22nd September 2012 was two times greater than that for the Aller catchment (Table 4.9).

Both methods of SS yield calculation indicate an enhanced SS flux from the Aller catchment (Table 4.9, Fig. 4.11) and a proportionally greater SS export from this catchment normalised by both area and total discharge for the period (Table 4.9, Fig. 4.12).

One method of TPC yield estimation methods shows a greater TPC export from the Aller catchment (Table 4.9, Fig. 4.11) and both indicate a proportionally greater TPC export from this study catchment when normalised by the total discharge (Table 4.9, Fig. 4.12).

Both DOC yield estimation methods show a greater DOC export from the Horner Water catchment (Table 4.9., Fig. 4.11). One method shows a proportionally greater DOC export, normalised by total discharge, from the Horner Water catchment and one from the Aller catchment (Table 4.9, Fig. 4.12).

DOC:TPC ratio is lower in the Aller than in the Horner Water catchment (Table 4.9).

		Yield ($t\ km^{-2}$)		Normalised yield ($kg\ mm^{-1}$)	
		Horner Water	**Aller**	**Horner Water**	**Aller**
SS estimated from turbidity record	median	30.44	38.56	3.00	7.80
	min	21.69	25.51	2.14	5.16
	max	39.16	58.75	3.86	11.89
SS estimated using conc. / Q rating equation	median	44.99	76.32	4.44	15.45
	min	32.13	36.41	3.17	7.37
	max	57.76	116.23	5.70	23.52
TPC estimated from turbidity derived SS load and average % TPC content	median	5.17	3.82	0.51	0.77
	min	3.69	2.53	0.36	0.51
	max	6.66	5.82	0.66	1.18
TPC estimated from SS conc. / Q rating equation derived load and average % TPC content	median	7.65	8.40	0.75	1.70
	min	5.46	4.01	0.54	0.81
	max	9.82	12.79	0.97	2.59
DOC estimated from inst. load / Q rating equation	median	2.59	2.37	0.26	0.48
	min	2.46	2.18	0.24	0.44
	max	2.62	2.56	0.26	0.52
DOC estimated Walling formula 5		3.25	1.29	0.32	0.26
DOC:TPC ratio	min	0.25	0.15		
	max	10.02	1.01		
Total discharge for the period (ML)		10,140	4,941		
Total water yield ($ML\ km^{-2}$)		460.91	337.49		
Discharge record completeness (%)		98.83	96.64		

Table 4.9 Yields of SS, DOC and TPC in the two study catchments for an eight month period between 26th January 2012 and 22nd September 2012 for which a reliable continuous turbidity record was available and yields normalised for total discharge during the study period. Minimum and maximum yield estimates were calculated from the 95 % confidence intervals of rating equations presented in Fig. 4.6 and Table 4.2. Minimum and maximum DOC:TPC ratio was calculated as a ratio of the minimum estimated DOC yield to the maximum estimated TPC yield and *vice versa*. Confidence intervals were not calculated for the DOC estimate using the Walling formula Method 5 (Formula 4.2).

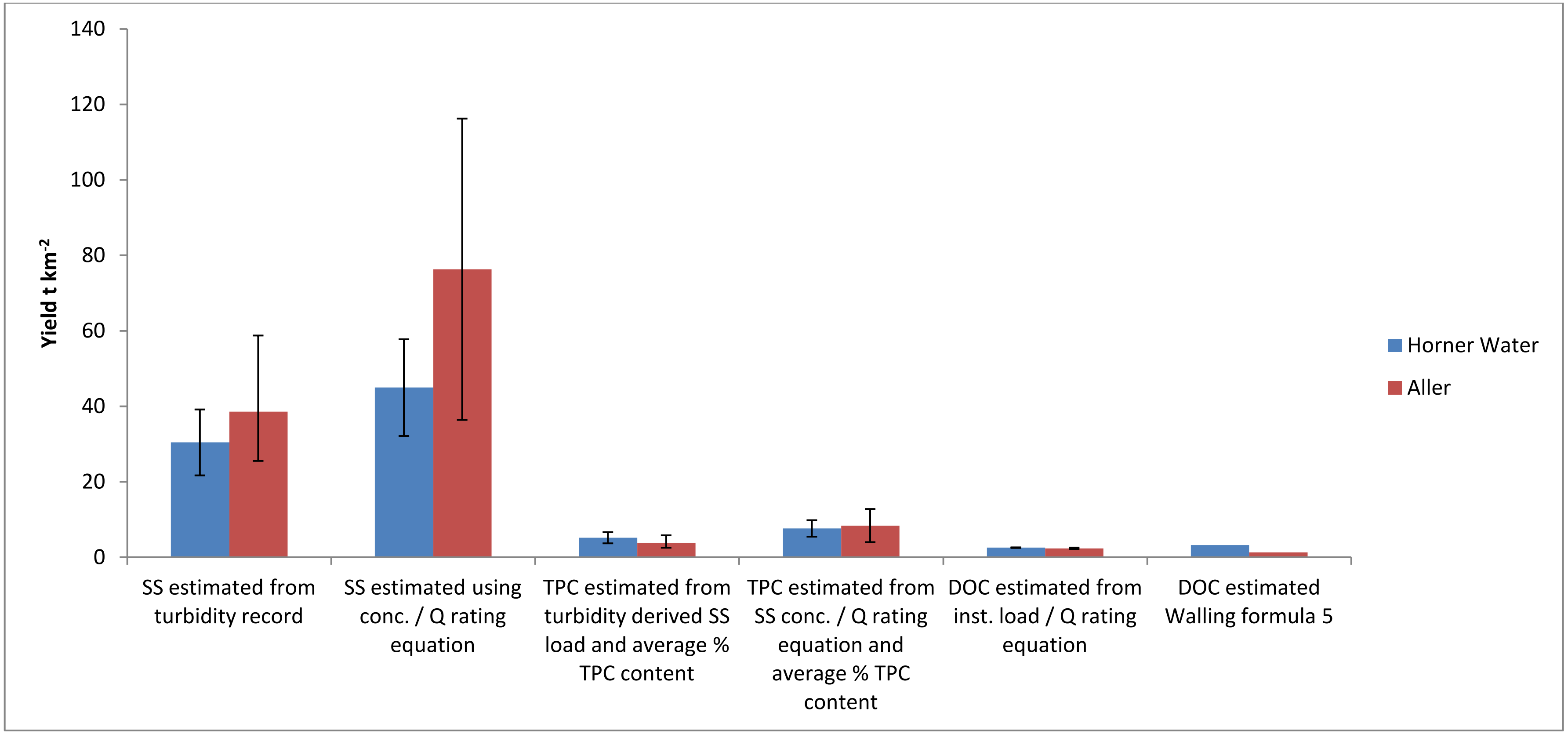


Fig. 4.11 Estimated SS, TPC and DOC yields calculated for the period between 26th January 2012 and 22th September 2012 show a greater SS flux from the Aller catchment. One method also shows a greater TPC flux from this catchment, while Horner Water supports a greater DOC flux. The error bars show 95 % confidence intervals. No error was calculated for the DOC yield estimated with the Walling Method 5 formula (Formula 4.2).

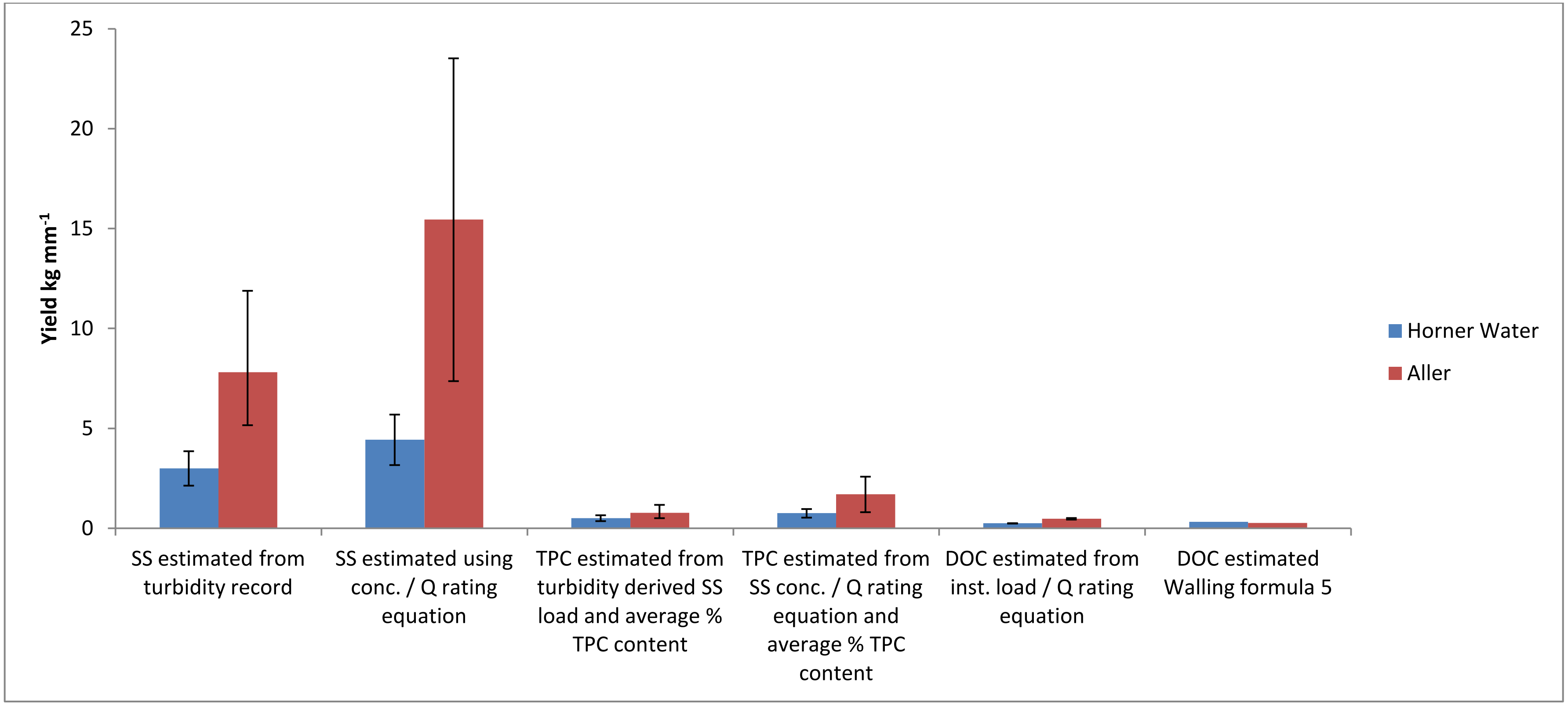


Fig. 4.12 Estimated SS, TPC and DOC yields calculated for the period between 26th January 2012 and 22nd September 2012 show a proportionally greater SS and TPC flux from the Aller catchment, normalised by the total discharge for the study period. DOC yield normalised by the total discharge shows no clear difference between the two catchments. The error bars show 95 % confidence intervals. No error was calculated for the DOC yield estimated with the Walling Method 5 formula (Formula 4.2).

V. DISCUSSION

A. Differences in event-based hydrological characteristics between the two study catchments

Conceptual understanding of hydrological processes operating within a catchment is critical for the interpretation of land use impacts on water quality (Soulsby et al., 2002). However, catchments are complex systems, therefore the prevailing hydrological processes can often only be inferred (Kirchner et al., 2000). The climatic, geomorphological and vegetation characteristics of the two study catchments described in Chapter 3 influence the observed event-based hydrological differences (Soulsby et al., 2006). The higher mean annual rainfall and higher water yield in the Horner Water catchment results in significantly higher total and peak event discharge, while the steeper slope gradients likely lead to a greater contribution of shallow sub-surface flow (as opposed to deep groundwater-fed sub-surface flow) to the event hydrograph and thus a higher rainfall/runoff coefficient (Burt and Pinay, 2005). Conversely, the faster hydrograph response (shorter lag from start of event to peak discharge) in the Aller catchment indicates a greater contribution of overland flow along preferential pathways such as paved roads and tracks to the event hydrograph. Higher soil bulk density, sparse vegetation cover and reduced soil organic matter content in the Aller catchment are also likely to contribute to the faster hydrological response through reduced infiltration rates and increased propensity for infiltration excess overland flow in parts of the catchment (Bracken and Croke, 2007). Further, hydrologically more responsive clay soils (HOST type 21) in the eastern part of the catchment and seasonally saturated loams (Wigton Moor soil series, Fig. 3.3) in the riparian corridor are conducive to seasonal saturation excess overland flow (Boorman et al., 1995), while preferential flow through sub-surface drainage is also likely to contribute to the quick hydrological response. The lower rainfall-runoff coefficient in the Aller catchment suggests greater groundwater storage. However, the precise contribution of groundwater to the hydrograph in both study catchments would require further study. Even in upland catchments, groundwater may make a more important contribution to the hydrograph than previously thought (Soulsby et al., 2002) and McDonnell (2003) commented that both flow, source and age of water would need to be determined in order to describe fully the hydrological processes operating within a catchment.

B. Controls on SS, TPC and DOC export from the two study catchments

a. Suspended sediment and particulate carbon

In line with the research hypothesis 1) that anticipated higher SS concentrations, fluxes and yields in the agricultural catchment, the Aller catchment supported higher peak event SS concentrations and a higher SS yield. However, there was no significant difference in peak event instantaneous SS fluxes between the two study catchments, likely due to the counter-balancing effect of higher SS concentrations in the Aller and higher discharge in Horner Water.

Contrary to hypothesis 2) that anticipated higher TPC concentrations, fluxes and yields in the semi-natural catchment, the Horner Water catchment did not support higher peak TPC concentrations, fluxes and yields. As TPC is associated with suspended sediment and thus related to rates of soil erosion (Oeurng et al., 2011), this lack of difference perhaps reflects the increased SS concentration in the Aller catchment, which counter-balances the higher sediment % TPC content and higher discharge in Horner Water.

The significantly higher peak event SS concentration in the Aller catchment is likely due to enhanced mobilisation and transport of sediment from both surface and sub-surface sources in arable and intensively managed grassland land uses (Russell et al., 2001, Bilotta et al., 2010). The lower % TPC in the Aller catchment is likely to be linked to reduced soil % carbon content in the mineral soils prevalent in this catchment as well as to arable land use practices such as tillage and inorganic fertilisers which have been shown to result in soil organic matter degradation (Brady and Weil, 1999, Graeber et al., 2012) through more rapid decomposition of soil organic matter (Kuzyakov et al., 2000, Senbayram et al., 2008), as discussed in Chapter 3.

The mean peak TPC concentrations in both study catchments exceeded those between 0.4 and 3.8 mg L^{-1} reported from agricultural watersheds in mid-western US (Kronholm and Capel, 2012), between 0.01 and 7.22 mg L^{-1} reported from two upland streams in the UK (Dawson et al., 2002), and between 0.1 and 0.8 mg L^{-1} from two river systems in NE Scotland (Hope et al., 1997a), although the latter two studies did not include storm-integrated sampling and were therefore likely to underestimate mean TPC concentrations. As particulate C is associated with sediment and thus related to rates of erosion (Oeurng et al., 2011), the lack of significant difference in TPC concentrations between the two catchments is interesting. It perhaps reflects the contrasting effects of higher total SS concentration in the Aller catchment, due to higher rates of soil erosion, and higher % suspended sediment C content in the Horner Water catchment, reflecting more C rich soils in this catchment, as characterised in Chapter 3. However, given the greater discharge from the larger Horner Water, the lack of significant difference in total SS and TPC instantaneous fluxes suggests a proportionally greater TPC export from the agricultural catchment. Correll et al. (2001) also found higher TPC fluxes from cropland than from an upland forested watershed, primarily due to enhanced soil erosion. Such a finding suggests a strong link between land use and the carbon fluxes from the land to water, which in turn suggests that less intensive management of the land may result in lower losses of carbon from soil to water.

Event duration and peak discharge exert a significant control over total SS and TPC concentrations and fluxes in the Aller catchment. This may be linked to greater amount of mobilised sediment from larger contributing source areas during longer and bigger events. Oeurng et al. (2011) also found a strong relationship between total precipitation, event duration, event discharge, total water yield and SS and POC fluxes during flood events. In the Horner Water catchment, peak discharge and the time lag between peak rainfall intensity and peak discharge account for a significant amount of variability in total SS and TPC concentrations. Total SS and TPC fluxes in the Horner Water catchment also increase with peak discharge, however this relationship is weaker than in the Aller catchment, until extreme events are encountered. The greater responsiveness of SS and TPC concentrations and fluxes in the Aller catchment to discharge indicates a lower response threshold to sediment mobilisation, transport and delivery, linked to an enhanced fluvial particulate carbon loss. This is likely due to the greater erosion potential of soils on agricultural land (Evans, 1990) and increased hydrological connectivity along anthropogenically altered hydrological pathways (Lexartza-Artza and Wainwright, 2009), such as roads (Bracken and Croke, 2007), tramlines (Deasy et al., 2010), compacted field surfaces and subsurface drains (Russell et al., 2001, Deasy et al., 2009). Conversely, these results suggest that very large events are necessary to mobilise sediment and carbon in the semi-natural Horner Water catchment, as soils with lower bulk density, greater organic matter content and good vegetation cover are likely to support greater infiltration and reduce the opportunities for the generation of overland flow (Bracken and Croke, 2007). Thus comparison between these two study catchments suggests that sustainable management of agricultural catchments could increase their resilience to more extreme hydrological regimes anticipated as a result of climate change (Whitehead et al., 2009), with multiple benefits for water quality and carbon sequestration.

b. **DOC**

Contrary to Hypothesis 2) which anticipated that higher DOC concentrations, fluxes and yields would occur in the semi-natural catchment, peak event DOC concentrations in Horner Water catchment did not differ significantly from those in the Aller catchment; however peak instantaneous DOC fluxes were still higher. Conversely, in baseflow conditions, DOC concentrations in the agricultural Aller catchment were significantly higher than those in Horner Water.

The median peak storm flow DOC concentrations of 5.26 mg L^{-1} in the Aller and 6.19 mg L^{-1} in Horner Water were within the mean annual values of 1.8-13 mg L^{-1} reported for European rivers (Mattsson et al., 2009) and near the upper end of the range 2.1 – 6.8 mg L^{-1} reported for 13 diverse agricultural watersheds in the US (Kronholm and Capel, 2012). The higher baseflow DOC concentrations in the Aller catchment and the lack of significant difference in peak DOC concentrations between the two study catchments in stormflow seems counter-intuitive, as soils with a higher carbon content and a higher C:N ratio, as those in the Horner Water catchment, have been shown to be important sources of fluvial DOC concentrations (Aitkenhead et al., 1999). However, other factors such as climate and geomorphology (Mattsson et al., 2009), vegetation (Mattsson et al., 2009), hydrology (Wilson and Xenopoulos, 2008, Oeurng et al., 2011) and soil type (Van den Berg et al., 2012), have also been shown to be important controls of DOC concentrations in different environments. A number of these factors may be responsible for the observed pattern of DOC concentrations in the two study catchments, resulting in different sources and delivery pathways of DOC during baseflow and storm flow conditions. Firstly, the higher water flux (Buckingham et al., 2008) and steeper slopes (Zhang et al., 2011) in the Horner Water catchment may be a factor in reducing DOC concentrations in baseflow through the dilution of soil DOM, reduced soil water residence time and predominance of shallow sub-surface flow paths (Zhang et al., 2011). Although the total catchment soil carbon pool (Aitkenhead et al., 1999) and soil C:N ratio (Aitkenhead and McDowell, 2000, Van den Berg et al., 2012) are often related to higher DOC concentrations, particularly in small peaty catchments, in mineral soils and shallow peats DOC concentrations decrease with soil depth (Hope 1994). As in baseflow conditions DOC is mostly derived from the lower mineral soil layers of the soil profile (Vidon et al., 2008), the B horizon of the podzolic soils in the lower reaches of the Horner Water catchment may act as a significant sink of DOC through reaction with Al^{3+} and Fe^{2+} ions (Hope et al., 1994). In addition, higher rainfall, typical of the Horner Water catchment, has been shown to be negatively related to DOC concentrations in soils (Van den Berg et al., 2012), due to a dilution effect. Therefore, the greater quantities of water moving through lower soil horizons with reduced DOC concentrations in Horner Water catchment may dilute the DOC signal when compared to the Aller catchment response. Conversely, in stormflow, the carbon rich upper soil layers become more important sources of DOC in Horner Water, thus reducing the difference between stormflow DOC concentrations in the two study catchments.

Secondly, land use may be an important contributing factor to the observed differences in DOC concentrations between the two catchments, principally through enhanced carbon cycling as a result of anthropogenic nutrient addition in the agricultural catchment (Dawson et al., 2012). Molinero and Burke (2009) found that DOC concentrations increased along a gradient of land use intensity with the proportion of pasture, while a study of headwater catchments in Central Europe (Graeber et al., 2012) found consistently higher concentrations of DOC in agricultural than in forested catchments. This apparent increase in DOC concentrations in the agricultural catchment may be due to the application of organic manures (Heitkamp et al., 2009), incorporation of crop residues in arable rotations and intensive grazing of pasture that have all been shown to enhance soil dissolved organic matter (DOM) concentration through a stimulation of microbial activity and increased oxygenation of the soil profile (Chantigny, 2003). About half of this increase has been attributed to the turnover of the indigenous soil organic matter, while the other half was shown to be derived from the decomposition of the added organic matter (Chantigny, 2003).

While many studies have found a positive relationship between DOC concentrations and stream discharge (Hope et al., 1994), peak discharge is not a significant control over DOC concentrations in the Horner Water catchment, although DOC concentrations do increase during storm events. In the Aller catchment, peak discharge accounts for 44 % of variability in DOC concentrations, however the relationship is weak ($P < 0.04$). Reviewing available literature, Dalzell (2007) found that positive correlations between discharge and DOC concentrations were more commonly observed in catchments with altered land use, due to anthropogenic alterations of hydrological pathways (Dalzell et al., 2011). In accordance with the findings of other studies (Hope et al., 1994, Worrall et al., 2011), peak discharge exerts a significant control over DOC fluxes in both study catchments.

These results illustrate that SS, TPC and DOC exports respond differently to hydrological controls. While hydrology controls a significant amount of variability in total SS and TPC concentrations and fluxes, the controls over DOC exports are more complex, making the “understanding [of] anthropogenic impact on DOC cycling at the watershed ... scale ... an enormous challenge” (Hernes et al., 2008, p. 5275). Whilst in unsaturated conditions DOC is unlikely to be derived from the most carbon rich top soil, especially in shallow peat and mineral soils, the enhanced sediment and TPC input into the fluvial environment from more intensive land use may be partly responsible for the increased DOC concentrations via in-stream processing. Hernes (2008) found a linear relationship between the concentration of lignin, a polyphenol unique to vascular plants and an important component of DOC, and total suspended sediment concentration in an agricultural watershed, suggesting that mobilisation of SS through agricultural practices is likely to influence both the quality and quantity of DOC.

C. Qualitative differences in DOC composition

The initial exploration of the qualitative composition of DOC shows a marked difference between the contrasting study catchments. Both specific absorbance $SUVA_{254}$, and the two absorption ratios indicate that DOC in the Aller catchment is composed of more complex, humic DOC compounds, as compared to a greater prevalence of lower molecular weight fulvic acids in Horner Water. This difference may reflect different inputs and hydrological pathways (Wallage et al., 2006, Strauss et al., 2007, Vidon et al., 2009). However, "the mechanisms which induce these alterations of DOM, as well as their effects on aquatic ecosystems are still largely unknown" (Graeber et al., 2012, p. 445) and should be the subject of further research (Stanley et al., 2011).

Agricultural land use, including tillage and addition of organic and inorganic fertilisers, aids soil organic matter mineralisation (Brady and Weil, 1999) and potentially enhances the availability of DOC for fluvial transport (Graeber et al., 2012). While agriculture has been shown to affect the qualitative composition of DOC, the direction of change is still equivocal as DOC in agricultural catchments has been found to be composed of both simpler (Chantigny, 2003), and more complex (Graeber et al., 2012) molecules than in other land uses. A higher turnover of organic carbon in the agricultural catchment could result in the preferential removal of simpler compounds through enhanced microbial respiration and the observed greater proportion of humic substances in fluvial DOC (Holl et al., 2009).

The bioavailability of DOC is not solely determined by its qualitative composition but also by the availability of other limiting macro-nutrients. Addition of N and P into the aquatic environment increases microbial respiration (Stelzer et al., 2003) and in-stream processing of DOC (Johnson et al., 2009, Johnson et al., 2012). Mineau et al. (2012) have shown that nutrient addition is more important than DOC composition in determining DOC uptake, allowing microbes to access more recalcitrant DOM pools (Stelzer et al., 2003, Dawson et al., 2012), which may otherwise resist immediate decomposition in the fluvial environment (Kaplan et al., 2008).

This study provides only an initial insight into the qualitative differences in DOC composition between these study catchments and extended sampling would be necessary to fully characterise the seasonal variation in the observed qualitative differences (Dalzell et al., 2007).

D. Annual export of SS, DOC and TPC from the two study catchments

DOC is typically the dominant component of the fluvial organic carbon flux (Hope et al., 1994, Dawson and Smith, 2007, Worrall et al., 2011). DOC:TOC ratios observed in temperate ecosystems in Europe range between 3.3-6.5 (Hope et al., 1994). However, DOC ratios below 1 have been observed in temperate forests and grasslands in North America. It has been suggested that the lower DOC:TPC ratios between 0.07-1.01 observed in the Aller catchment, may be linked to an increasing amount of arable land and increased rates of soil erosion (Hope et al., 1997a).

Mean soil erosion rates in Britain are estimated between 22 and 1,130 t km^{-2} yr^{-1} (Brazier, 2004, Dawson and Smith, 2007). The amount of this potential sediment and carbon source delivered to watercourses can be expressed as a ‘connectivity ratio’ and is higher on slopes and lower permeability soils (Cooper et al., 2008). The median SS yield, estimated in the Aller catchment over an eight month period, between 26-116 t km^{-2} is within the range commonly encountered in UK catchments, however it exceeds the proposed target yield of 20 t km^{-2} yr^{-1} for low lying permeable catchments (standard % runoff < 40%) (Cooper et al., 2008). The range of SS yield estimated for the Horner Water catchment between 22-58 t km^{-2} for the same eight month period are below the lower quartile of 50 t km^{-2} yr^{-1} estimated from other high altitude peaty catchments in the UK (Cooper et al., 2008).

The median estimates of TPC yield from the Horner Water catchment between 36.9-76.5 kg C ha^{-1} and 25.3-120.8 kg C ha^{-1} from the Aller catchment for the eight month period are within the range of 1-500 kg C ha^{-1} yr^{-1} found in rivers in the UK and globally (Hope et al., 1997b, Dawson and Smith, 2007) and within 0.9-120 kg C ha^{-1} yr^{-1} TPC found in agricultural watersheds (Kronholm and Capel, 2012). However, compared to estimated extreme losses of particulate carbon of up to 2,063 kg C ha^{-1} yr^{-1} from actively eroding upland peatland catchments in the UK (Worrall et al., 2011), the rates of carbon export in the present study are modest.

The median estimated DOC yields between 25.9-32.5 kg C ha^{-2} from Horner Water and 12.9-25.6 kg C ha^{-2} from the Aller are comparable with estimates of DOC export from world rivers between 1.4-212 kg C ha^{-1} yr^{-1} (Hope et al., 1994), those of 8.7-40 kg C ha^{-2} yr^{-1} estimated for European rivers (Mattsson et al., 2009) and the range of 2-130 kg C ha^{-1} yr^{-1} found in agricultural watersheds (Dalzell et al., 2007, Kronholm and Capel, 2012). However, the values in the present study are an order of magnitude lower than those of 130-956 kg C km^{-2} yr^{-1} estimated from small actively eroding upland peatland catchments in the UK, although these latter values may be over-estimated and not be typical of upland catchments in general (Worrall et al., 2011).

E. Database for the evaluation of the effectiveness of water quality mitigation measures

This dataset provides a comprehensive baseline to allow the evaluation of the effectiveness of future land use mitigation interventions in these two study catchments that are further discussed in Chapter 6. Decreasing soil carbon content and unsustainable rates of soil erosion as a result of intensive agricultural practices have been reported world-wide (e.g. Sleutel et al., 2006, Montgomery, 2007b, Bell et al., 2011). Therefore, mitigation measures that reduce soil erosion and enhance soil organic matter conservation in the agricultural catchment could have a positive impact on ecosystem services, including food production and carbon storage.

The underlying mechanisms, ecological consequences (Stanley et al., 2011) and the significance of the enhanced fluvial carbon fluxes for the global carbon cycle (Dawson et al., 2012) remain poorly understood. However, Kronholm (2012) suggested that as the total organic carbon export from agricultural watersheds represents only a small proportion of the total carbon sequestered within these ecosystems, enhancing carbon storage in agricultural catchments could make a significant contribution to climate change mitigation. The comparison with the semi-natural catchment in this study suggests that enhancing natural vegetation, such as woodland and rough grassland, within agricultural catchments could be an effective means of reducing fluvial sediment and carbon losses, however the spatial extent of a ‘minimum cost-effective intervention’ remains to be determined.

VI. CONCLUSIONS

This research adds significantly to the limited number of studies examining the impact of agricultural land use on total fluvial organic carbon export. Hydrology exerts a greater control over fluvial organic carbon dynamics in the agricultural catchment, with a lower response threshold of SS, TPC and DOC to hydrological drivers, particularly peak discharge. Both the differences in the qualitative composition of DOC between the two study catchments and the lack of significantly higher TPC and DOC instantaneous fluxes and yields from the catchment with a greater soil carbon pool and a greater discharge, indicate that agricultural land use has a significant effect on both the quality and quantity of fluvial organic carbon export. Therefore, these results suggest that sustainable management of agricultural catchments that enhances soil quality and semi-natural vegetation could increase their resilience to more extreme hydrological regimes anticipated as a result of climate change, with multiple benefits for the ecological status of water courses and carbon sequestration.

Chapter 5

Testing the pressure-specific invertebrate index (PSI) as a tool for determining ecologically relevant water quality sedimentation targets

I. ABSTRACT

Sedimentation is a major cause of river impairment and water pollution worldwide. However, setting an ecologically meaningful sedimentation target is proving challenging due to significant gaps in the understanding of quantitative links between sedimentation and ecological response as well as variability between different types of surface waters. This study evaluates the utility of a new pressure-specific macro-invertebrate index Proportion of Sediment-sensitive Invertebrates (PSI) to act as a simple tool for measuring sedimentation impacts and setting ecologically relevant sedimentation targets.

Five macro-invertebrate indices were calculated from 51 samples taken from 13 sampling locations across two neighbouring, but contrasting study catchments in spring and autumn 2010 and 2011. For four of these, Environmental Quality Indices (EQIs) were also calculated as a proportion of observed to expected (O:E) macro-invertebrate scores, which were predicted for a theoretical pristine invertebrate community using the River Invertebrate Prediction and Classification System (RIVPACS) model.

Principal Component Analysis has shown a clear hydromorphological and sedimentation gradient within the two study catchments. A generalised hierarchical mixed model with site as a random factor and % fine bed sediment as a fixed factor found a significant relationship between PSI and O:E PSI and % fine bed sediment cover at reach-scale sampling resolution over a moderate gradient of impact ($P = 0.002$ and $P = 0.014$). Lotic Index for Flow Evaluation (LIFE) scores and *Ephemeroptera-Plecoptera-Trichoptera* (EPT) % abundance were also related to % fine bed sediment cover ($P = 0.014$). However, PSI was more strongly related to % fine bed sediment cover than either LIFE or EPT %

abundance. While PSI and O:E PSI were correlated with LIFE and O:E LIFE (r = 0.58-0.91), with the strength of the relationship increasing over the sampling period, PSI was not correlated with EPT % abundance, which suggests a differentiated response of these metrics to multiple stressors. The relationship between PSI and other invertebrate metrics should be subjected to further testing along a pronounced gradient of multiple stressors, as our findings suggest that PSI and % fine bed sediment cover have the potential to provide simple, sensitive and effective tools for setting of 'twin' ecological and physical sedimentation targets and add additional explanatory power to the existing suite of macro-invertebrate indices.

II. INTRODUCTION

Sedimentation is acknowledged as a major cause of river impairment worldwide (Bilotta and Brazier, 2008). While a range of physical sedimentation metrics have been proposed internationally for setting and monitoring water quality targets (Collins et al., 2011), their ecological relevance and practical applicability are often questioned (Walling et al., 2007, Bilotta and Brazier, 2008). Monitoring freshwater macro-invertebrate populations is an effective and well established approach for the understanding of anthropogenic impacts on water quality and for setting of ecologically meaningful water quality targets (Hawkes, 1997, Friberg et al., 2005, Bonada et al., 2006). Macro-invertebrate indices can provide a relatively straightforward alternative to more involved physico-chemical methods of impact monitoring, including the identification of outcomes of landscape and river restoration that may be otherwise hard to identify (Clews and Ormerod, 2009, Extence et al., 2013). Furthermore, invertebrate indices can be used to assess departures from 'reference conditions' using multivariate models such as RIVPACS (Wright, 2000) or its successor RICT (Davy-Bowker et al., 2008) and in combination with physico-chemical data may help to inform 'good ecological condition' or target setting under the Water Framework Directive (Álvarez-Cabria et al., 2010). Such multivariate models were found to at least partially satisfy nine out of 12 criteria of an 'ideal' bio-monitoring tool (Bonada et al., 2006), thus making them a relatively cost-effective option for setting and monitoring of water quality targets. In addition, Clews and Ormerod (2009) found that a combination of simple univariate indices can conclusively identify different pressures on riverine ecological status and help to guide management action. Hence, the development of further pressure-specific indices, including those for the assessment of sedimentation impacts, has been suggested as the next step in the evolution of bio-assessment metrics (Clews and Ormerod, 2009, Relyea et al., 2012).

Pressure-specific indices for the monitoring of mild eutrophication/organic pollution (Walley and Hawkes, 1997, Czerniawska-Kusza, 2005); for antecedent flow evaluation (Extence et al., 1999, Dunbar et al., 2009a, Dunbar et al., 2009b), for evaluation of community conservation value (Chadd and Extence, 2004) and for the assessment of acidification impacts (Davy-Bowker et al., 2005) have been developed. However, internationally, few univariate metrics for monitoring of sedimentation impacts exist (Zweig and Rabeni, 2001, Bryce et al., 2010, Relyea et al., 2012) and only recently has such a pressure-specific index Proportion of Sediment-sensitive Invertebrates (PSI) been developed in the UK (Extence et al., 2013). This research aims to test the utility of the new PSI index for setting of water quality sedimentation targets by examining the relationship between physical measures of sedimentation and PSI. It is hypothesised that unlike non-pressure specific indices, the PSI will relate to physical measurements of sedimentation across a moderate impact gradient and thus ad explanatory power to the existing suite of macroinvertebrate indices.

III. METHODS

A. Study area

Two adjacent, yet contrasting, study catchments, the Aller and Horner Water were chosen as they represent a broad hydromorphological and land use gradient, typical of the south west of the UK. The study area is described in detail in Chapter 3, Section III.A.

B. Field sampling and laboratory analysis

Freshwater macro-invertebrate samples were taken on four occasions (25th-26th May 2010, 25th-30th November 2010, 4th-19th May 2011 and 18th October-22nd November 2011) at 13 locations across the two study catchments, except for one site (A8) which was not sampled in May 2010 (Fig. 5.1). Samples were taken using the standardised semi-quantitative UK TAG sampling methodology (Environment Agency, 2009) that involves a 3 minute kick-sample of the stream bed along a 5-20 m long transect using a pond net (25 x 22 cm, 1 mm mesh), with an additional 1 minute manual search split evenly between surface dwelling taxa (prior to kick-sampling) and substrate/macrophyte attached animals (after kick-sampling), with all habitats sampled in proportion to their occurrence.

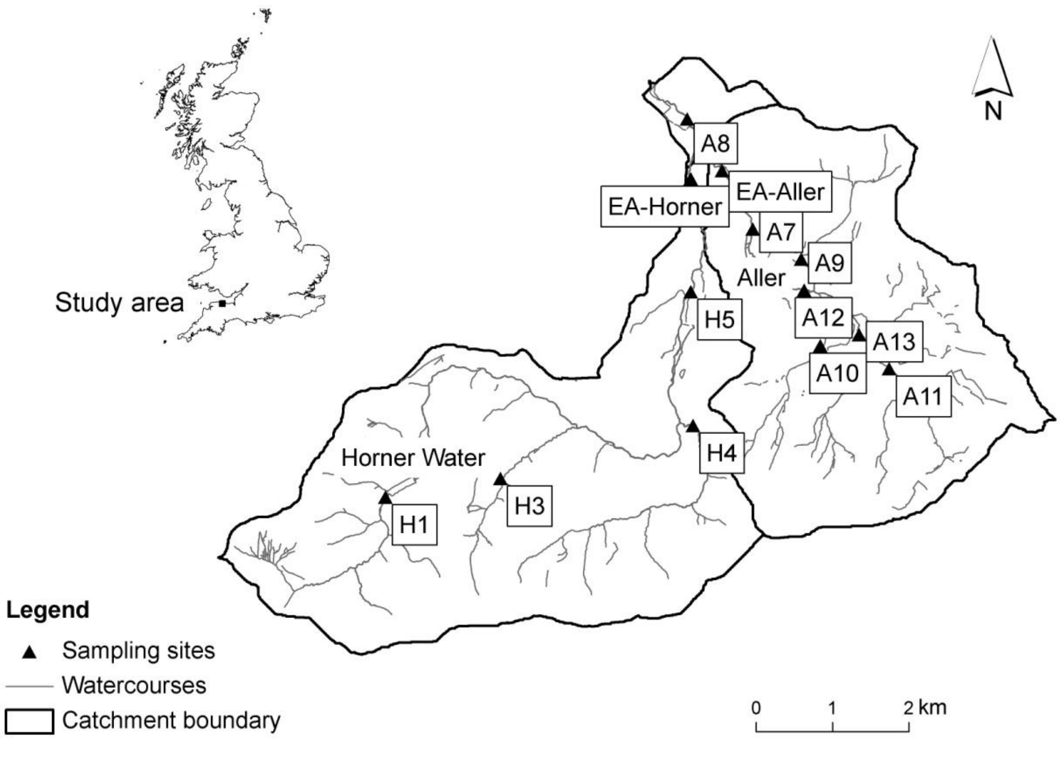


Fig 5.1 Map of the study area showing the Aller and Horner Water catchments, 11 regular monthly water quality monitoring points (H1-A13) and two Environment Agency invertebrate sampling points (EA-Aller and EA-Horner).

All samples were preserved in 100 % ethanol immediately on return to the laboratory and refrigerated. All taxa were identified to family level under a light microscope (x45 magnification) using standard identification keys. Although it is acknowledged that higher-resolution species-level data are more likely to produce significant model components (Monk et al., 2012), family-level identification was pursued in this study to allow time for the exploration of spatial variability across the 13 sites. Family-level identification is still used in routine bio-monitoring protocols, thus making it relevant for the achievement of the objectives of this study.

Sedimentation was quantified in four different ways. First, on each invertebrate sampling occasion, percentage fine bed sediment cover (approximate particle size < 0.06 mm) was estimated visually and by manual testing to determine that sediment was 'soft in texture and not abrasive to the hands when rubbed', as used in the standard UK Environment Agency methodology (Environment Agency, 2009). Second, total suspendable bed sediment concentration was measured on each invertebrate sampling occasion using a sediment re-suspension technique described by Lambert and Walling (1988). A steel cylinder with 40 cm diameter was pushed into the river bed and the substrate was disturbed up to c. 2 cm depth for c. 20-30 seconds. At each sampling site, three approximately evenly spaced samples were taken across the river channel from one bank, the middle of the channel and from the other bank. A 1-litre water sample was taken from the measurable volume within the cylinder, the sediment was then dried, weighed, calculated as g m^{-2} and the values from the three samples were combined and the mean determined for each sampling site. Third, suspended sediment was sampled monthly at all but the EA monitoring sites by taking a 1-litre grab sample. To calculate the total suspended sediment concentration, each water sample was allowed to settle for at least 3 days. The supernatant was then decanted into a measuring cylinder without disturbing the sediment. The remaining sample was agitated, measured in a measuring cylinder and then dried for 48 hours in desiccated pre-weighed ceramic evaporation dishes at 80^{o}C. The sediment concentration was then calculated as per Formula 4.1. Fourth, at five sampling sites (A7, A8, A11, A12, H5) flow-integrated storm sediment samples were taken using ISCO samplers programmed to sample on discrete, high-resolution time-steps of 30 (Aller) and 60 (Horner Water) minutes respectively, based on the examination of the catchment hydrological response. The samples were collected as soon as possible after each rainfall event within 24 hours and immediately transferred to a refrigerator on return to the laboratory where suspended sediment concentration was determined as above. At all stormflow monitoring locations, the cumulative suspended sediment frequency for all samples was calculated (in 5 mg L^{-1} increments) for the 6 months preceding the invertebrate sampling and the % time for which the arbitrary WFD 25 mg L^{-1} target was achieved was noted (% exceedance). All four techniques measured a similar particle size range as care was taken to sample only suspended sediment, which has been shown to be largely composed of particles < 0.06 mm (Knighton, 1998).

C. Data analysis

Average suspended sediment concentrations were calculated for the preceding 6 months for the 11 regular monthly sampling sites. Fixed environmental variables including altitude above sea level, distance from source and local river bed slope were calculated for all 13 sampling sites in ArcGIS 9.3.1. using a 5 m resolution Nextmap Digital Elevation Model. Each sampling location was assigned to a discharge category (1-3), representing mean annual discharge of <0.31, <0.62 and <1.25 m^3 s^{-1} respectively.

Macro-invertebrate community structure was summarised by calculating five metrics:

1. Proportion of sediment-sensitive invertebrates (PSI) present in the sample. This approach is designed to provide a biological alternative to physical/visual methods for the assessment of the extent to which the surface of the river bed is composed of, or covered by, fine sediment (Extence et al., 2013). Freshwater macro-invertebrates were assigned one of four Fine Sediment Sensitivity Ratings (A-D), from highly sensitive to highly insensitive. The PSI index was calculated as the ratio of the sum of ratings allocated to the most sensitive groups A+B to the total sum of ratings (Extence et al., 2013).
2. Lotic-invertebrate Index for Flow Evaluation (LIFE), which measures the response of the benthic macro-invertebrate communities to prevailing flow regimes by calculating a weighted average of flow scores that are based on the allocation of each taxon to a Flow Group ranging from I to VI in order of reducing preference for higher flow velocities (Extence et al., 1999).

3. Average Score per Taxon (ASPT) index which reflects a macro-invertebrate response to mild eutrophication/organic pollution (Armitage et al., 1983, Walley and Hawkes, 1997).
4. Number of taxa (NTAXA) which represents the total invertebrate taxon richness and is a measure of organic pollution stress and general environmental degradation (Clarke et al., 2011).
5. *Ephemeroptera-Plecoptera-Trichoptera* (EPT) % abundance, calculated as the proportion of individuals belonging to these orders within each sample, as a further measure of organic pollution/environmental degradation used by researchers worldwide (e.g. Wagenhoff et al., 2012).

In addition, the first four indices were standardised across sites and catchments by deriving a proportion of observed versus expected (O:E) Environmental Quality Indices (Extence et al., 2013). The expected scores were calculated for a theoretical pristine macro-invertebrate community that was predicted from measured site-specific environmental variables by the freely available RIVPACS III+ model (Wright, 2000).

Where necessary, data sets were $Log_{10}(x+1)$ transformed to ensure normality and homogeneity of variance for statistical tests. All statistics were considered significant where $P < 0.05$. Student's t-test was used to examine the differences in temporal variability of PSI and O:E PSI. Pearson's correlation was used to examine the association between PSI, O:E PSI and other invertebrate metrics on each sampling occasion, and the association between the four sedimentation variables, averaged by site. Mann-Whitney U-test was used to examine the difference between the observed % fine bed sediment cover and reference % bed sediment cover associated with 'pristine' sites for the predicted macro-invertebrate end groups in the RIVPACS III+ model.

Principal Component Analysis (PCA) was used to examine hydromorphological and sedimentation gradients in the two study catchments, using SPSS Version 16. The number of environmental variables was chosen to ensure a minimum of five cases per component (Tabachnick and Fidell, 2001, Pallant, 2007). Prior to performing the PCA, the suitability of data for factor analysis was assessed by inspecting the correlation matrix for presence of any coefficients of 0.3 and above, checking the Kaiser-Meyer-Oklin value exceeding the recommended value of 0.6 and the Bartlett's Test of Sphericity reaching statistical significance (Tabachnick and Fidell, 2001, Pallant, 2007). Ordination axes with eigenvalues exceeding 1 were retained and Varimax rotation was used for the interpretation of the axes as preliminary analysis using the Direct Oblimin rotation revealed low correlation between components (< 0.078).

Given the hierarchical structure of the data (repeated sampling occasions nested within 13 sampling sites), multi-level regression using a generalised linear mixed model (Gelman and Hill, 2007, Wright, 2009) was used to investigate the functional relationship between hydromorphological and sedimentation variables and macroinvertebrate indices using the lmre function in the lme4 library in 'R' version 2.15.0 (2012-03-30, The R Foundation for Statistical Computing). Site was used as a grouping variable and treated as a random effect, sedimentation variables were treated as fixed effects at the level of individual observations (Dunbar et al., 2009a). Sampling occasion was also included in the initial model as a random effect; however, it was later dropped during model simplification as it was shown not to be statistically significant, suggesting that unlike site, the repeated sampling occasions contributed little variation around the overall response. Generalised linear mixed models can cope with unbalanced experimental design. In this case, there were unequal numbers of observations (3-4) across the different sites as site A8 was only sampled on three occasions. The minimal adequate model was selected using likelihood ratio tests of nested models fitted by maximum likelihood under Chi-square distribution with 1 degree of freedom. The final model was then re-fitted using Residual or Restricted Maximum Likelihood estimation (REML) in order to produce unbiased estimates of the random effects (Dunbar et al., 2009a).

IV. Results

A. Temporal variability in macro-invertebrate indices and sedimentation variables

A total of 25,093 individuals were identified in 51 invertebrate samples, belonging to 65 families. Summary statistics for the macro-invertebrate indices and environmental variables recorded at the 13 study sites are presented in Tables 5.1 and 5.2, respectively.

There was no significant difference in PSI and O:E PSI scores between seasons, however, PSI and O:E PSI scores were significantly higher in 2010 than in 2011 ($P < 0.05$). Similarly, there was no significant difference in % fine bed sediment cover between seasons but the % fine bed sediment cover was significantly higher in 2011 than in 2010 ($P < 0.03$).

Site	PSI	O:E PSI	LIFE	O:E LIFE	ASPT	O:E ASPT	NTAXA	NTAXA	EPT % abundance
A10	59.04(8.32)	0.97(0.13)	7.20(0.60)	0.98(0.09)	5.78(0.65)	0.95(0.09)	18.00(2.71)	0.83(0.11)	4.98(3.97)
	4	4	4	4	4	4	4	4	4
A11	76.82(6.56)	1.30(0.10)	8.11(0.15)	1.06(0.02)	6.79(0.37)	1.12(0.03)	20.25(1.71)	0.93(0.07)	8.50(4.12)
	4	4	4	4	4	4	4	4	4
A12	73.25(4.99)	1.25(0.09)	8.15(0.25)	1.07(0.03)	6.82(0.22)	1.13(0.02)	21.25(4.50)	0.94(0.20)	15.23(7.64)
	4	4	4	4	4	4	4	4	4
A13	75.52(6.99)	1.29(0.12)	8.09(0.09)	1.03(0.07)	6.60(0.03)	1.10(0.04)	23.75(2.87)	1.07(0.14)	16.07(8.67)
	4	4	4	4	4	4	4	4	4
A7	76.33(8.63)	1.34(0.15)	7.92(0.24)	1.06(0.03)	6.66(0.36)	1.12(0.03)	22.75(5.91)	0.96(0.25)	10.49(3.50)
	4	4	4	4	4	4	4	4	4
A8	68.81(3.38)	1.19(0.05)	7.82(0.31)	1.02(0.06)	6.42(0.21)	1.09(0.01)	23.33(3.06)	0.98(0.18)	20.57(11.70)
	3	3	3	3	3	3	3	3	3
A9	68.17(5.99)	1.14(0.08)	7.70(0.30)	0.99(0.07)	6.34(0.39)	1.05(0.04)	26.50(0.58)	1.21(0.05)	7.55(6.59)
	4	4	4	4	4	4	4	4	4
EA-Aller	59.32(12.37)	1.02(0.21)	7.60(0.40)	1.02(0.03)	6.43(0.38)	1.08(0.03)	23.50(4.65)	1.01(0.20)	12.16(9.42)
	4	4	4	4	4	4	4	4	4
EA-Horner	72.33(5.14)	1.24(0.09)	7.94(0.34)	1.06(0.04)	6.57(0.31)	1.05(0.05)	22.00(1.83)	0.82(0.09)	36.00(22.27)
	4	4	4	4	4	4	4	4	4
H1	84.38(7.36)	1.36(0.09)	8.27(0.23)	1.08(0.03)	6.95(0.24)	1.07(0.03)	21.25(2.06)	0.93(0.14)	12.57(4.30)
	4	4	4	4	4	4	4	4	4
H3	88.01(3.99)	1.44(0.05)	8.27(0.26)	1.07(0.03)	6.90(0.30)	1.06(0.06)	21.75(1.26)	0.94(0.08)	22.23(3.27)
	4	4	4	4	4	4	4	4	4
H4	78.00(4.24)	1.30(0.08)	8.13(0.14)	1.05(0.02)	6.88(0.24)	1.06(0.05)	23.25(3.30)	1.02(0.17)	33.99(9.69)
	4	4	4	4	4	4	4	4	4
H5	77.87(10.44)	1.31(0.21)	8.02(0.21)	1.03(0.03)	6.69(0.38)	1.03(0.04)	22.00(2.94)	0.91(0.09)	32.53(8.73)
	4	4	4	4	4	4	4	4	4
Total	73.78(10.42)	1.24(0.17)	7.94(0.39)	1.04(0.05)	6.61(0.43)	1.07(0.06)	22.25(3.42)	0.96(0.16)	17.86(13.07)
	51	51	51	51	51	51	51	51	51

Table 5.1 Descriptive statistics for macro-invertebrate indices at the 13 sampling sites showing mean, standard deviation (in brackets) and sample size.

Site	Discharge category	Altitude (m)	Slope (m km^{-1})	Distance (km)	Average 6-months SS baseflow concentration (mg L^{-1})	25mg/l frequency exceedance (%)	Percentage fine sediment cover (%)	Suspendable bed sediment (kg m^{-2})
A10	1	63.00	23.93	0.56	25.80 (7.09) 3	-	31.25 (30.10) 4	11.36 (6.18) 4
A11	1	63.00	22.73	1.96	33.81 (4.24) 3	5.38 (1.35) 3	25.00 (10.80) 4	7.03 (6.45) 4
A12	2	36.00	9.84	3.84	34.13 (8.58) 3	2.52 (1.33) 3	13.75 (7.50) 4	10.62 (4.63) 4
A13	1	51.00	12.50	2.67	35.76 (9.47) 3	-	22.52 (23.95) 4	7.27 (6.27) 4
A7	2	36.00	6.82	5.04	41.64 (4.22) 3	8.28 (7.34) 3	9.00 (11.58) 4	2.94 (0.63) 4
A8	3	0.00	12.82	13.40	14.90 (5.01) 3	23.96 (9.49) 3	0.02 (0.03) 3	0.52 (0.19) 3
A9	1	55.00	42.92	2.03	40.92 (10.73) 3	-	13.75 (4.79) 4	1.63 (0.77) 4
EA-Aller	2	22.00	13.30	6.24	-	-	22.50 (15.00) 4	9.83 (7.07) 4
EA-Horner	2	18.00	0.10	13.00	-	-	10.38 (13.79) 4	0.88 (0.32) 4
H1	1	307.00	69.44	2.97	12.23 (5.45) 3	-	0.00 (0.00) 4	2.41 (1.96) 4
H3	1	251.00	116.20	1.55	11.12 (1.65) 3	-	0.50 (1.00) 4	3.61 (6.31) 4
H4	1	104.00	53.48	3.80	13.30 (4.54) 3	-	3.75 (4.79) 4	3.20 (3.81) 4
H5	2	50.00	23.81	10.90	15.44 (4.89) 3	70.53 (15.04) 3	1.00 (1.15) 4	1.31 (0.90) 4
Total	-	-	-	-	25.37 (13.00) 33.00	21.20 (27.73) 15.00	12.03 (15.59) 51.00	4.90 (5.41) 51.00

Table 5.2 Descriptive statistics for hydromorphological and sedimentation variables recorded at the 13 sampling sites showing mean, standard deviation (in brackets) and sample size.

B. Environmental gradients within the study area

The suitability of the data for factor analysis was confirmed (the Kaiser-Meyer-Oklin value was 0.702 and Bartlett's Test of Sphericity was highly significant P < 0.001). Principal component analysis revealed the presence of two ordination axes with eigenvalues exceeding 1, explaining 44.65 % and 38.56 % the variance, respectively (Table 5.3). The two ordination axes explained a total of 83.21 % of the variance. The first axis represents a hydromorphological gradient along the river continuum with increasing distance and discharge and decreasing altitude and slope, while the second axis reflects a sedimentation gradient with increasing suspended sediment concentration, % fine bed sediment and bed sediment concentration and decreasing slope (Fig. 5.2). Distance from source is also weakly loaded onto this gradient. Fig. 5.3 shows the position of the 13 sampling sites along the two ordination axes.

Axis	1	2
Discharge category	**-.962**	-.138
Log altitude	**.901**	-.070
Log distance from source	**-.849**	**-.377**
Log slope	**.724**	**-.632**
Log % fine bed sediment cover	.217	**.885**
Log suspendable bed sediment	.123	**.864**
Susp. sediment concentration	-.082	**.824**
Initial eigenvalues	3.13	2.70
% variance	44.65	38.56

Table 5.3 Loading scores of seven environmental variables, initial eigenvalues and % total variance accounted for by the two retained PCA components with eigenvalues > 1. Loading scores > 0.3 used in the interpretation of axes are highlighted.

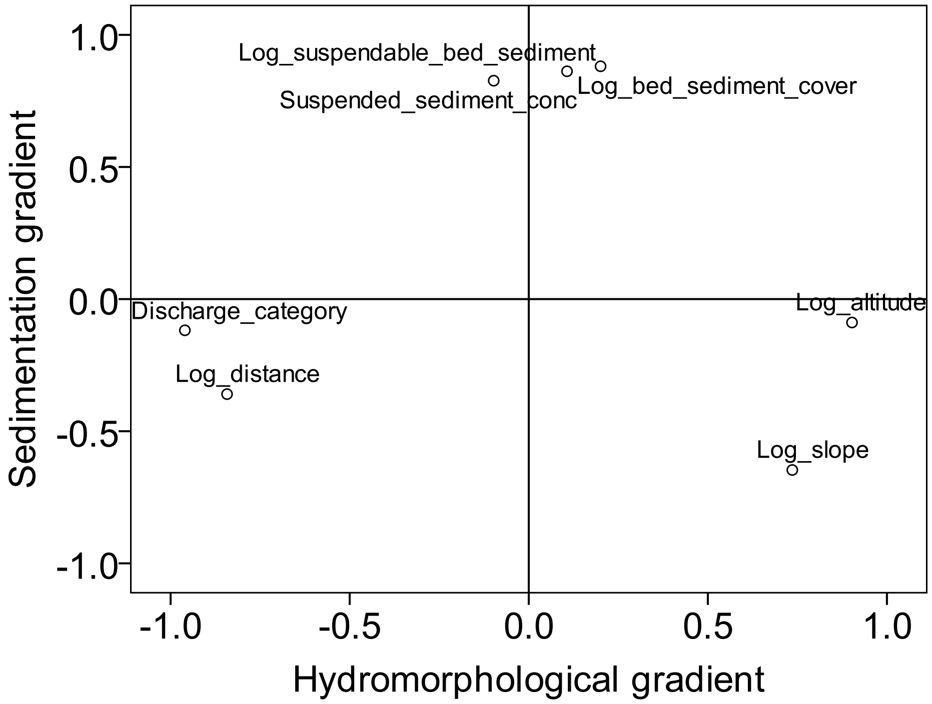


Fig. 5.2 Two-dimensional plot of variable distribution in rotated space along two PCA principal components revealed a hydromorphological and a sedimentation gradient.

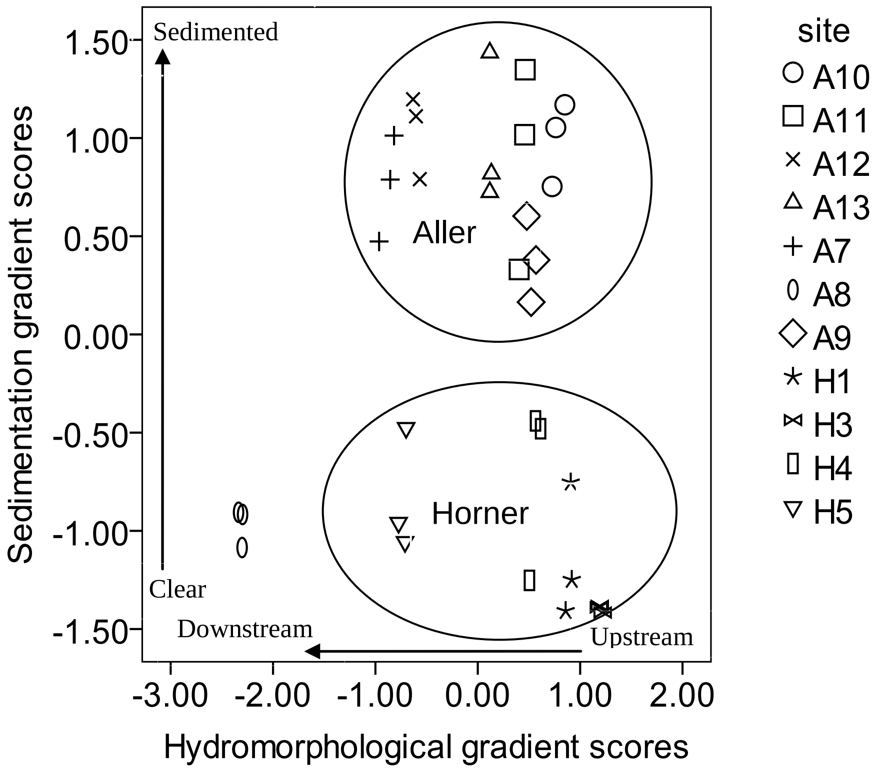


Fig. 5.3 Two-dimensional plot of sampling site loading scores on the two PCA principal components shows a clear hydromorphological and sedimentation gradient within and between the two study catchments, respectively.

C. Relationships between hydromorphological and sedimentation variables and the PSI index

A simple random-intercept model using restricted maximum likelihood estimation (REML) showed a statistically significant relationship between PSI scores and % fine bed sediment cover and altitude (Fig. 5.4, Table 5.4, p. 224) ($P = 0.009$) and between O:E PSI scores and % fine bed sediment cover ($P = 0.013$) (Fig. 5.5, Table 5.4). Suspended sediment concentration and 25 mg L^{-1} frequency exceedance also appeared to be significant predictors of PSI (but not O:E PSI), however, the models were rejected on account of non-random distribution of residuals.

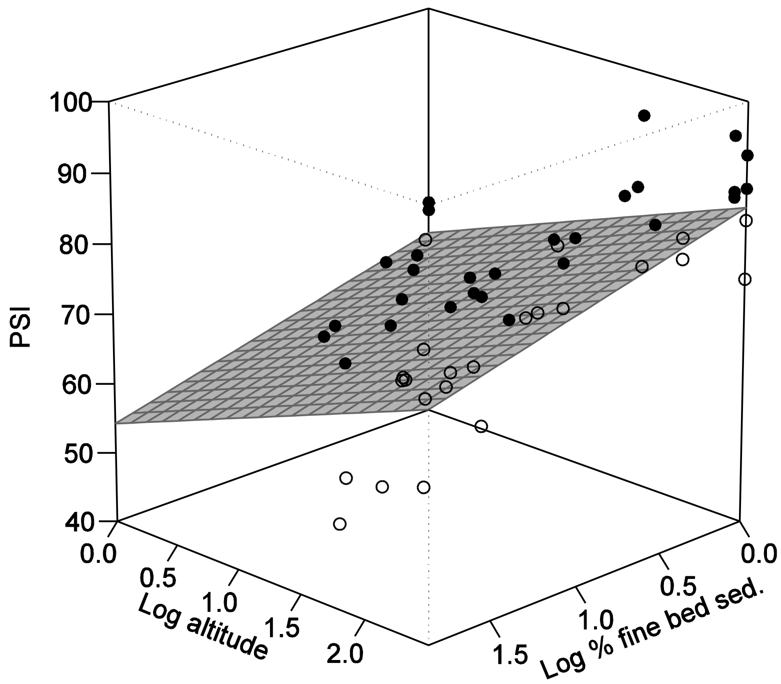


Fig. 5.4 Three-dimensional plot of the multi-level hierarchical mixed model, showing the relationship between % fine bed sediment cover, altitude and PSI, with highest PSI scores predicted for sites with lowest % fine bed sediment cover at high altitude. Observed data (for the 13 sampling locations, with 3-4 repeated measures per site) that lie above the surface are solid and those below are open.

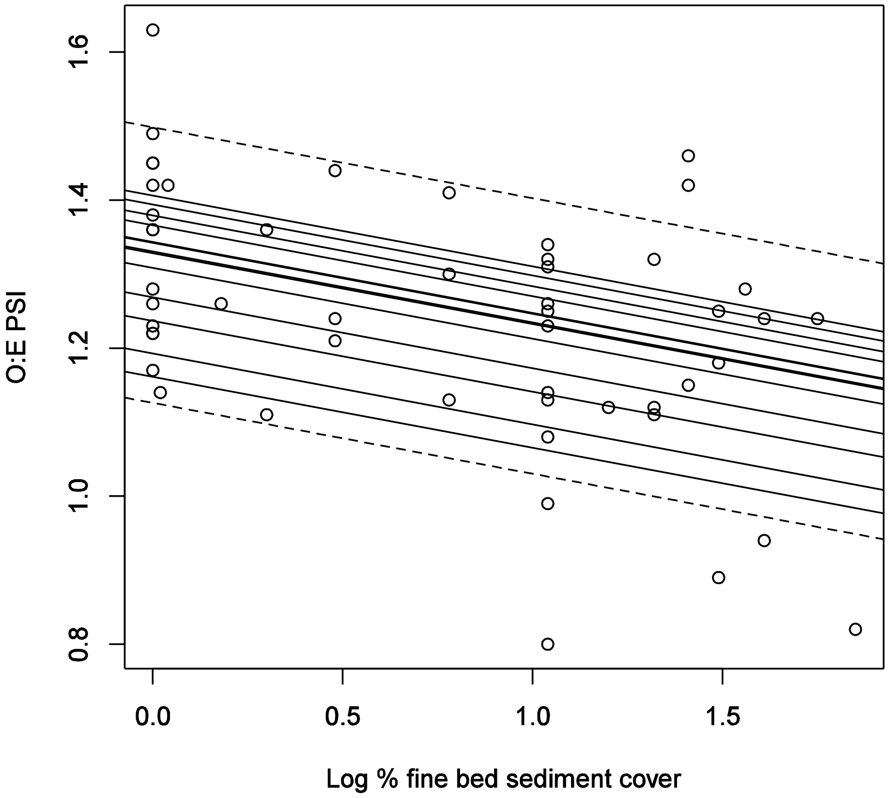


Fig. 5.5 Multi-level linear model with random intercept using restricted maximum likelihood estimation for the 13 sampling locations, with 3-4 repeated measures per site, showing a functional relationship between % fine bed sediment cover and O:E PSI. Dashed lines represent 95% confidence intervals of the fixed effects intercept (P = 0.013).

D. The utility of PSI as a method for assessing riverine sedimentation

LIFE, O:E LIFE and EPT % abundance were also related to % fine bed sediment cover (P = 0.012, P = 0.029 and P = 0.012, respectively). PSI was significantly correlated with LIFE, with the strength of the relationship increasing over the sampling period (Table 5.5).

Mean percentage fine bed sediment cover at each sampling site was significantly correlated with mean suspendable bed sediment concentration (R = 0.788, P < 0.001).

	Season	LIFE	ASPT	NTAXA	EPT % abundance
PSI	Spring 2010	0.630*	ns	ns	ns
	Autumn 2010	0.771**	0.744**	ns	ns
	Spring 2011	0.799**	0.731**	ns	ns
	Autumn 2011	0.899**	0.843**	ns	ns
		O:E LIFE	O:E ASPT	O:E NTAXA	
O:E PSI	Spring 2010	0.578*	ns	ns	
	Autumn 2010	0.781**	0.664*	ns	
	Spring 2011	0.822**	0.646*	ns	
	Autumn 2011	0.911**	0.840**	ns	

Table 5.5 Correlation between PSI, O:E PSI and other macro-invertebrate indexes over the sampling period. ** = P < 0.01, * = P < 0.05, ns = not significant.

The PSI values recorded in this study ranged between 46.81 and 94.74 (mean = 73.78, N=51). The O:E PSI values ranged between 0.80 and 1.63 (mean = 1.24, N = 51), while the % fine bed sediment values ranged between 0 and 70 % (mean = 12.03, N = 51) (Tables 1 and 2). There was no significant difference between the observed % bed sediment cover and reference % bed sediment cover associated with 'pristine' sites for the predicted macro-invertebrate end groups in the RIVPACS III+ model (n.s., N = 123) (Fig. 5.6).

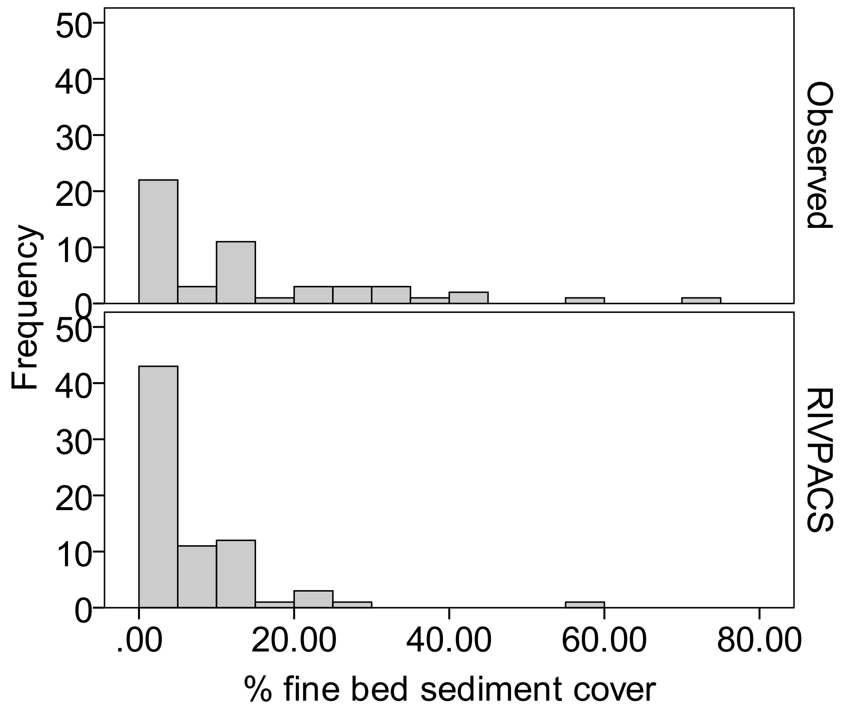


Fig. 5.6 Histogram of observed and reference % fine bed sediment cover values for the RIVPACS III+ predicted macro-invertebrate end-groups.

V. DISCUSSION

The results of this research only partially support the research hypothesis that anticipated that PSI would be the only index related to physical measurements of sedimentation across a moderate gradient of impact at a reach-scale sampling resolution. While the existing non-pressure specific indices LIFE and EPT % abundance were also related to a physical measure of sedimentation, the relationship between % fine bed sediment cover and PSI was statistically more significant.

A. Temporal variability and environmental gradients

Contrary to other studies (Wood et al., 2011), there was no seasonal difference in PSI scores in this study. However, the PSI scores were significantly higher in 2010 than in 2011, whilst % bed sediment cover exhibited an inverse response. This was probably due to the start of a prolonged drought period in 2011 that facilitated lower flows and resulted in a greater sediment deposition in the river channel.

The longitudinal hydromorphological gradient was more pronounced in the Horner Water catchment. The sedimentation gradient largely reflected the lower sedimentation impacts in the higher upland reaches of the Horner Water catchment through to the lowlands where reduced local slope facilitates sediment deposition on the river bed. The counter-intuitive negative loading of distance from source onto the sedimentation axis reflects higher bed sedimentation levels in the upper reaches and in smaller tributaries in the Aller catchment and may reflect increased diffuse anthropogenic sediment input into this river system.

B. Relationship between hydromorphological and sedimentation variables and the PSI

The relationship between raw PSI scores (but not O:E PSI) and altitude reflects a decreasing land use intensity in the uplands and hence lower sediment input, as well as a coarser substrate. Wood et al. (2011) also found higher PSI scores at sites dominated by coarser substrate.

Of the four variables that measured sedimentation in this study, only % fine bed sediment cover was significantly related to the ecological index PSI. Although substrate is an important variable in the prediction of expected macro-invertebrate scores by the RIVPACSIII+ model (Clarke et al., 2011), the significant relationship between raw PSI and % fine bed sediment cover shows that the relationship between O:E PSI and % fine bed sediment cover is not simply a modelling artefact. Hydromorphology-independent models that are currently being developed (Clarke et al., 2011) may allow examination of this relationship in the absence of substrate as a predictive variable.

The lack of a significant relationship between suspended sediment concentration, % exceedance and PSI may be due to a number of factors. First, sediment in suspension may have a less direct impact on the aquatic biota than river bed fines (Kefford et al., 2010), especially if the increased sediment concentrations are confined to short periods during hydrological events, as was the case in this study. It has been shown that 90 % of annual suspended sediment load can leave the catchments during 6 % of hydrological events (Knighton, 1998) and it is likely that suspended sediment concentrations only significantly impact on the health of macro-invertebrate communities during prolonged periods of high exposure (Larsen and Ormerod, 2010b). However, as a relatively small sample size was available for the evaluation of these variables (N = 33 and N = 15, respectively), further work involving a wider range of ecosystems across an impact spectrum is needed to fully evaluate the link between these variables and PSI and to establish whether duration of exposure expressed as a % threshold exceedance, as proposed by Bilotta and Brazier (2008), is indeed an ecologically meaningful measure of sedimentation impacts.

C. The utility of PSI as a method for assessing riverine sedimentation

LIFE, O:E LIFE and EPT % abundance were also related to % fine bed sediment cover, however this relationship was statistically less significant than with PSI. The increasing correlation between PSI and LIFE during our study period concurs with the work of Matthaei *et al.* (2010) who found that hydrological stress exacerbates the negative effects of sedimentation on aquatic macro-invertebrates. Conversely, PSI was not correlated with EPT % abundance, possibly reflecting a differentiated response of the two metrics to multiple stressors such as sedimentation, hydrological stress and nutrients (Matthaei et al., 2010, Wagenhoff et al., 2011, Wagenhoff et al., 2012). The potentially differentiated response of PSI to multiple stressors, as compared with existing metrics such as EPT, merits further investigation as PSI could become a useful tool in distinguishing between alternative causes of river impairment.

Mean % fine bed sediment cover was positively correlated with the mean total suspendable bed sediment concentration. Although PSI was not related to the total suspendable bed sediment concentration, this may be due to the difference in sampling resolution (Smiley and Dibble, 2008, Larsen et al., 2009). Whereby in this study sedimentation was measured at a patch scale by taking three systematic samples across the river channel, the invertebrate sampling was undertaken at a reach scale with habitats sampled in proportion to their availability. Previous studies have found that the choice of sampling scale may influence the ability to detect treatment effects (Smiley and Dibble, 2008). Further, the different relationships between the PSI and the two bed sedimentation variables found in this study demonstrate the difficulty in measuring sediment settling rates that are likely to change both temporally and spatially (Kefford et al., 2010).

The % fine bed sediment cover estimation technique used in this study could be criticized as at best semi-quantitative and prone to surveyor errors. Therefore, it has to be noted that the estimation of fine bed sediment grain size in this survey method is approximate and some particles greater than the 0.06 mm threshold may have been included in the % bed cover estimation. In other similar studies, all particles smaller than 2 mm were regarded as fine sediment (e.g. Zweig and Rabeni, 2001, Matthaei et al., 2006, Larsen et al., 2009). However, despite its semi-quantitative basis, it is argued that this straightforward technique, which is used in routine bio-monitoring protocols across the UK (Environment Agency, 2009) has proven here to be an ecologically meaningful measure of sedimentation impacts.

Many reach-scale confounding factors and patch-scale sources of variation (Angradi, 1999), such as presence of refugia, make the detection of sedimentation effects challenging. Impacts of sedimentation using non-sediment-specific invertebrate metrics have previously been detected at a patch scale where finer resolution measurements allowed for the sedimentation effects to be detected at lower values of % sediment cover than could be done at reach scale (Larsen et al., 2009). At reach-scale, sediment effects are harder to detect (Larsen et al., 2009), with weaker and more subtle relationships between invertebrate metrics and fine sediment (Angradi, 1999) as refugia may allow sediment-sensitive taxa to maintain their density (Matthaei et al., 2006). Hence, the ability of PSI to detect impacts at a reach-scale sampling resolution, across a relatively modest gradient of impact, makes it a suitable tool for practical river management applications in bio-monitoring programmes routinely carried out at this scale. Similarly to the approach suggested by Extence et al. (1999) for the assessment of impaired flows using the LIFE index, PSI and % fine bed sediment would be well suited to setting of 'twin targets' for the monitoring of sedimentation impacts and the achievement of 'Good ecological status' under the Water Framework Directive as the failure to meet the sedimentation target may not necessarily mean a corresponding failure in the ecological standard or *vice-versa*. Collins et al. (2011) recently reviewed international approaches to setting of sedimentation targets. PSI could be used alongside or *in lieu* of some of the existing approaches or indeed as part of the proposed new modelling techniques. The twin approach proposed in this thesis goes some way towards satisfying the need for the use of 'holistic and ecologically meaningful approaches' (Page et al., 2012) to setting and measuring of desired river restoration outcomes.

In a review paper Kemp et al. (2011) state that aquatic biota can be adversely affected by extremely low sediment concentrations. Analysis of reference values for % fine bed sediment composition in different ecosystems at benchmark sites such as those used in the RIVPACS model is a useful starting point for the setting of sedimentation targets. For the sites included in this study, the reference values for RIVPACS predicted macroinvertebrate end-groups range between 0-57 %, whilst the observed values ranged between 0-70 %. Impairment of the macro-invertebrate communities in this study, defined as O:E PSI value < 1, was observed on three occasions at the most impacted sites (A10 and EA-Aller) when % fine bed sediment values exceeded > 10% (Fig. 6.). However, at other sites, high O:E PSI values between 1.15 and 1.42 were still recorded at % fine bed sediment values between 25-40 %. As the observed % bed sediment cover in the study catchments did not differ significantly from the reference values for the RIVPACS-predicted end-groups, it can be concluded that the sampling sites in this study were close to reference conditions.

In the literature, reported threshold values for % fine bed sediment impairment range from 0.8-0.9 % of fine sediment composition in riffle substrate (Kaller and Hartman, 2004), through 3 % of streambed silt cover (Bryce et al., 2010), fine sediment deposit of 10-20 % (Relyea et al., 2012) and 12-17 % in fine interstitial sediment content to 75 % of substrate embeddedness (Collins et al., 2011). Larsen et al. (2009) found tolerance values for a range of taxa between c. 1-12.5 % sediment cover. Kemp et al. (2011) noted that aquatic biota can be adversely affected by extremely low sediment concentrations and Larsen and Ormerod (2010b) found that even small increases in sediment loads to stony streams increased invertebrate drift and reduced benthic density. Their results suggest that any water quality target for good ecological status related to % sediment cover is likely to be low and will vary between different ecosystems.

Clearly, further research is needed to inform the development of twin ecological and sedimentation targets by testing the relationship between PSI and % fine bed sediment cover along the full environmental gradient of sedimentation impacts (Clarke et al., 2011) and multiple stressors (Townsend et al., 2008). However suitable datasets with simultaneous biological and abiotic measurements are scarce (Dunbar et al., 2010), making the results of the present study even more valuable.

VI. Conclusions

This Chapter examined the utility of a new pressure-specific macro-invertebrate index PSI to act as a simple tool for setting and monitoring of sedimentation targets. PSI was found to be related to % fine bed sediment cover at reach-scale sampling resolution, across a moderate gradient of impact. While other metrics, LIFE and EPT % abundance, were also related to % fine bed sediment cover, this relationship was weaker. While PSI was correlated with LIFE, this relationship changed over time and was strongest in the presence of hydrological stress. PSI and EPT % abudance were not correlated, suggesting a differentiated response to multiple stressors. While further testing of PSI along a full gradient of multiple stressors is recommended, this research shows the potential of PSI to become a new, simple and cost-effective tool for the setting and monitoring of twin sedimentation targets and to add explanatory power to the existing suite of macro-invertebrate indices.

Chapter 6

EVALUATING THE EFFECTIVENESS OF AN ECOSYSTEM MANAGEMENT APPROACH TO DELIVER WATER QUALITY OBJECTIVES

I. ABSTRACT

Over the past three decades, many plot and field scale studies elucidated the processes controlling the mobilisation, transport and delivery of pollutants from intensive agricultural land use and their impact on receiving watercourses. While the effectiveness of different mitigation measures has been examined, the effectiveness of a suite of measures on multiple pollutants at a catchment scale is still unclear and likely to vary with local catchment characteristics and socio-economic conditions. This chapter addresses this knowledge gap by establishing a firm baseline against which the effectiveness of a suite of present and future land use changes in the agricultural Aller catchment can be evaluated and examines the impact of a single large scale land use intervention - upland ditch blocking - on multiple physico-chemical and biological water quality parameters in Horner Water catchment one year after restoration.

The conceptual understanding of the hydrological processes operating within the study catchments and the baseline water quality characterisation indicate that the proposed arable conversion and construction of flood alleviation levées in the Aller catchment are likely to lead to reduced sediment and nitrate export from the most intensively farmed central part of the catchment. However, extended flooding of floodplain grassland and new areas of intensively managed grassland may also lead to enhanced export of dissolved reactive phosphorus (DRP), unless a low-input, extensive management regime of these areas can be practiced. Additional wooded buffer strips in the riparian corridor of the river Aller are likely to lead to reduced sediment input through stabilisation of river banks.

No clear positive or negative impact of the extensive ditch blocking in the Horner Water catchment could be detected one year after habitat restoration. While this may be due to the short time scale of post-restoration monitoring, it may also indicate that these extensive earth-moving works have not had any detrimental effect on the ecological status of this high quality semi-natural environment.

II. INTRODUCTION

Over the past decades, plot and field scale studies elucidated the processes and mechanisms responsible for the negative impact of enhanced anthropogenic nutrient inputs on altered biogeochemical cycles (Dungait et al., 2012) and water quality (McGonigle et al., 2012) in agricultural systems. While measures to ameliorate the effects of intensive agricultural production on biodiversity and the wider environment have been in place since the 1990s (Carey et al., 2003), the effectiveness of a suite of mitigation measures on multiple pollutants at a catchment scale is still unclear (McGonigle et al., 2012) and is likely to differ between sites and observation scales. In this Chapter, the potential effectiveness of a suite of water quality mitigation measures is evaluated at a catchment scale, using a nested monitoring approach in the agricultural Aller catchment. The measures include re-wetting of floodplain grassland through the construction of flood alleviation levées, planting of riparian woodland and wooded buffer strips, conversion of arable land to permanent grassland and restoration of off-line mill ponds.

In the upland Horner Water catchment, the implemented flood risk and water quality mitigation measures include peatland restoration through the blocking of drainage ditches. Upland peatlands in the UK have been managed and altered by humans for millennia (Ramchunder et al., 2009). Particularly extensive draining of upland peatland has occurred since the 2nd World War with a drive for improved agricultural production, with UK peatlands now considered to be some of the most extensively drained in the world (Holden et al., 2004). The increasing concentrations of DOC over the past two decades, reported from rivers in the UK, north-west Europe and north America (Evans et al., 2005) give rise to concerns over the destabilisation of the terrestrial soil carbon pool, particularly in peatlands which are important stores of terrestrial carbon (Billett et al., 2012). Over the past decade, conservation efforts to revert the environmental degradation of peatlands have increased, with a particular focus on biodiversity benefits (Wilson et al., 2011a). However, peatland restoration could potentially bring multiple benefits for a number of ecosystem services, including water quality and carbon storage and research on quantifying the effects of upland restoration on these multiple benefits is now underway (Grand-Clement et al., 2013). To date, several studies have found contradicting effects of upland ditch blocking on fluvial carbon fluxes, likely to reflect the different effects of complex controls on peatland hydrology and biogeochemistry in differing local conditions (Wilson et al., 2011b). Furthermore, the effects of conservation measures are likely to vary with observation scale and time-span, therefore monitoring of restoration measures needs to be undertaken at a catchment scale (Wilson et al., 2011b) and over an extended period (Grand-Clement et al., 2013).

This chapter aims to address some of these knowledge gaps by evaluating:

1. The likely impact of the proposed land use mitigation measures in the Aller catchment on the water quality determinands at a catchment scale;
2. The response of physico-chemical determinands of water quality at a sub-catchment scale to upland ditch blocking one year after habitat restoration in the Horner Water catchment;
3. The response of freshwater macro-invertebrate communities at a sub-catchment scale to upland ditch blocking one year after habitat restoration in the Horner Water catchment.

III. METHODOLOGY

A. Land management interventions

In the Aller catchment, old mill ponds were cleared and restored for increased flood water storage between 2nd and 18th November 2011 (Fig. 6.1 and 6.2a-b) and a small area of floodplain woodland was planted in spring 2012 (Fig. 6.1). The flood alleviation works in the Aller catchment, including construction of levées and lowering of ground were undertaken between 6th May and 26th July

2013 (Fig. 6.1, 6.2c-d). Two tenant farmers agreed to enter into a Higher Level Stewardship scheme from 1st June 2013, whereby 4 arable fields on the steepest ground in the central part of the catchment will be converted to permanent pasture and 6 m wide woodland buffer strips will be created in the upper reaches of the river Aller in 2014 (Fig. 6.1).

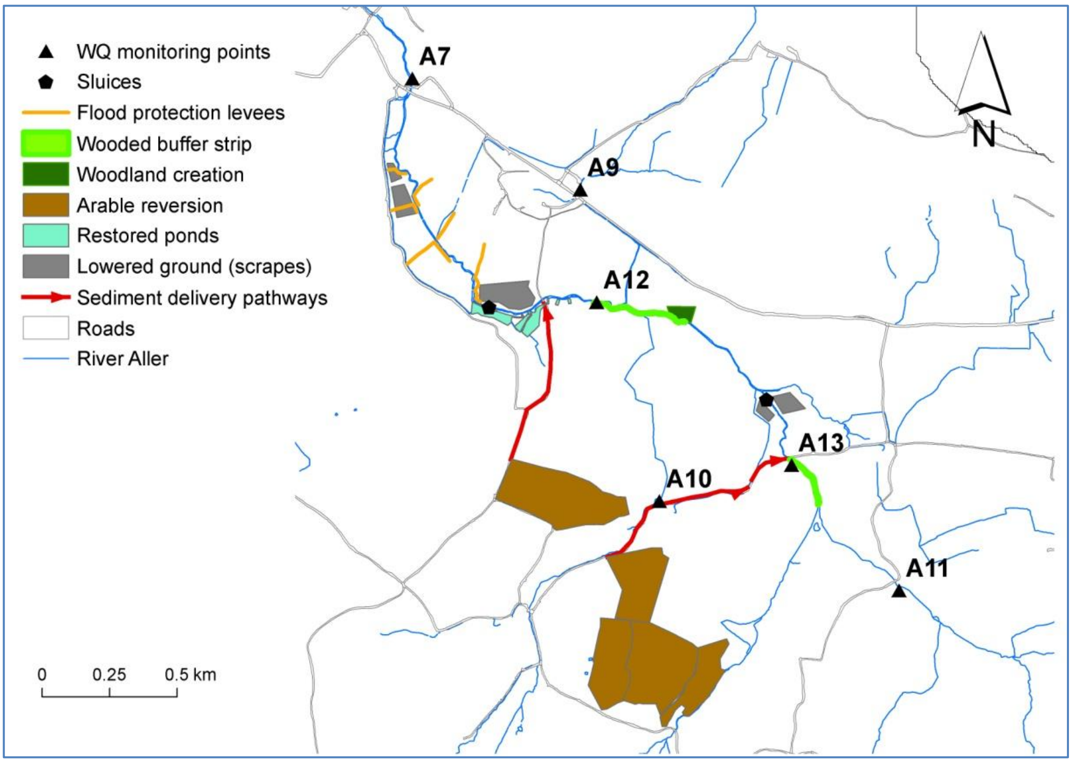


Fig. 6.1 Map of land management interventions carried out in the Aller catchment, including restoration of old ponds (2nd-18th November 2011), woodland planting (spring 2012), construction of flood alleviation levées and shallow habitat scrapes (6th May- 26th July 2013). Conversion of arable land to permanent pasture and 6 m wide wooded riparian buffer strips will be implemented in 2014. Observed known preferential sediment delivery pathways from arable fields to the watercourse along paved roads are highlighted in red.

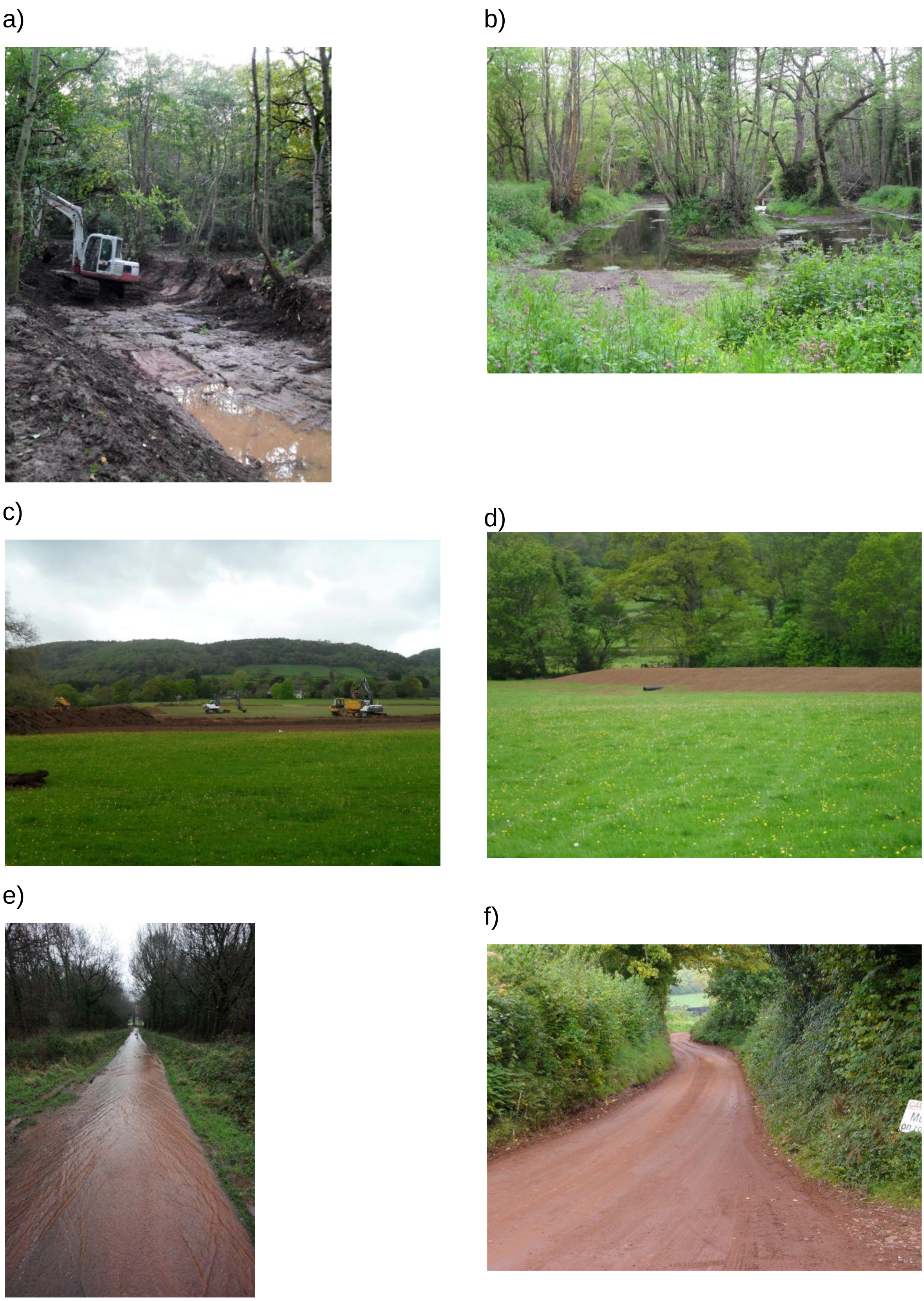


Fig. 6.2 a) Restoration of former mill ponds for flood water storage 17th November 2011, b) restored ponds 24th May 2013, c) and d) construction of flood alleviation levées in the Aller Vale 24th May 2013, e) and f) preferential overland sediment pathways along paved roads delivering eroded topsoil to the river Aller from the fields targeted for arable conversion.

In the Horner Water catchment, upland ditch blocking was undertaken between the 8th September and 14th October 2011 (Fig. 6.3). The extent of works is illustrated in Fig. 6.4. Five % of sub-catchment H1, 35 % of sub-catchment H3 and 80 % of sub-catchment H4 were affected.

Originally, all the works were scheduled to take place between summer 2010 and 2011, allowing 1 year for pre- and 1 year for post-restoration monitoring. However, delays due to difficulties with obtaining statutory consents and agreement of tenant farmers meant that the present study can only report on the *potential* of the ecosystem management approach to deliver water quality improvements in the Aller catchment and offer an assessment of the short-term impacts of upland ditch blocking on water quality and biodiversity of upland streams in Horner Water catchment.

Fig. 6.3 Upland ditch blocking undertaken by the National Trust in the upper reaches of the Horner Water catchment between 8th September and 14th October 2011 with the aim of increasing water storage and reducing the velocity and magnitude of discharge response to rainfall events.

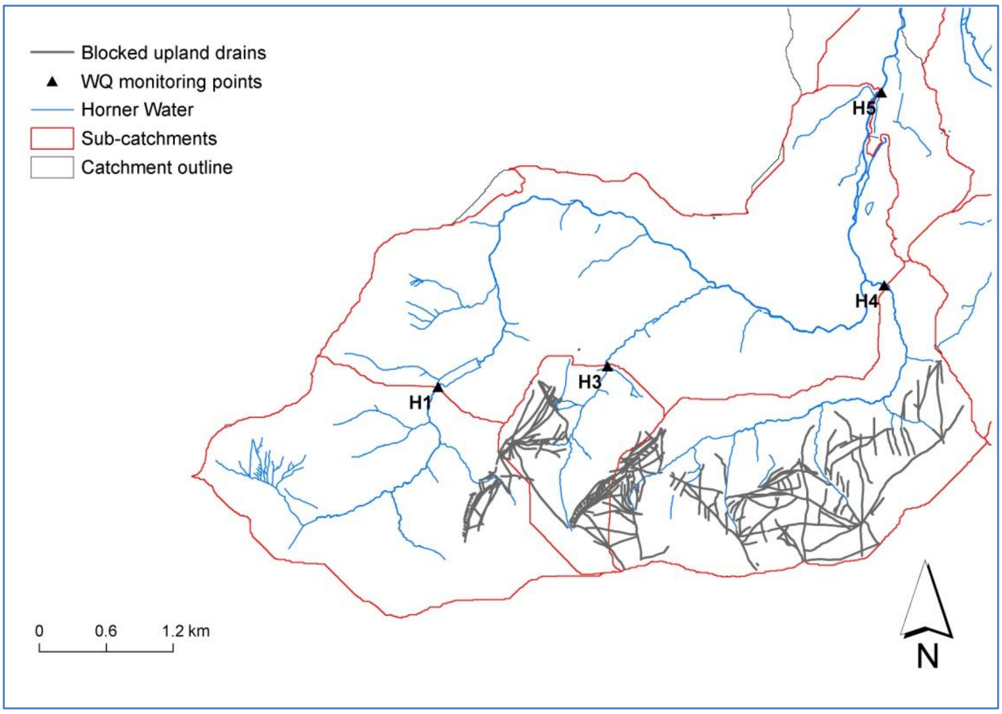


Fig. 6.4 The extent of upland ditch blocking in sub-catchments H1-H3 carried out between 8th September and 14th October 2011. Approximately 5 % of sub-catchment H1, 35 % of H3 and 80 % of H4 were affected.

B. Water quality sampling

Monthly water quality grab-samples were collected between 25th February 2010 and 26th November 2012 at six monitoring sites (H1, H3, H4, H5, A7, A8) (Fig. 5.1), with November 2011 treated as the first month of the post-restoration period. At a further five sites in the Aller catchment (A9, A10, A11, A12, A13) (Fig. 5.1), monthly grab-samples were collected between 25th February 2010 and 3rd November 2011 to establish a baseline against which the impacts of future land use change can be measured. Flow-integrated sampling was undertaken between 10th July 2010 and 31st January 2013 at three sampling locations (H5, A7, A8), with the period between 29th July 2010 and 18th November 2011 taken as a pre-restoration period on the basis of the timing of lowland pond restoration works in the Aller catchment. At a further two sites (A11, A12), flow-integrated sampling was undertaken between 10th July 2010 and 18th November 2011 to establish a baseline against which the effects of future land use change in the Aller catchment can be measured.

Invertebrate samples were collected at 13 sites as described in Chapter 5 (Fig. 5.1). At five sites (H1, H3, H4, EA-A and EA-H) samples were collected on six occasions with May 2010, November 2010 and May 2011 representing the pre-restoration and November 2011, May 2012 and November 2012 representing the post- restoration period with reference to the Horner Water restoration works. At the remaining eight sites (H5, A7, A8, A9, A10, A11, A12, A13) samples were collected on four occasions in May and November 2010 and 2011 to establish a baseline against which the impact of future land use change in the Aller catchment can be measured.

On each monthly sampling occasion, temperature was measured using a digital test thermometer with a stainless steel probe (Brannan Thermometers, Cumbria, UK) and pH was measured using a Checker pocket size pH meter (until 23rd October 2012) and H198129 pH meter (26th November 2012 only) (Hannah instruments, Bedfordshire, UK). The pH meters were calibrated in 4 and 7 pH solution on each sampling day.

Continuous stage data were collected at three sites (A7, A8, H5) using the same instrumentation as described in Chapter 4, Section III.B. At a further five sites (H3, H4, A9, A11, A12), continuous 15 minute stage data were collected by consultants commissioned by the National Trust, using OTT Orpheus Mini loggers (OTT Hydromet GmbH, Kempten, Germany). At H1, discharge was calculated from the Wessex Water Nutscale Reservoir compensation flow record by area-subtraction method, due to problems with OTT instrumentation at this site. Environment Agency rainfall data was used for both study catchments, as described in Chapter 4 (Fig. 4.1).

For 9 out of the 11 water quality monitoring sites (Fig 5.1), rating curves were constructed using the standard flow/area discharge measurement method (YSI, 2009). The Environment Agency supplied the discharge data at its hydrometric monitoring station 51002 at H5 (Marsh and Hannaford, 2008) and hence no rating curve was constructed for this site. Between three and nine rating datasets were used at each site, in line with the UK Environment Agency practice (Hazel Grace, pers. comm. 9th July 2012). A higher number of rating points was collected at stormflow monitoring sites, while the lowest number was collected at two sites (A10 and A13) which were only monitored in baseflow and where stage fluctuations were small (within 5 cm). Rating data were collected by a team of scientists, employed by the National Trust on the larger Defra project. To ensure comparability of datasets, a strict protocol was used throughout the data collection work as specified in the ISO standards 748 (1997) and 9196 (1992) using the mid-section discharge equation method (YSI, 2009). Additional data were collected at A7 and A8 to ensure satisfactory coverage of high flows at these stormflow monitoring sites. 95 % confidence intervals were fitted to best-fit regression curves using the lm and nls functions in the ‘stats’ library in ‘R’ version 2.15.0 (2012-03-30, The R Foundation for Statistical Computing) to illustrate the uncertainty associated with discharge calculations (Table 6.1, Fig. 6.5). Median regression parameters were used for the purposes of instantaneous discharge calculations.

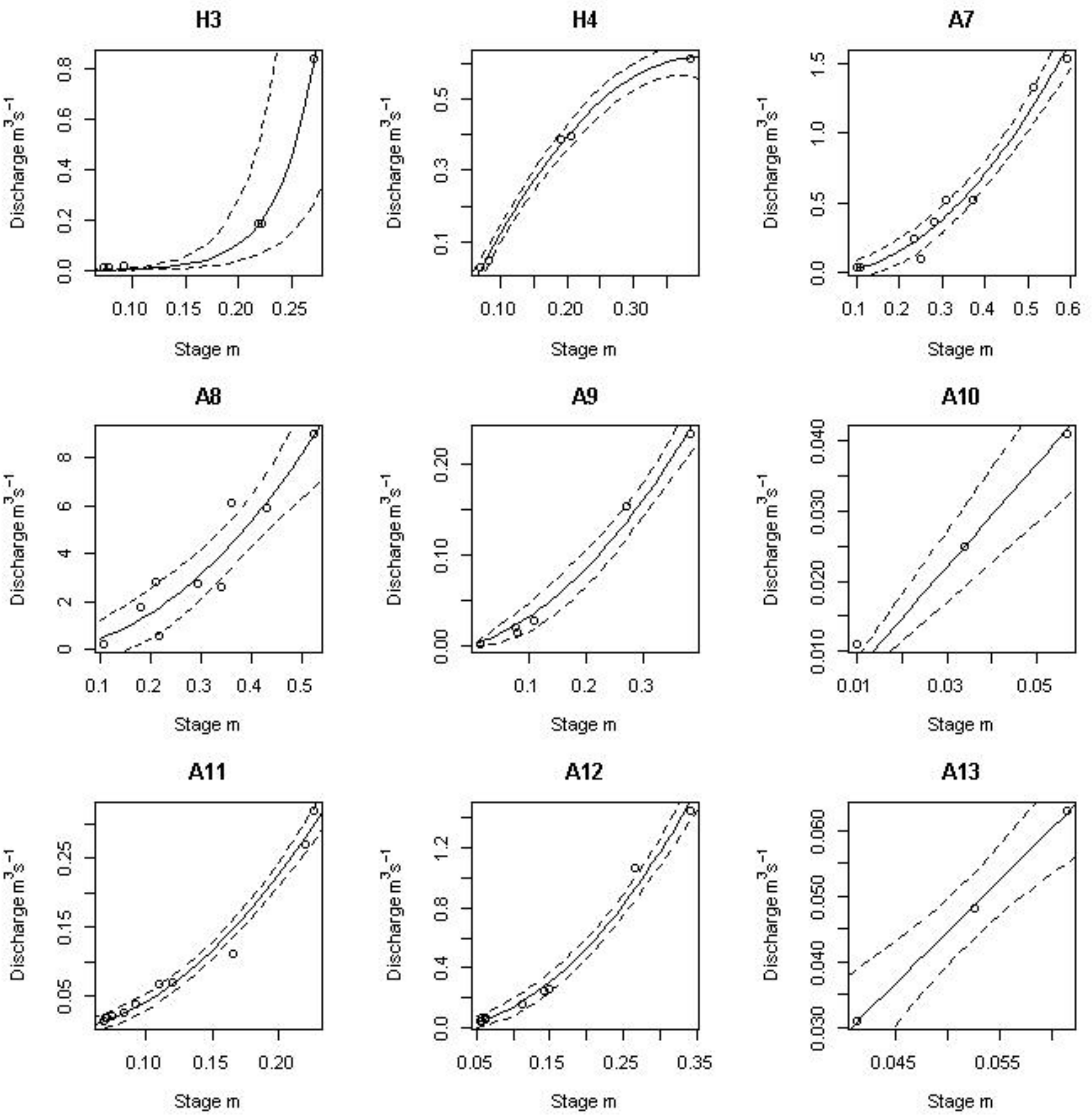


Fig. 6.5 Lines of best fit of stage/discharge rating equations for nine monitoring sites with 95 % confidence intervals.

C. Laboratory analysis

Invertebrate samples were preserved and identified in the laboratory using the protocol described in Chapter 5, Section III.B. For both baseflow and stormflow samples, SS was quantified as described in Chapter 4, equation 4.1. Monthly DOC samples were analysed on the Skalar Formacs^{HT} CA14 TOC Analyser and stormflow DOC samples were analysed using the Trios UV spectrometer and recalculated as described in Chapter 4, Section III.C. Suspended sediment total particulate carbon (TPC) content in stormflow samples was quantified using an elemental analyser, as described in Chapter 4, Section III.C.

For both stormflow and baseflow samples, total oxidised nitrogen (TON), unfiltered dissolved ortho-phosphate (DRP) and alkalinity were determined colourimetrically using the continuous flow Auto-analyzer 3 (Bran+Luebbe, Norderstedt, Germany). During this analysis, nitrate is reduced by hydrazine in alkaline solution with a copper catalyst, then reacted with sulphanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride to form a pink compound measured at 550 nm with a detection limit of 6 µg L^{-1}, accuracy 93.09 % and precision 89.18 %. Alkalinity is measured with a methyl orange indicator in water with a detection limit of 3.4 mg L^{-1}. DRP in stormflow samples was determined by reaction with molybdate and ascorbic acid to form a blue compound measured at 660 nm with a detection limit of 38 µg L^{-1}, accuracy 61.24 % and precision 79.93 %. A number of baseflow samples (Table 6.4, p. 227) were also analysed at Rothamstead Research North Wyke laboratories to characterise the spatial variability of baseflow DRP concentrations across the two study catchments, as these were consistently below the detection limits of the Auto-analyser. This analysis was carried out on Aquakem 250 (Thermo Fisher Scientific Inc., Vantaa, Finland) discrete photometric analyser with detection limit 1.5 µg L^{-1}.

D. Data analysis

Total annual rainfall was calculated for each calendar year for the period of record from the available EA rain gauge data for both study catchments. The % of total annual rainfall as compared to the longer term mean was calculated for each year of the study period (2010-2012).

The total discharge, total water yield and Q5:Q95 ratio were calculated for the nine sites with continuous discharge record for the period between 29th July 2010 and 18th November 2011 to characterise and compare the spatial distribution of hydrological variables across the two study catchments before restoration. Q5:Q95 ratio was used as an indicator of the hydrological flashiness at each site (Jordan et al., 2005, Jordan et al., 2012b).

Sub-catchments with the contributing area at each sampling location were delineated in ArcGIS 9.3.1 (Esri Inc., Redlands, CA) using the ArcHydro tools and a 5 m resolution DEM. The total area of each sub-catchment, the proportion of each land use type (arable, grassland, moorland, woodland), the proportion of each soil type (peat, clay, loam) and median soil properties (median BD, TC, TN, C:N ratio, $\delta^{15}N$, C storage and N storage) within each sub-catchment were calculated.

Principal Component Analysis (PCA) was used to examine the relationship between land use (% moorland, woodland, grassland and arable within sub-catchments), soil characteristics (% peat, loam and clay within sub-catchments) and monthly water quality data (SS, DOC, TON, alkalinity, pH and temperature) across all 11 spatially distributed sampling sites in the two study catchments. Prior to performing the PCA, the suitability of data for factor analysis was assessed by inspecting the correlation matrix for presence of any coefficients of 0.3 and above, checking the Kaiser-Meyer-Oklin value exceeding the recommended value of 0.6 and the Bartlett's Test of Sphericity reaching statistical significance (Tabachnick and Fidell, 2001, Pallant, 2007). Environmental variables with the lowest loading on the component axis were sequentially removed until a definitive matrix could be achieved (Pallant, 2007). Principal components with eigenvalues exceeding 1 were retained and Varimax rotation was used for the interpretation of the components as the correlation between the components was low.

SS, DOC and TON yields were calculated for all 11 monitoring sites for the pre-restoration period between 29th July 2010 and 18th November 2011 using formula 4.2 (Chapter 4) and monthly baseflow samples. SS, DOC, DRP, TPC and TON yields were also calculated for the five stormflow monitoring sites for the same time period using formula 4.2 but including all baseflow and stormflow samples to give the best possible estimate of total pre-restoration yields and to compare the processes controlling pollutant concentrations, loads and yields in baseflow and stormflow.

Pearson's correlation was used to examine the relationship between median baseflow and stormflow concentrations and determinand yields at the five stormflow monitoring locations and the % of four land use types (arable, grassland, moorland and woodland), % of soil type (clay, loam, peat) and soil properties (median BD, TC, TN, C:N ratio, $\delta^{15}N$, C storage and N storage) in each sub-catchment.

The relationship between land use within the riparian corridor and water quality deteminands was examined within the 5 sub-catchments with stormflow monitoring. First, 10 m buffer zones were delineated along the watercourses in ArcGIS 9.3.1 (Esri Inc., Redlands, CA). The % of arable, grassland, moorland and woodland land use within each buffer was then calculated and related to the median baseflow and stormflow SS, DOC, DRP, TON and TPC concentrations, using the Pearson's correlation coefficient.

Frequency duration curves (Bilotta and Brazier, 2008) of concentrations of SS, DOC, TON and DRP were plotted at the five stormflow monitoring locations to set a baseline for comparison following future habitat restoration works. Hysteresis analysis (McDonnell, 2003, Bowes et al., 2005) was undertaken on two events (medium and extreme) recorded simultaneously at the two catchment outlets (A7 and H5) to compare the response between the two study catchments and aid the understanding of pollutant delivery pathways. Another medium-size event recorded simultaneously from the upstream to downstream monitoring sites (A11, A12, A7) in the Aller catchment was also examined to elucidate different sources and delivery pathways operating at nested scales.

Repeated measures Anova with pre- and post- restoration as a repeated measure and site as a fixed factor (Bryman and Cramer, 2011) was used to examine the response of 2nd order sub-catchments H1-H3 to upland ditch blocking. The monthly water quality data and invertebrate samples collected between the 25th February 2010 and 5th October 2011 represented the pre-restoration and those between 6th October 2011 and 26th November 2012 represented the post-restoration period. A statistically significant interaction effect between site and pre-/post- restoration factors indicates a differentiated response of a response variable at one of the sites, as compared to the other two sites, between the pre- post- restoration years. Examination of the interaction plots allows visualisation of this differentiated response.

IV. RESULTS

A. Rainfall and discharge characterisation over the study period

Total rainfall for the three years of monitoring and the % of long-term average in the two study catchments are presented in Table 6.2 and Fig. 6.6. Whilst at the beginning of the sampling period, the total annual rainfall was 78 % of the long-term average, at the end of the sampling period the total rainfall was up to 135 % of the longer-term average, reflecting the very wet year of 2012.

	Horner		Aller	
Year	total rainfall (mm)	% of long term average 1996-2012	total rainfall (mm)	% of long term average 2009-2012
2010	977.8	77.14	676.6	77.72
2011	1115.6	88.01	722.4	82.98
2012	1638	129.20	1177	135.19

Table 6.2 Total rainfall and rainfall as a % of long-term average over the three years of water quality monitoring in the two study catchments.

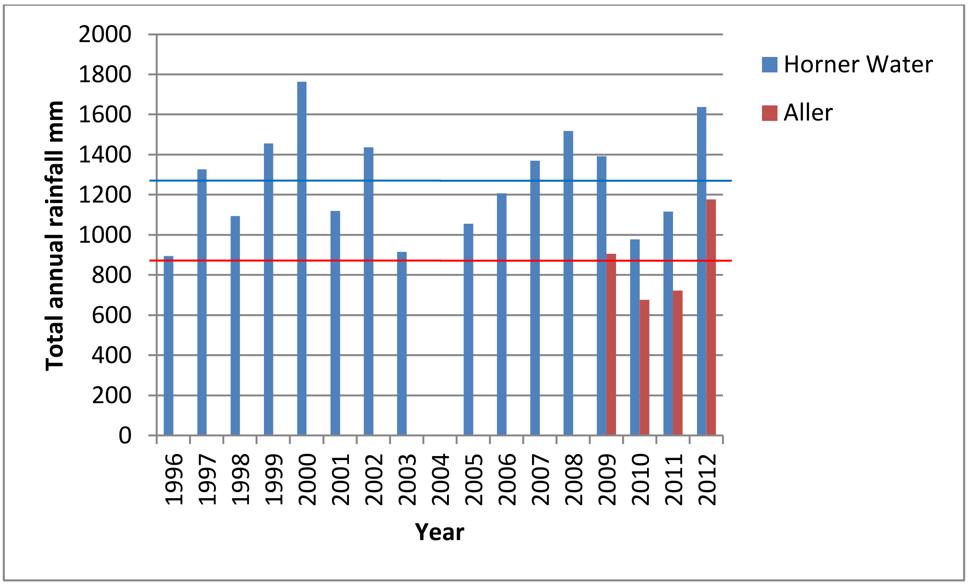


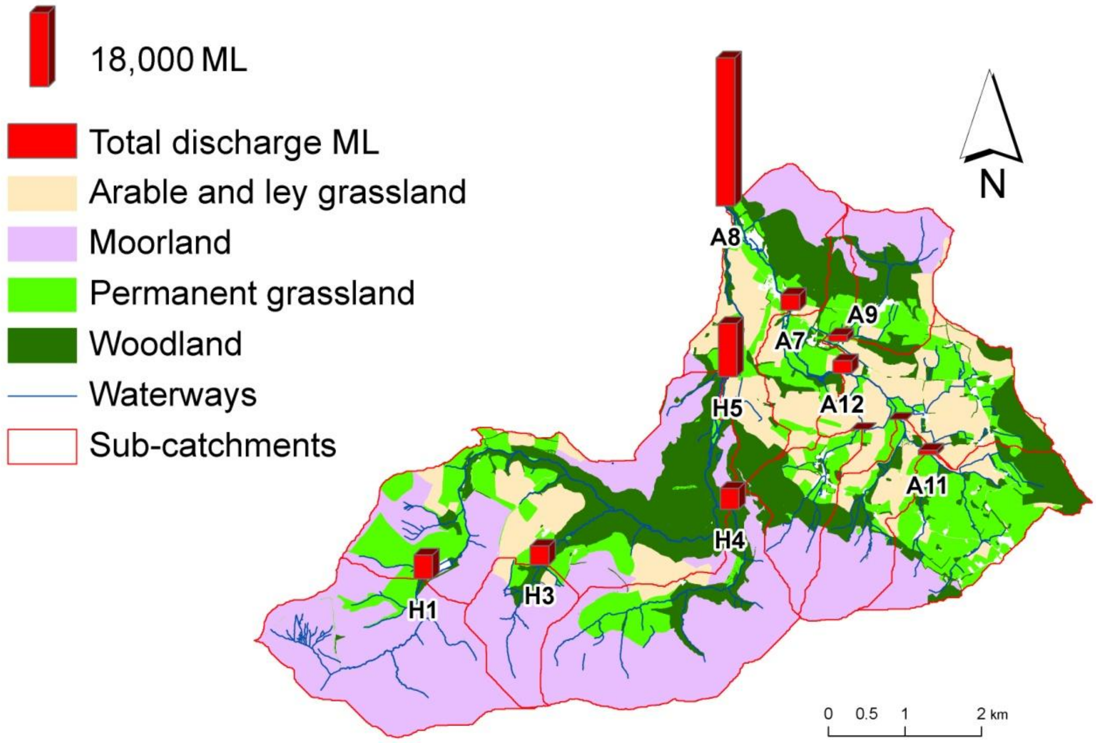
Fig. 6.6 Total annual rainfall over the period of record for the Horner Water and Aller catchments recorded at the EA rainfall monitoring stations. Blue line shows the mean annual rainfall of 1,268 mm for the period 1996-2012 for Horner Water catchment and the red line shows the mean annual rainfall of 871 mm for the Aller catchment for 2009-2012.

Total discharge, water yield and Q5:Q95 ratio over the pre-restoration period across nine water quality monitoring sites with continuous discharge record are presented in Table 6.3 and Fig. 6.7. The greatest total discharge was recorded at the catchment outlets at H5, A7 and the joint outlet at A8, while the greatest water yield was recorded in the upper reaches of Horner Water catchment at H3 and H1. H3 and A9 were the flashiest sub-catchments with Q5:Q95 ratios of 34.5 and 30.0, respectively.

Site	Area (km^2)	Total discharge (ML)	Record completeness (%)	Water yield ($ML\ km^{-2}$)	Q5:Q95
A10	1.68	-	-	-	-
A11	3.39	1144	100	337.36	6.27
A12	12.75	3156	82	247.50	8.06
A13	5.48	-	-	-	-
A7	14.64	3864	99	263.93	9.40
A8	38.82	36490	96	939.97	6.27
A9	2.04	1623	100	795.49	30.00
H1	4.63	5900	100	1274.20	16.87
H3	1.68	4663	100	1683.47	34.50
H4	5.04	5128	100	1017.43	6.76
H5	20.23	13178	99	651.40	11.48

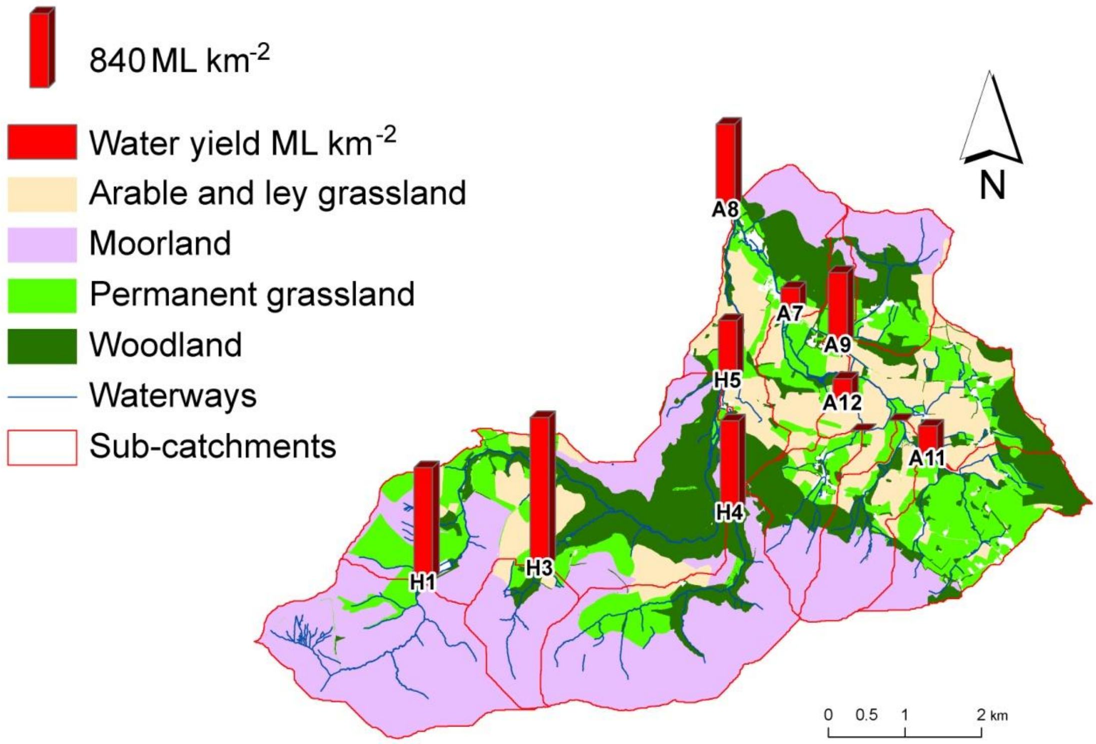
Table 6.3 Hydrological characteristics of the nine sub-catchments with continuous discharge record show an increasing discharge in downstream direction, greater water yields in the uplands at H3, H1 and H4 and within the Aller catchment at A9. Greatest flashiness was recorded in sub-catchments H3 and A9.

a)



18,000 ML
Total discharge ML
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
N
A8
A9
A7
A12
H5
A11
H4
H1
H3
0 0.5 1 2 km

b)



840 ML km-2
Water yield ML km-2
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
N
A8
A7
A9
H5
A12
A11
H4
H1
H3
0 0.5 1 2 km

c)

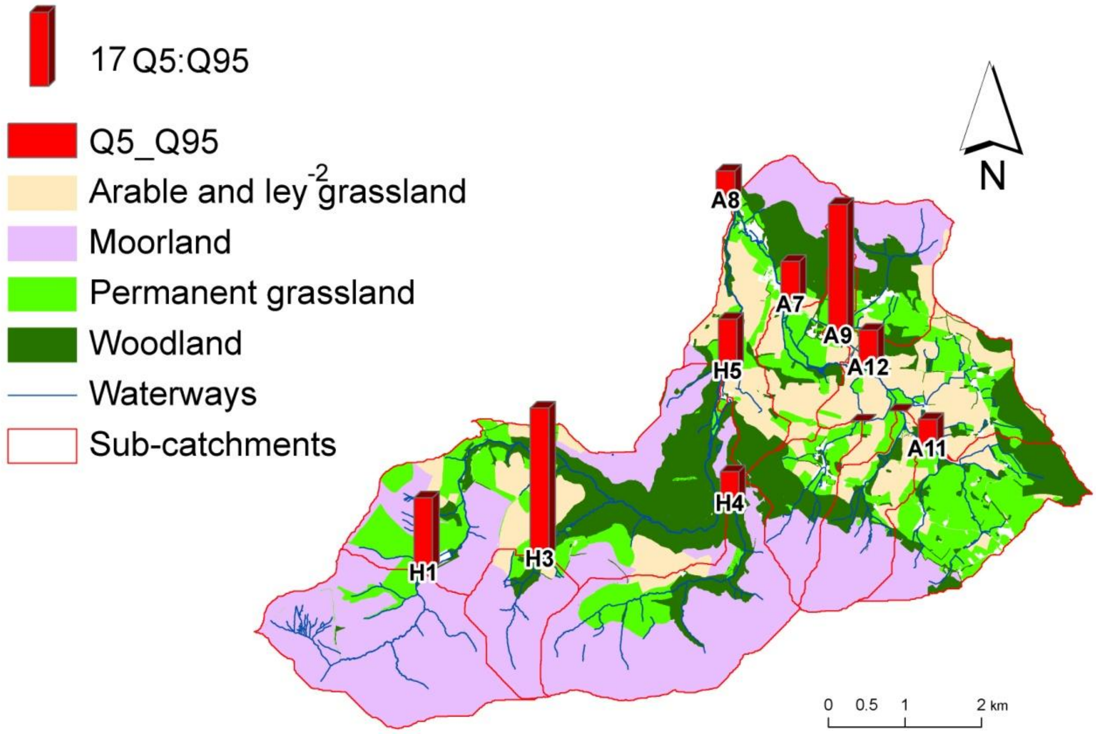


Fig. 6.7 The spatial distribution of hydrological variables across the nine monitoring sites with continuous discharge record shows a) the greatest discharge at the joint catchment outlet at A8, b) greatest water yield in the upland reaches of Horner Water at H3 and H1 and c) greatest flashiness at H3 and A9.

B. Exploring the impact of land use mitigation measures in the Aller catchment on water quality determinands at a catchment scale.

a. Relationship between monthly water quality observations and environmental variables

Table 6.4 (p. 227) shows the summary statistics for all monthly water quality samples collected at all 11 monitoring locations across the two study catchments. Table 6.5 (p. 228) shows the % of land use, soil type and measured soil properties within each sub-catchment.

The Principal Component Analysis of land use, soil type, soil properties and monthly water quality variables across all study sites revealed three principal components with Eigenvalues > 1. The first component accounted for the greatest proportion of variance (35 %) and was interpreted as a land use and water quality gradient. The second component accounted for 24 % of variance and was interpreted as a soil type gradient, while the third component accounted for 19 % of variance and could be interpreted as a larger scale climatic (temperature) and geological (alkalinity) gradient (Table 6.6).

	Gradient		
	Land use	Soil type	pH & temperature
SS conc.	**0.615**		0.387
DOC conc.	**0.684**		
TON conc.	**0.852**	0.344	
Alkalinity	**0.757**		0.482
pH			**0.763**
Temp			**0.851**
Arable %	**0.766**	0.439	
Grassland %	**0.637**	0.332	0.440
Moorland %	**-0.726**	-0.511	-0.391
Woodland %	0.456	0.628	0.442
Peat %	-0.343	**-0.866**	
Clay %	0.655	0.392	
Loam %		**0.934**	
% variance	35%	24%	19%

Table 6.6 Principal component analysis of water quality, land use, soil type and soil property variables revealed three gradients with eigenvalues > 1. The first gradient was interpreted as a land use gradient that is most closely related to water quality parameters, the second gradient was interpreted as soil type and the third gradient was interpreted as a large scale climatic (temperature) and geological (alkalinity) gradient. The variables used for the interpretation of gradients are highlighted.

The relationship between the main land use gradient and water quality determinands is illustrated in Fig. 6.8, whereby the most impaired sampling sites are located in the most intensively farmed central part of the Aller catchment, associated with arable cropping and short-term leys.

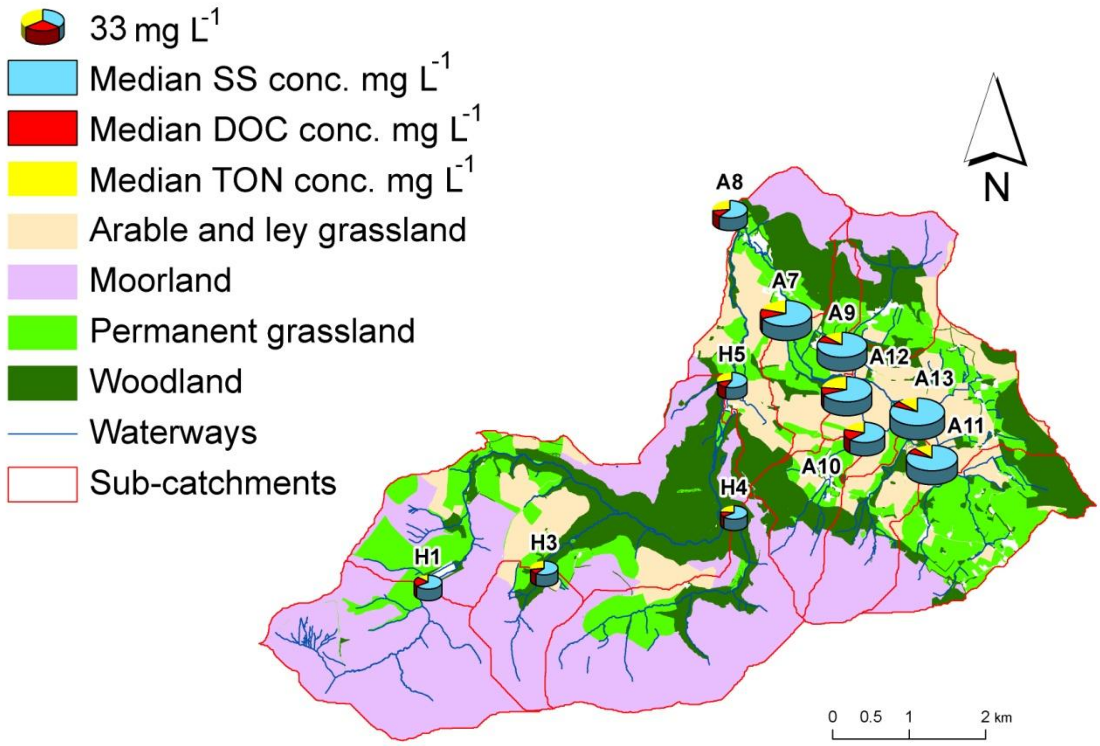


Fig. 6.8 Map showing the ranking of water quality determinands across the two study catchments, in relation to land use. The greatest water quality impairment can be observed in the most intensively farmed central part of the Aller catchment associated with arable land use. The size of the circles represents a sum of median values of the monthly SS, DOC and TON concentrations.

b. **Spatial variability of water quality between scales in baseflow and stormflow**

Table 6.7 shows the summary statistics for all stormflow data collected at the five stormflow monitoring sites. The full list of sampled events is included in the Appendices (Table 6.8, p. 232) and full chemographs are presented in Figs. 6.9-6.13 in the Appendix (pp. 234-238). In total, 141 events were captured across the five stormflow monitoring sites, amounting to a total of 1,971 individual water samples. Of these, 136 events were analysed for SS, 81 for TPC, 82 for DRP, 97 for TON and 53 for DOC. Determinand loads and yields calculated for all sites using the monthly baseflow data and for the five stormflow monitoring sites using both baseflow and stormflow data are presented in Table 6.9.

Site		Discharge ($m^3\ s^{-1}$)	SS (mg L^{-1})	DOC (mg L^{-1})	TPC (%)	TON (mg L^{-1})	DRP (µg L^{-1})
A7	median	0.11	77.85	4.98	11.63	9.46	45
	min	0.02	3.72	1.7	2.36	3.46	0
	max	10.72	3709.09	14.03	17.63	13.48	343
	N		545	251	279	506	464
A8	median	0.86	55.43	5.29	11.23	4.39	0
	min	0.16	1.41	0.49	1.53	2.14	0
	max	38.9	2998.86	19.44	25.63	8.68	143
	N		305	168	158	264	228
A11	median	0.04	59.37	4.46	12.14	6.76	77
	min	0.01	12.97	1.08	3.71	3.93	0
	max	6.91	2299.66	21.29	18.08	9.36	477
	N		384	145	214	290	272
A12	median	0.08	118.58	4.7	13.84	8.81	51
	min	0.02	17.32	1.65	4	3.29	0
	max	11.13	5102.4	7.81	24.45	13.47	683
	N		231	83	168	186	143
H5	median	0.32	21.93	5.25	18.09	3.6	0
	min	0.05	1.43	0.41	4.4	0.57	0
	max	32.2	1642.54	19.94	32.32	5.9	158
	N		482	226	176	376	293

Table 6.7 Summary statistics of water quality determinands and corresponding discharge for all stormflow samples collected at the five stormflow monitoring sites between 10th July 2010 and 31st January 2013.

i. Concentrations

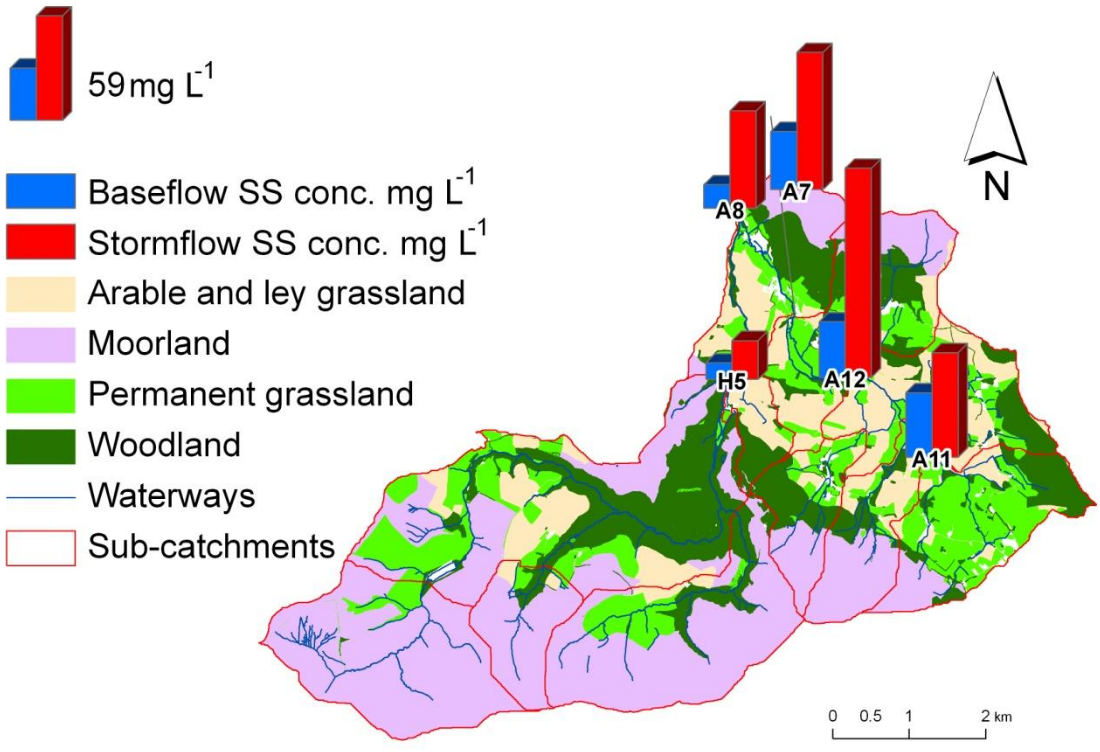
Fig. 6.14a-d shows the spatial distribution of median SS, DOC, DRP and TON concentrations across the five stormflow monitoring sites calculated separately from the baseflow and combined baseflow + stormflow datasets. The highest median baseflow SS concentrations are at A11 and A7, while in stormflow the highest SS concentrations were recorded at A12 and A7. The lowest SS concentrations in both baseflow and stormflow were found at the Horner Water outlet at H5 and at the joint outlet at A8.

Median baseflow DOC concentrations increased in a downstream direction from the upper reaches of the Aller at A11 to the outlet at A7 and were greater than median baseflow DOC concentrations at the Horner Water outlet at H5 and the joint outlet at A8. In stormflow, the highest median DOC concentration was recorded at the joint outlet at A8, followed by the Horner Water outlet at H5, while the ranking of sites within the Aller catchment did not change.

Highest median DRP concentration both in baseflow and stormflow were recorded in the upper reaches of the river Aller, while lowest DRP concentration were recorded at the outlet of the Horner Water catchment. While in baseflow, the outlet of the river Aller at A7 supported higher DRP concentrations than the middle reaches at A12, this ranking was reversed in stormflow.

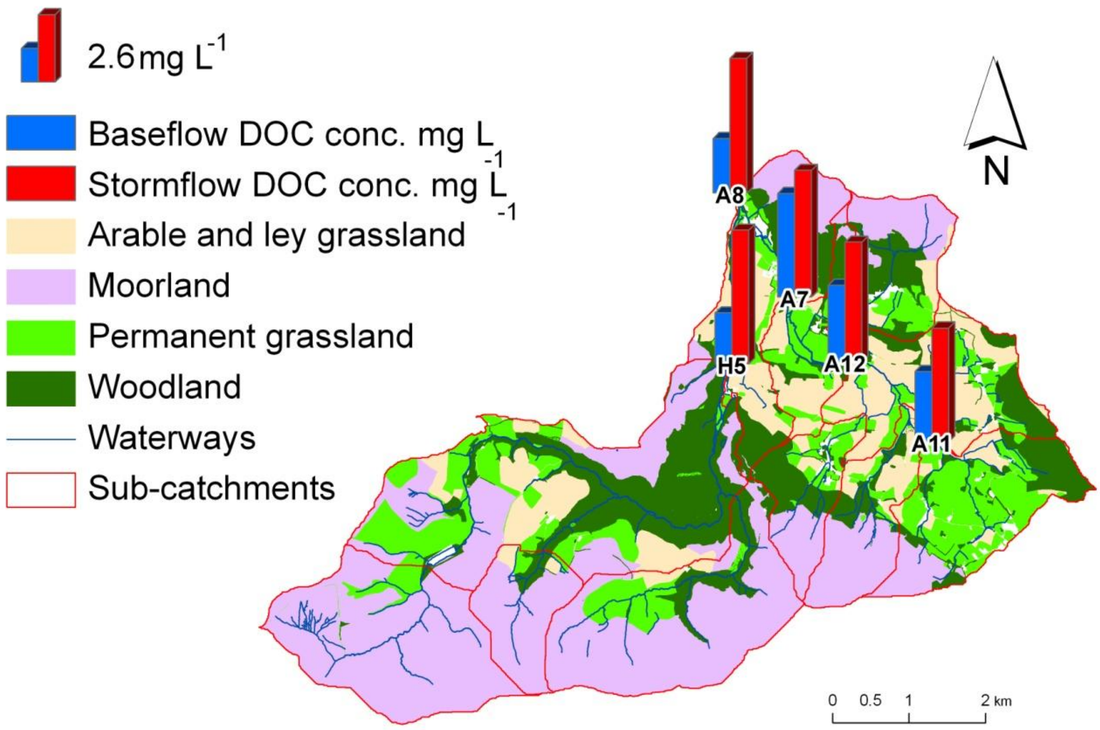
Median TON concentrations both in baseflow and stormflow were lowest at the outlet of Horner Water at H5, followed by the joint outlet at A8 and the upper reaches of the Aller at A11. While in baseflow, the highest TON concentrations were recorded in the middle reaches of the Aller catchment at A12, in stormflow the highest TON concentrations were recorded at the Aller catchment outlet at A7.

a)



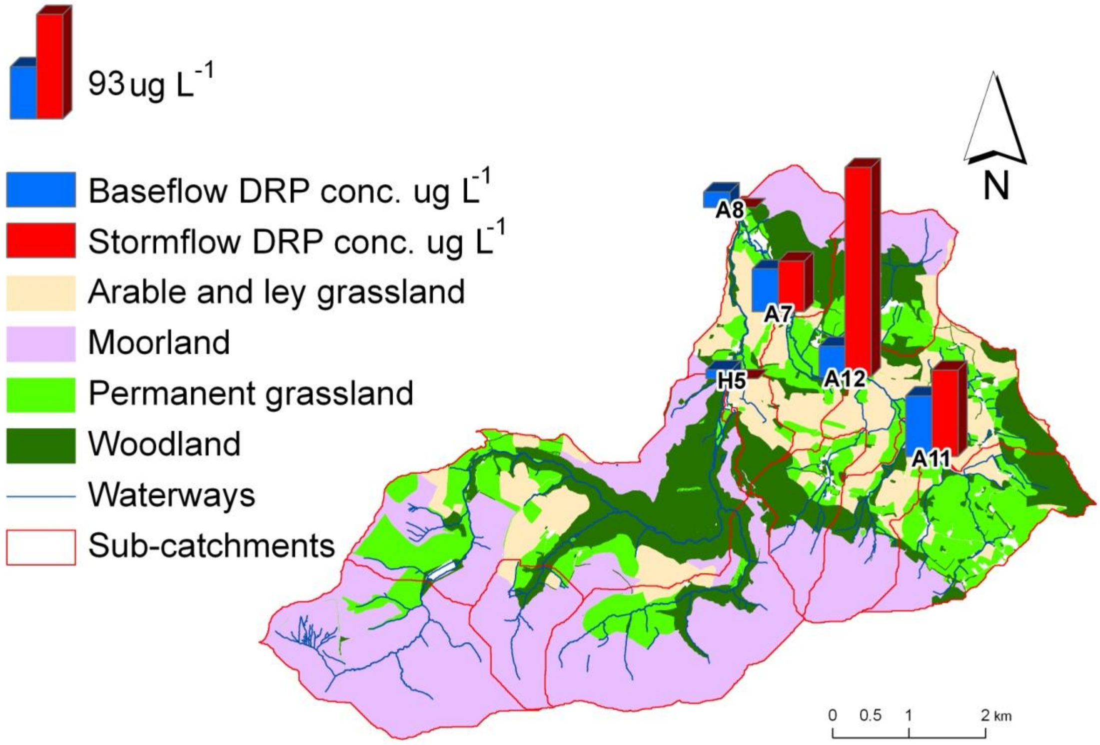
59mg L-1
Baseflow SS conc. mg L-1
Stormflow SS conc. mg L-1
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
A8
A7
H5
A12
A11
N
0 0.5 1 2 km

b)



2.6mg L-1
Baseflow DOC conc. mg L-1
Stormflow DOC conc. mg L-1
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
A8
A7
H5
A12
A11
N
0 0.5 1 2 km

c)



d)

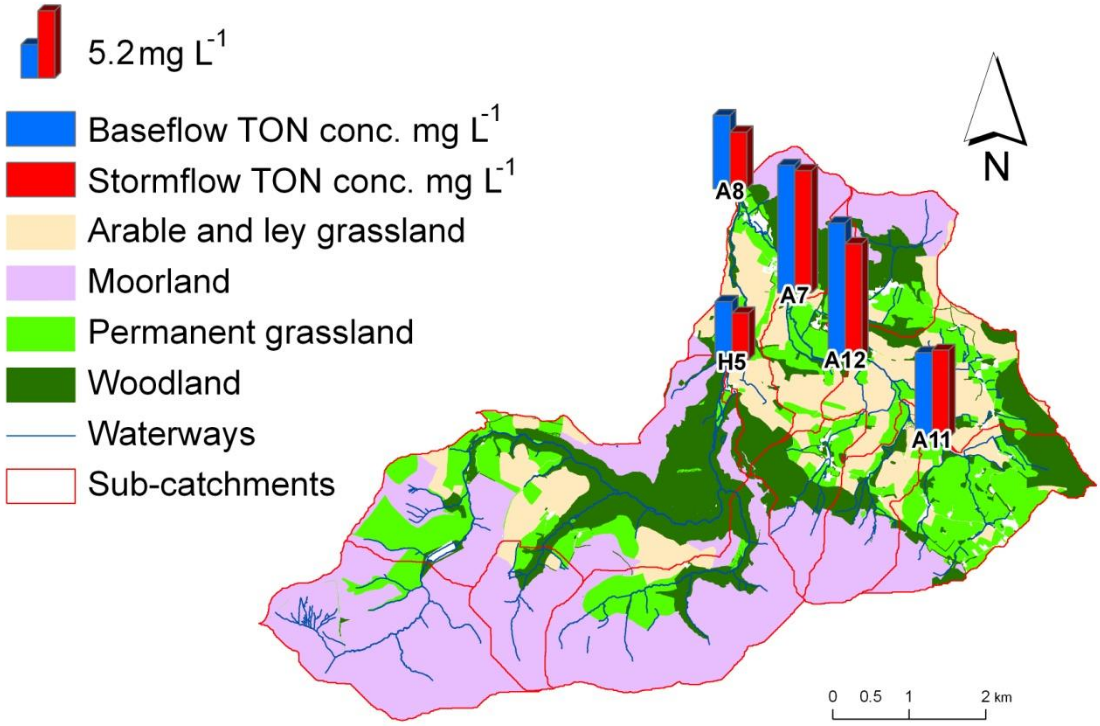


Fig. 6.14 Median concentrations of a) SS b) DOC c) DRP and d) TON in baseflow and stormflow at the five stormflow monitoring sites, showing the spatial distribution of water quality determinands and the ranking of sites both in baseflow and stormflow conditions. The Legend scale value refers to the red bar.

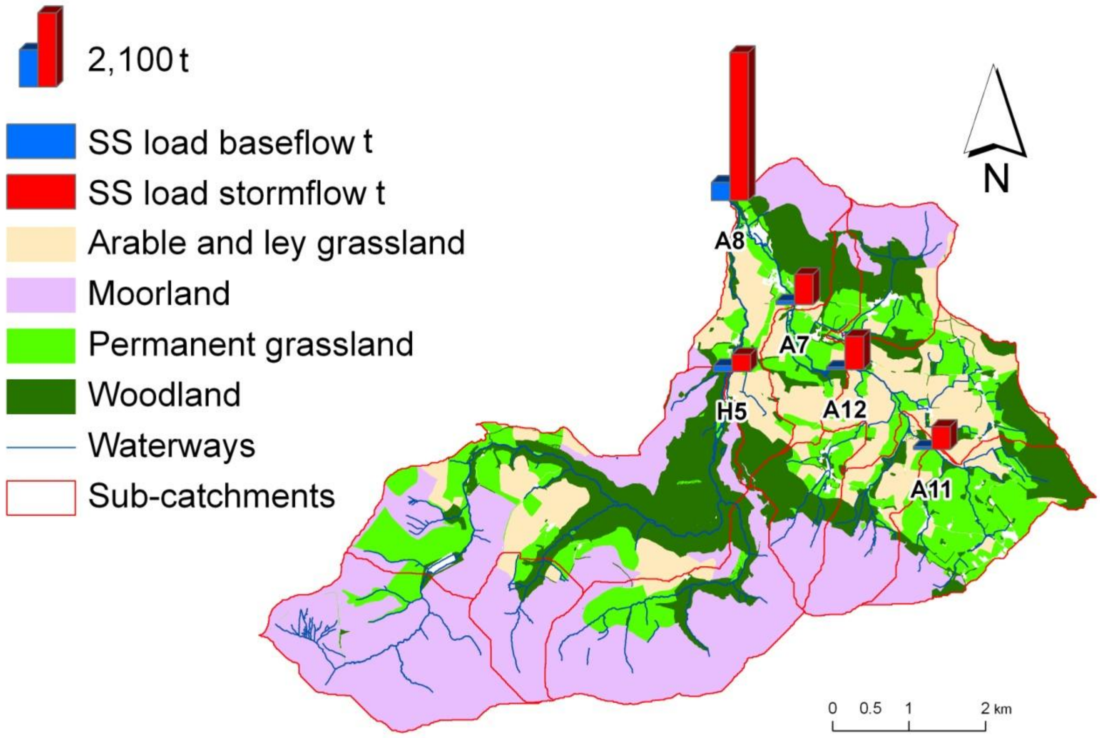
ii. Loads

Loads of DOC and TON calculated from baseflow data alone increased in line with discharge from the upper reaches of the river Aller at A11 to the joint outlet at A8 (Fig. 6.15b,c). The pattern was similar for SS loads calculated from baseflow data, except that the ranking of A11 and A12 was reversed by a small margin of 2.7 t (Fig. 6.15a).

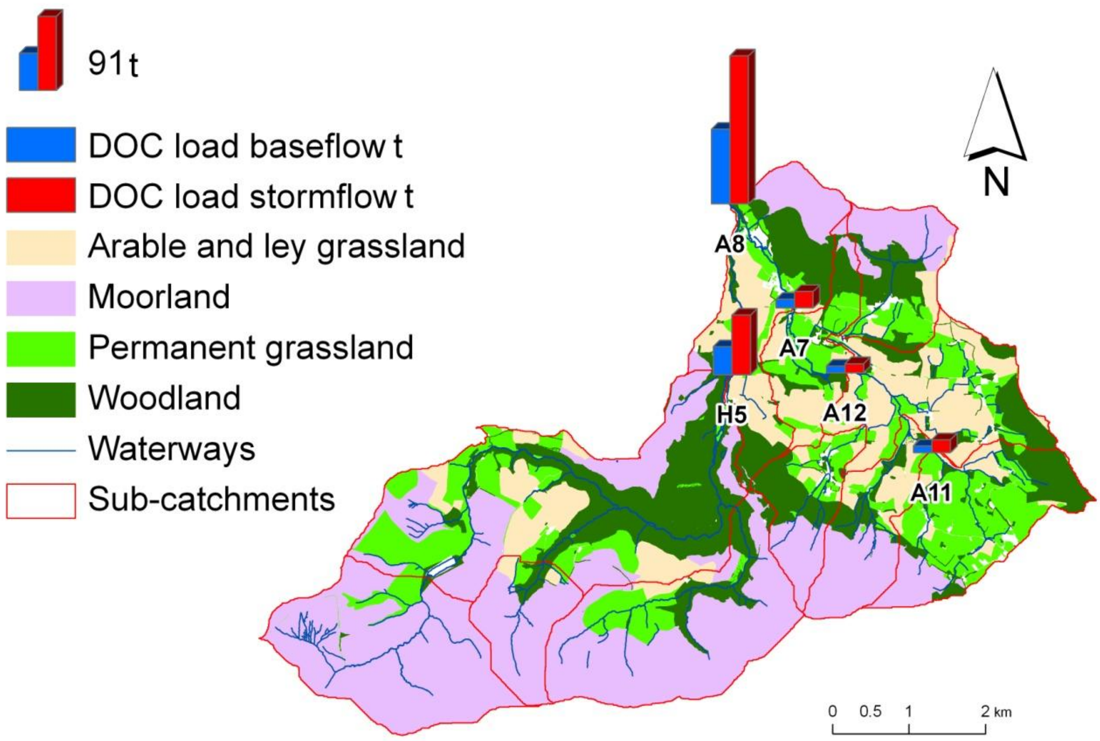
Loads calculated using the combined baseflow and stormflow datasets showed the highest load of SS at the joint catchment outlet at A8. However, the previously cleanest A12 (from baseflow conditions only) now had the highest estimated SS load, while the Horner Water outlet at H5 supported the lowest load. DOC load calculation using combined baseflow and stormflow data estimated greater DOC loads in the upper reaches of the Aller catchment at A11 than in the middle reaches at A12, with the ranking of other sites remaining the same. The ranking of sites according to TON load increased with increasing discharge and remained the same when either baseflow data or combined data were used in load estimation.

Only stormflow data were available for TPC and DRP calculations. TPC loads were lowest in the upper reaches of the Aller catchment at A11 and A12, followed by the Horner Water outlet at H5 and then the Aller outlet at A7 and the joint outlet at A8. DRP loads were greatest in the upper reaches of the Aller catchment at A11, followed by the joint outlet at A8, then the Aller outlet at A7 and the middle reaches of the river Aller at A12. The Horner Water outlet at H5 supported the lowest DRP loads.

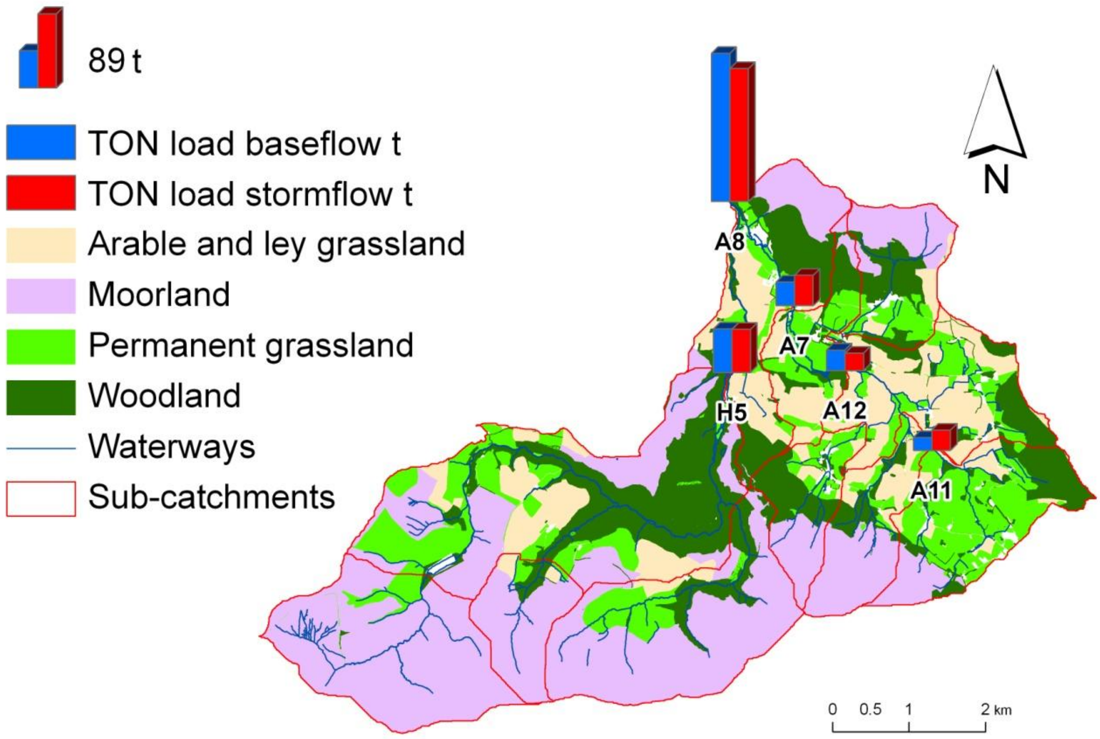
a)


2,100 t
SS load baseflow t
SS load stormflow t
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
N
A8
A7
H5
A12
A11
0 0.5 1 2 km

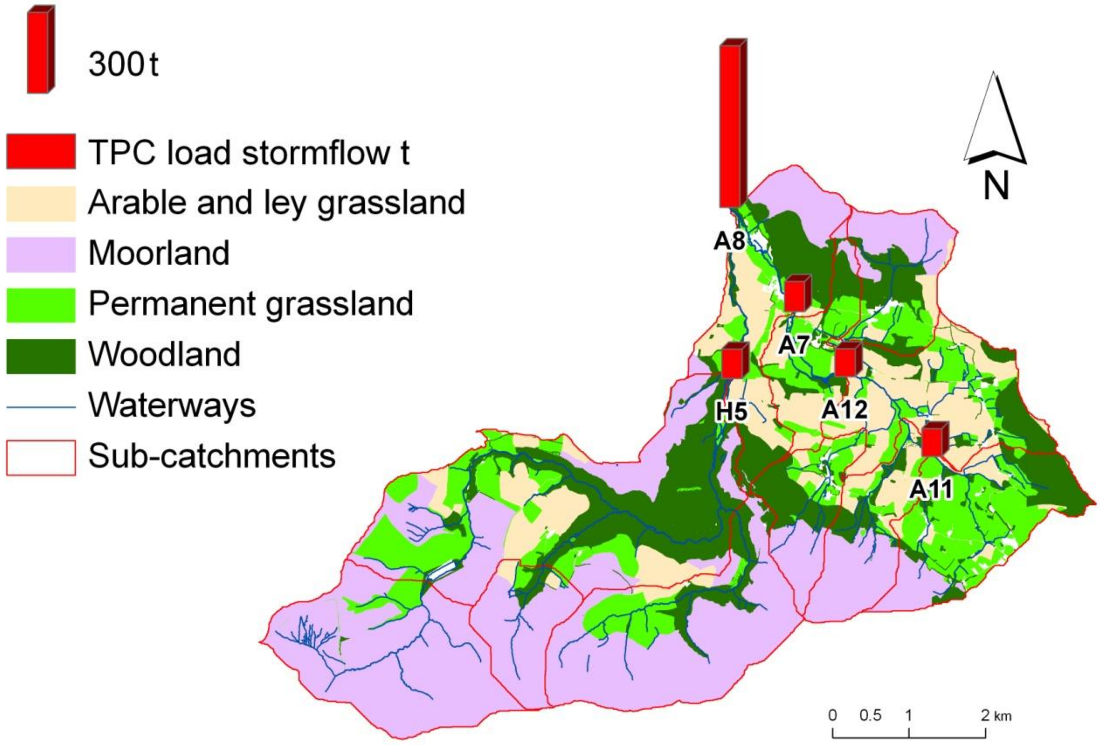
b)


91 t
DOC load baseflow t
DOC load stormflow t
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
N
A8
A7
H5
A12
A11
0 0.5 1 2 km

c)


89 t
TON load baseflow t
TON load stormflow t
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
A8
A7
H5
A12
A11
N
0 0.5 1 2 km

d)


300 t
TPC load stormflow t
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
A8
A7
H5
A12
A11
N
0 0.5 1 2 km

e)

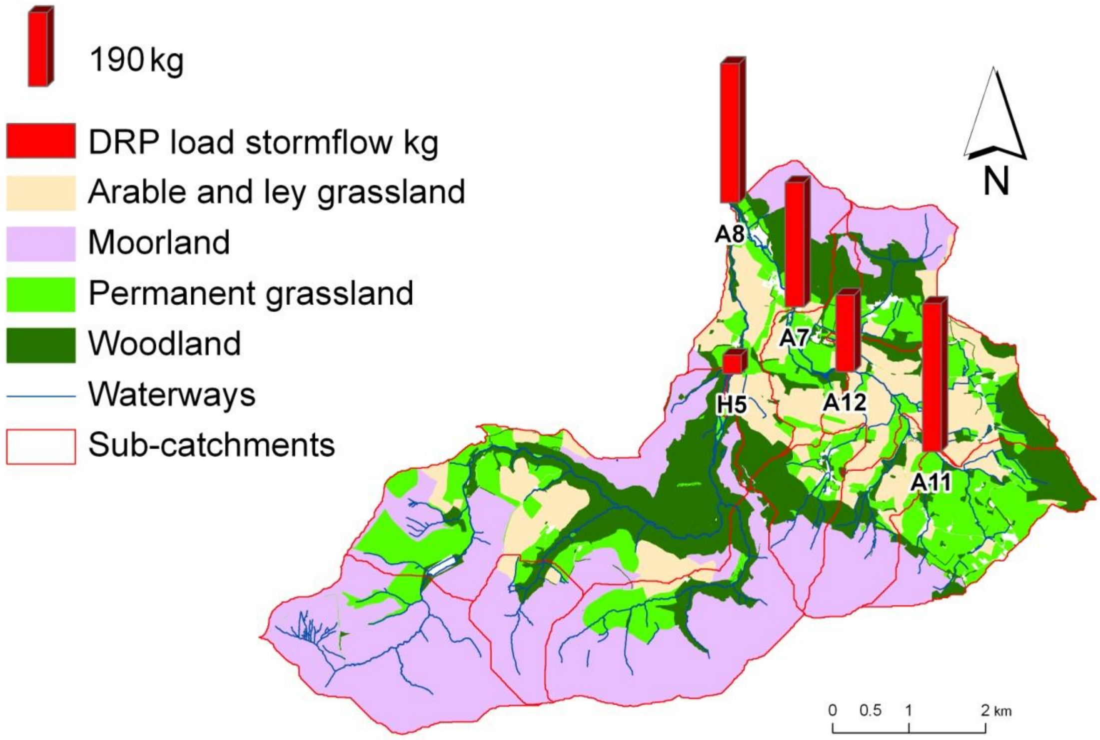
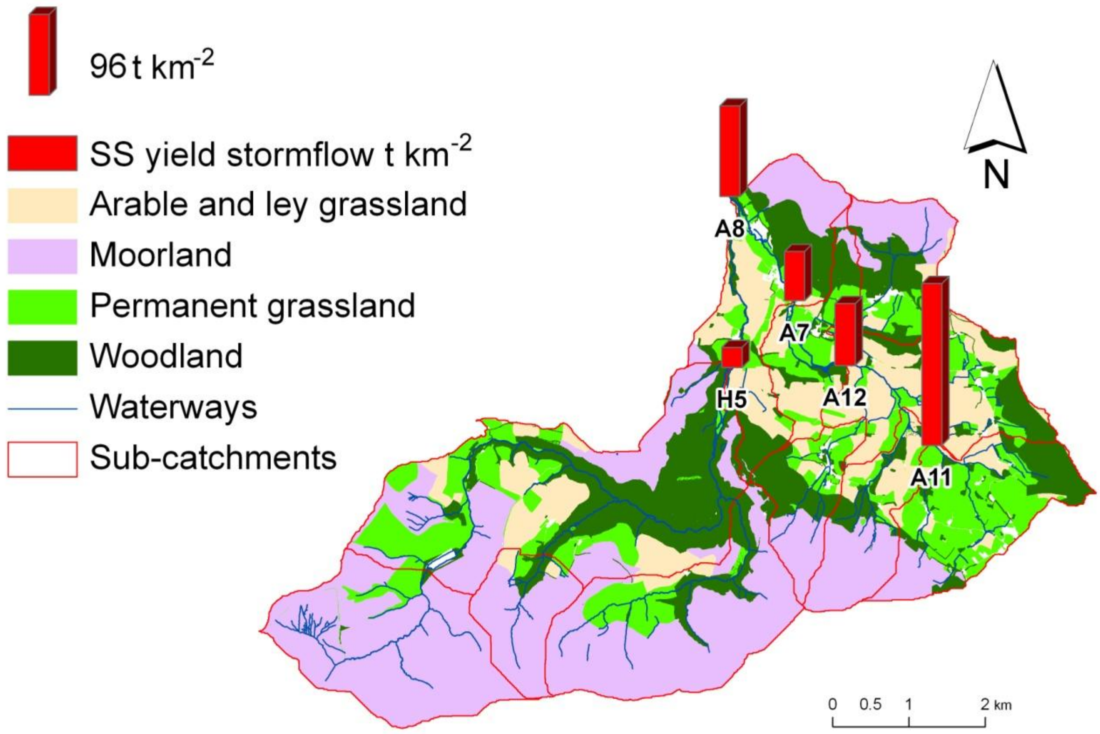


Fig. 6.15 Loads of a) SS b) DOC and c) TON calculated from baseflow data only and from all data at the five stormflow monitoring sites; d) DRP and e) TPC yields are calculated from stormflow data alone as no suitable baseflow data was available. SS loads show the greatest change in the ranking of sites and greatest proportional change in absolute values, when either baseflow measurements alone or all data are included in load calculations. The Legend scale value refers to the red bar.

iii. Yields

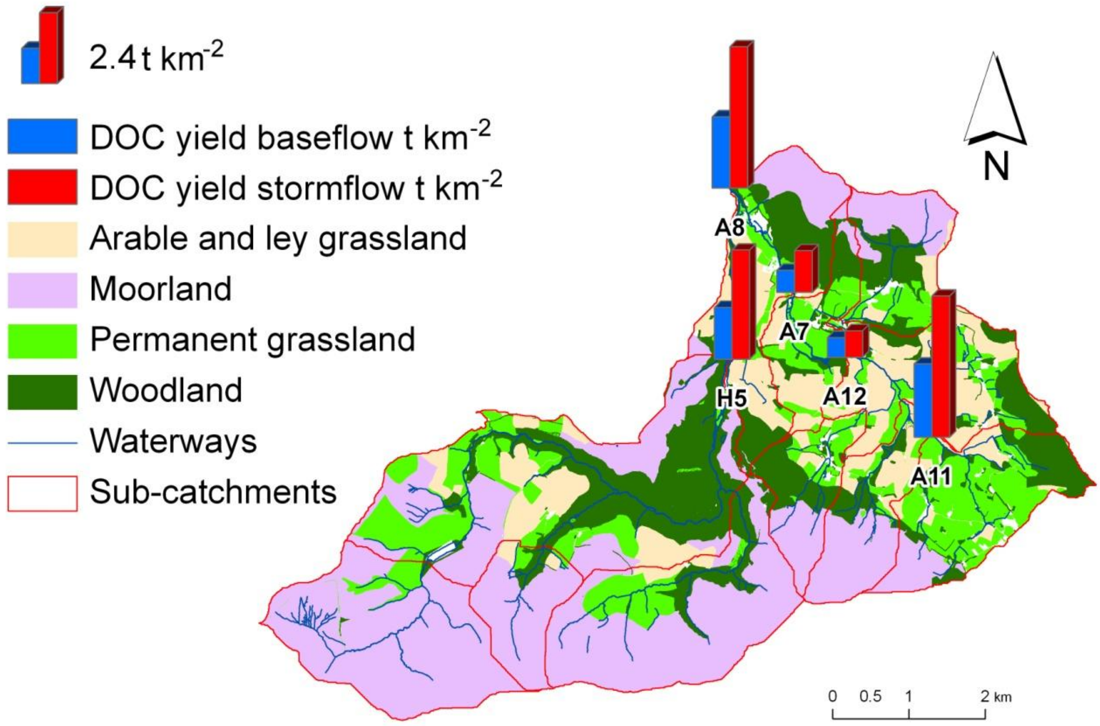
SS yields (Fig. 6.16a) were highest in the upper reaches of the river Aller at A11 and for both methods of yield estimation, the yields within the Aller catchment decreased in a downstream direction. Using baseflow data alone, the highest DOC yield was estimated in the upper reaches of the river Aller at A11, while using combined baseflow and stormflow data, the highest yield was estimated at the joint catchment outlet at A8 (Fig. 6.16.b). Highest TON yields (Fig. 6.16.c) were estimated in the upper reaches of the river Aller, using both data sets. Only stromflow data was available for TPC and DRP yield calculations (Fig. 6.16.d-e). This showed the highest estimated yields in the upper reaches of the river Aller at A11 and lowest yields at the Horner Water outlet at H5.

a)



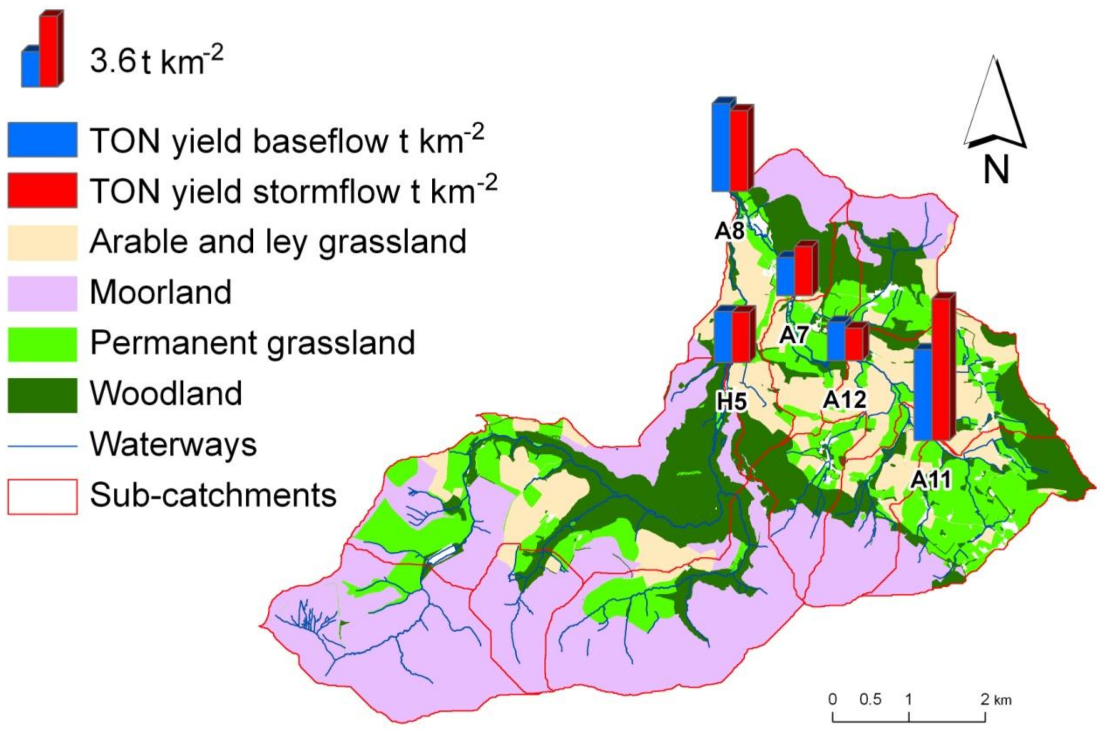
96 t km-2
SS yield stormflow t km-2
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
N
A8
A7
A12
H5
A11
0 0.5 1 2 km

b)

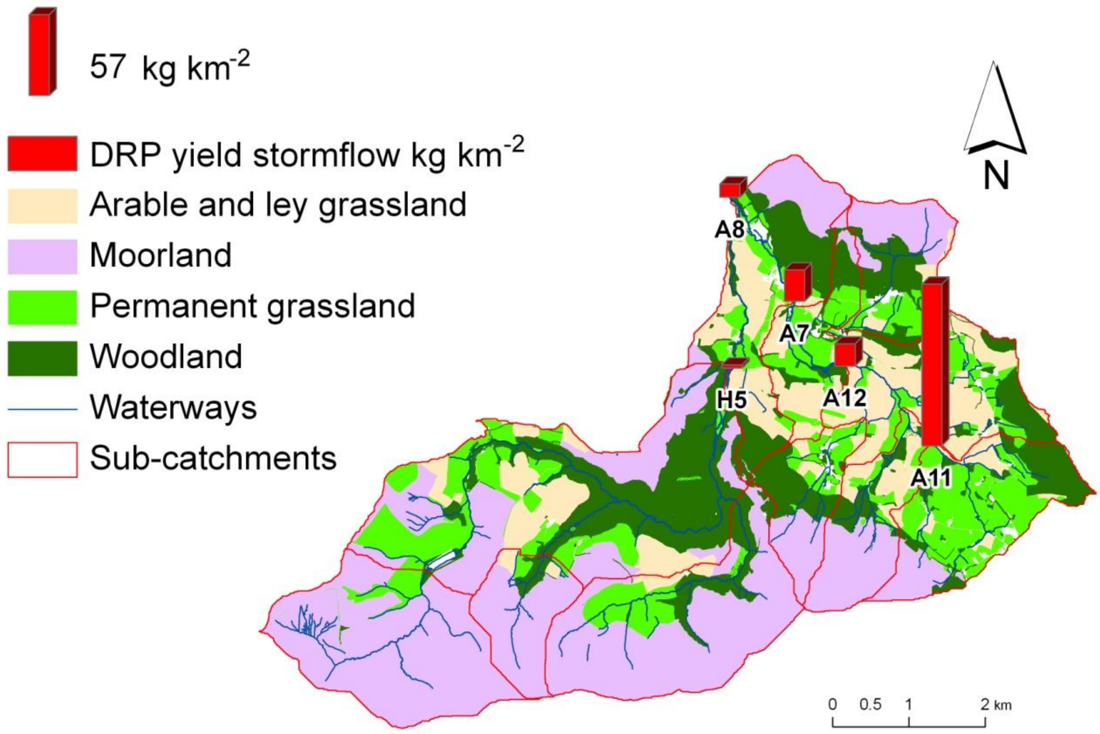


2.4 t km-2
DOC yield baseflow t km-2
DOC yield stormflow t km-2
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
N
A8
A7
A12
H5
A11
0 0.5 1 2 km

c)


3.6 t km-2
TON yield baseflow t km-2
TON yield stormflow t km-2
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
N
A8
A7
H5
A12
A11
0 0.5 1 2 km

d)


57 kg km-2
DRP yield stormflow kg km-2
Arable and ley grassland
Moorland
Permanent grassland
Woodland
Waterways
Sub-catchments
N
A8
A7
H5
A12
A11
0 0.5 1 2 km

e)

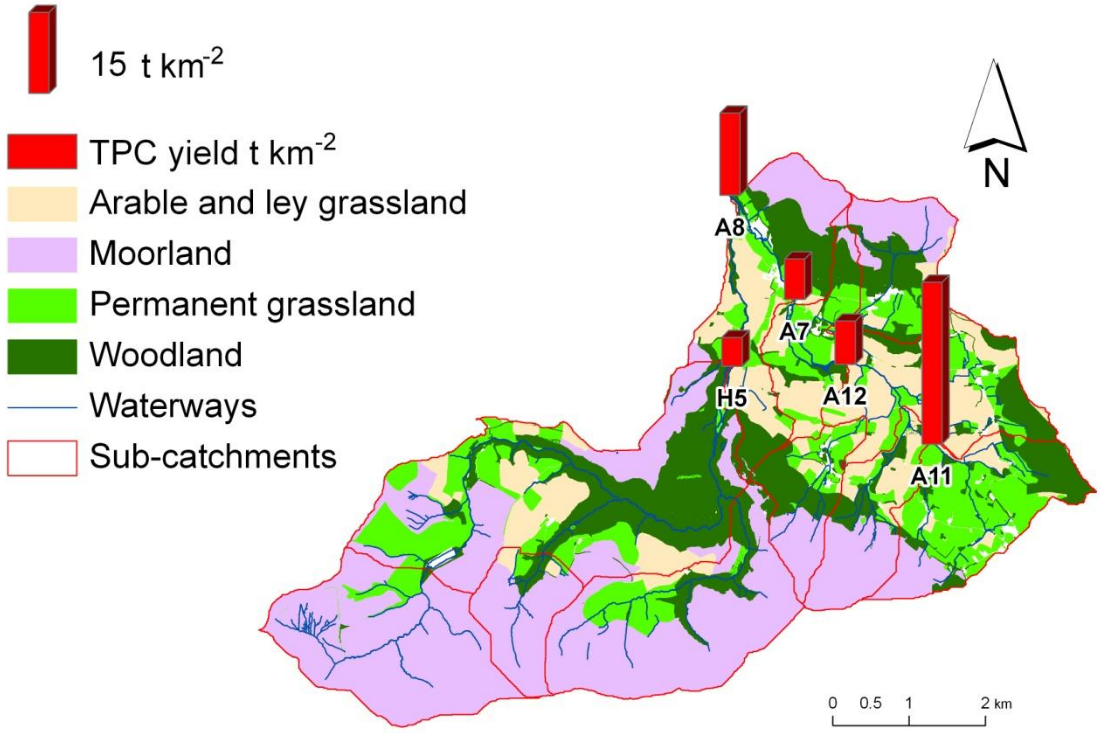


Fig. 6.16 Yields of a) SS b) DOC and c) TON calculated from baseflow data and from all data at the five stormflow monitoring sites; d) DRP and e) TPC yield calculation was based on stormflow data alone.

iv. Ranking of sites according to concentration frequency exceedance

The ranking of sites according to time frequency exceedance of pollutant concentration, using all available data (combined stormflow and monthly samples), at the five stormflow monitoring sites is shown in Fig 6.17. It shows a similar ranking of sites in relation to diffuse water pollution as discussed above. Greatest frequency exceedance, and hence greatest water quality impairment, was recorded at A12 for SS and at A7 for DOC and TON concentration. Greatest frequency exceedance of DRP concentration was recorded in the upper reaches of the Aller catchment at A11. The outlet of the river Horner at H5 was the most depleted in terms of SS, TON and DRP, however the lowest frequency exceedance for DOC was recorded in the upper reaches of the Aller catchment at A11 and A12.

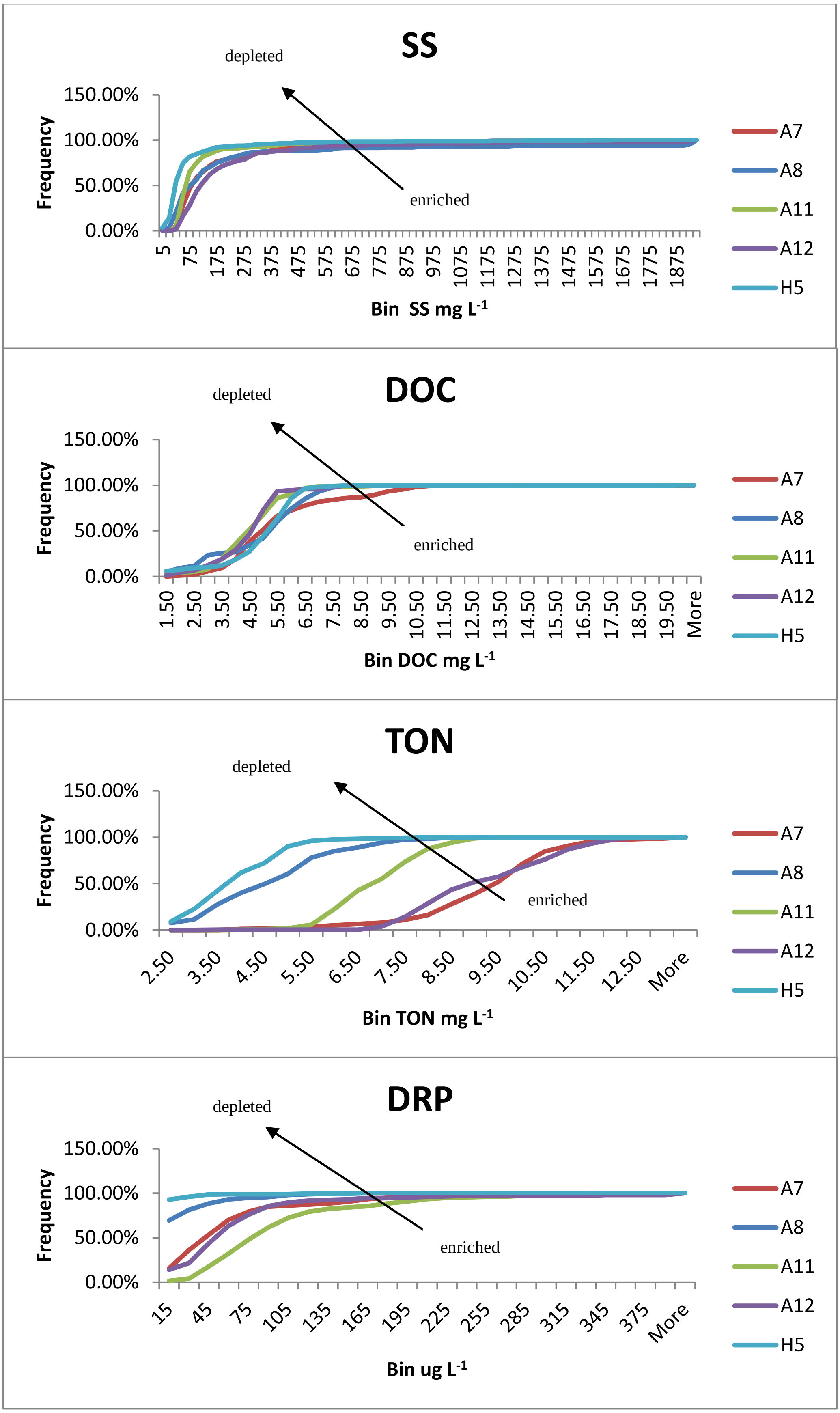


Fig. 6.17 Frequency exceedance curves of pollutant concentrations at the five stormflow monitoring sites using all monitoring data show ranking of sites from cleanest to the most polluted.

c. Relationship between riparian land use and water quality

Percentage of four land use types within a 10 m buffer along the riparian corridor within the five sub-catchments with stormflow monitoring are presented in Table 6.10. Table 6.11 shows significant correlations between median water quality determinands and land use variables within the five sub-catchments with stormflow monitoring.

site	% arable in 10 m buffer	% moorland in 10 m buffer	% grassland in 10 m buffer	% woodland in 10 m buffer
A11	0.26	0.06	0.46	0.23
A12	0.51	0.00	0.38	0.11
A7	0.08	0.00	0.68	0.24
A8	0.22	0.02	0.40	0.36
H5	0.01	0.22	0.18	0.60

Table 6.10 Percentage of land-uses in a 10 m riparian corridor in the five sub-catchments with stormflow monitoring was related to SS, DOC, TPC, TON and DRP concentrations in baseflow and stormflow and to best estimate yields.

Variables	**r**	**P <**
SS stormflow conc. & % woodland within 10 m buffer	-0.921	0.026
DOC baseflow conc. & % grassland within 10 m buffer	0.892	0.042
DOC stormflow conc. & % clay in the catchment	-0.887	0.045
TPC stormflow conc. & % moorland within 10 m buffer	0.882	0.047
TON baseflow conc.& % arable in the sub-catchment	0.915	0.029
DRP yield & % grassland in the sub-catchment	0.900	0.037

Table 6.11 Significant Pearson’s correlations between % of land use types in a 10 m riparian corridor and within the whole sub-catchment and median water quality determinand concentrations and yields for the 5 sub-catchments with stormflow monitoring data.

d. **Hysteresis analysis of pollutant sources and pathways**

Chemographs for one event recorded simultaneously at the three sampling locations within the Aller catchment (Fig. 6.18) show a clockwise hysteresis for TON and TPC, flat hysteresis for SS, anti-clockwise hysteresis for DOC and a slightly delayed anti-clockwise hysteresis for DRP.

Chemographs for a medium size event simultaneously recorded at both the outlet of Aller (A7) and Horner Water (H5) (Fig. 6.19, p. 242) shows the limited response of most water quality determinands to discharge in the Horner Water catchment during small and medium size events, with SS concentrations displaying flat hysteresis and DRP concentrations strong clock-wise hysteresis.

The response of water quality determinands to extremely large flows in both study catchments is illustrated in Fig. 6.20 (p. 244) in the Appendix. In both study catchments, TPC showed a clockwise hysteresis and DOC flat hysteresis. The response of DRP and SS differed between the two study catchments, whereby DRP exhibited a clockwise hysteresis in the Horner Water catchment and a flat response in the Aller, while SS showed a clockwise hysteresis in the Aller catchment and a flat response in Horner Water. TON shows a typical dilution effect.

C. The response of physico-chemical water quality deteminands in the Horner Water catchment to upland ditch blocking one year after habitat restoration

Analysis of variance (Tab. 6.12, Figs. 6.21 and 6.22, p. 245) shows significantly different SS and DOC concentrations, DOC load and discharge between the pre- and post-restoration years. Tukey's post-hoc test showed that TON concentrations and loads differed significantly between all three sites (Fig. 6.21). H3 supported significantly lower SS and DOC loads and lower discharge than the other two sites ($P < 0.001$). No statistically significant interaction between site and pre- and post-restoration factors was found, however the probability of the DOC load responding differently at the three sites during the two study years was near-significant ($P < 0.06$). The interactions plots for DOC load and for discharge at the three study sites are presented in Fig.6.23.

	Sites P <	Pre/post- restoration years P <	Interaction effects P <
SS concentration mg L^{-1}	0.893	**0.003**	0.861
DOC concentration mg L^{-1}	0.218	**0.001**	0.693
TON concentration mg L^{-1}	**0.001**	0.133	0.895
SS load mg L^{-1}	**0.001**	0.880	0.790
DOC load mg L^{-1}	**0.001**	**0.001**	0.060
TON load mg L^{-1}	**0.001**	0.065	0.475
Discharge $m^3 s^{-1}$	**0.001**	**0.002**	0.101

Table 6.12 Results of repeated-measures ANOVA with pre/post- restoration as repeated measures and site (H1, H3, H4) as fixed effect. All variables were $Log_{10}(x+1)$ transformed to improve normality. Statistically significant P-values are highlighted.

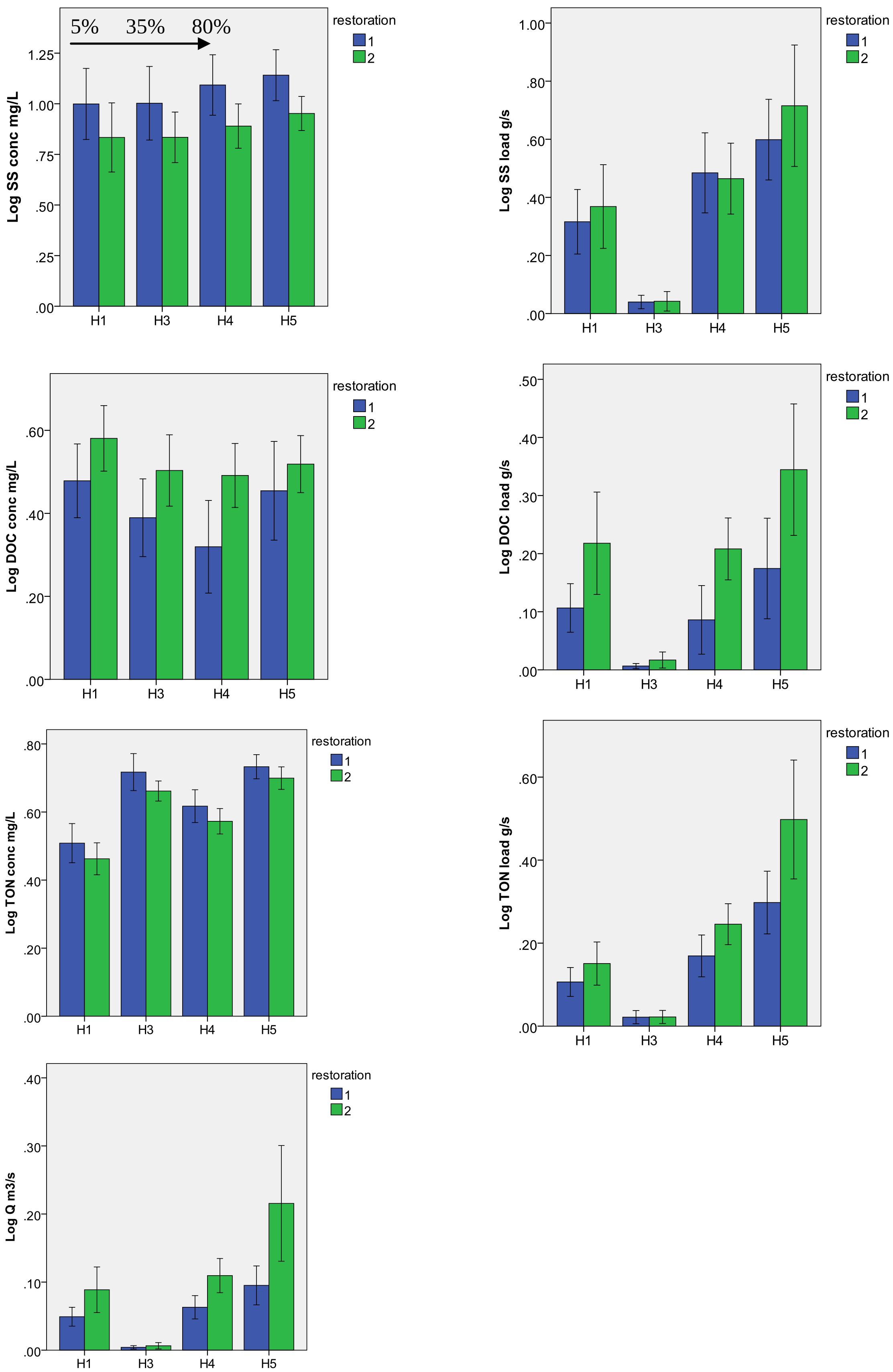


Fig. 6.21 Log-transformed mean values of concentrations and instantaneous loads for key water quality determinands and instantaneous discharge, with standard error bars: 1 - pre-restoration, 2 - post- restoration. The arrow illustrates the degree of restoration impact as a % of catchment affected by

ditch blocking. H5 at the catchment outlet is included to illustrate the between-years response at the catchment outlet, however it was not included in the repeated-measure ANOVA to avoid confounding effects of different scale comparisons.

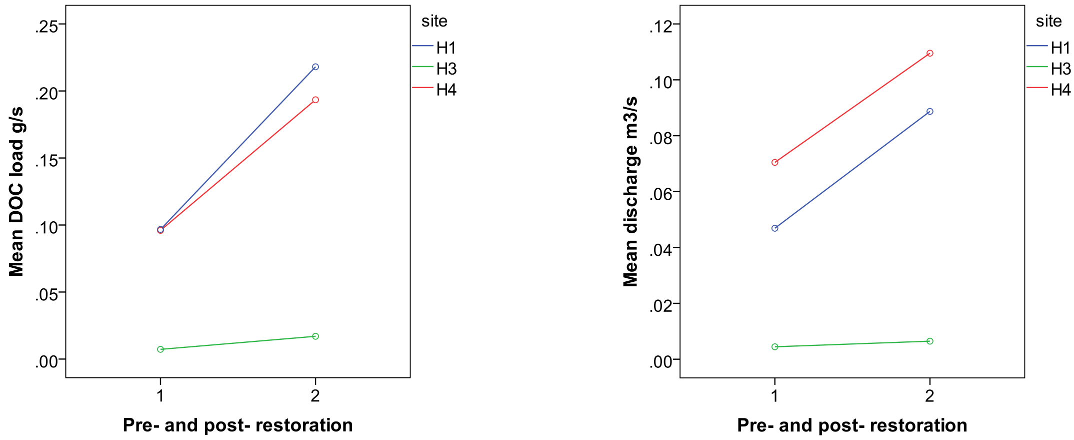


Fig. 6.23 Interaction plots showing the statistically near-significant difference between the response of DOC load and discharge at H3 as compared with H1 and H4 pre- and post- restoration. The slope of the line shows a different rate of response at the two sets of sites.

D. The response of macro-invertebrate indices in the Horner Water catchment to upland ditch blocking one year after habitat restoration.

Repeated measures ANOVA found no significant difference in macro-invertebrate indices between the three 2nd order tributaries of Horner Water, between study years and no significant interaction effects (Tab. 6.13, Figs. 6.24 and 6.25, p. 246). However, a near significant interaction effect ($P < 0.082$) was found in the response of O:E LIFE index between sites and the pre-/post-restoration periods, illustrated in Fig. 6.26. The summary data of all invertebrate indices across all study sites is presented in Table 5.1, Chapter 5.

	Sites	Restoration	Site*restoration
	P <	P <	P <
O:E PSI	0.085	0.559	0.232
O:E LIFE	0.070	1.000	0.082
O:E ASPT	0.874	0.224	0.106
O:E NTAXA	0.591	0.358	0.506

Table 6.13 Repeated-measures ANOVA with pre/post- restoration periods as repeated measure and site (H1, H3, H4) as fixed effect showed no significant difference in invertebrate indexes between sites and restoration years.

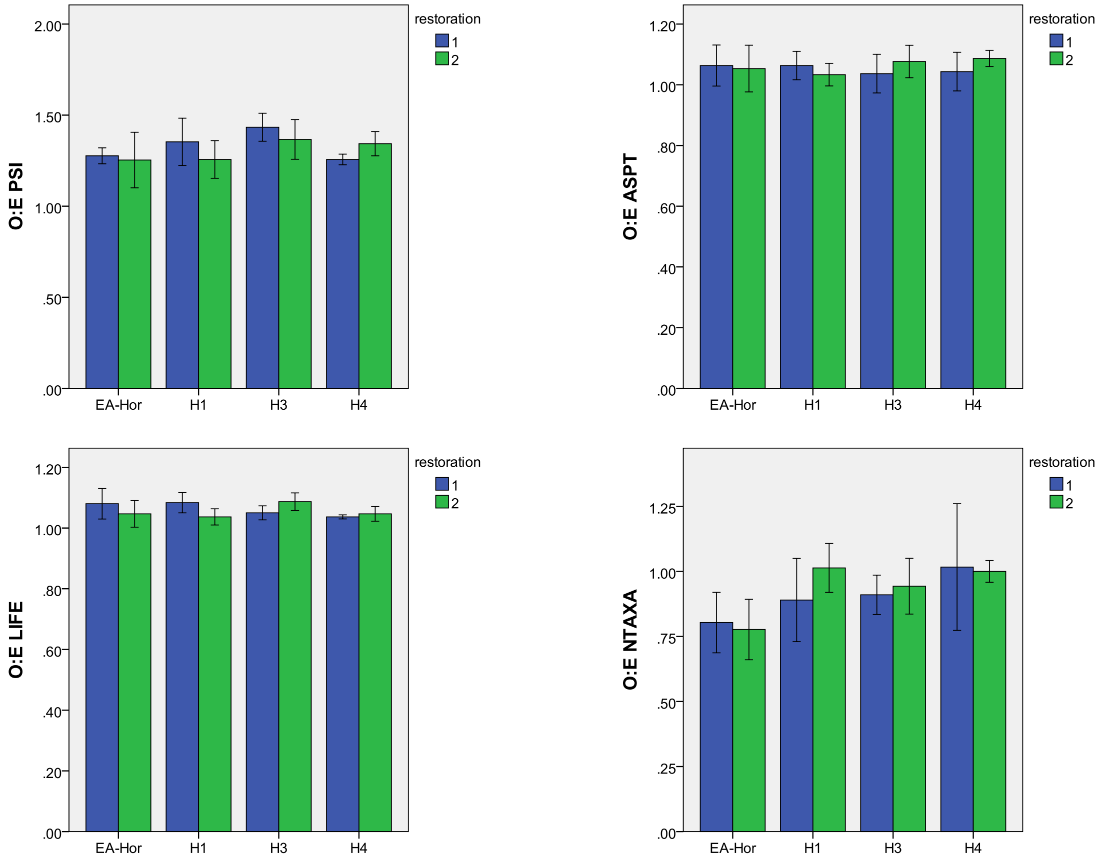


Fig. 6.24 Environmental Quality Indices for the four macro-invertebrate metrics with standard error bars: 1 - pre-restoration, 2 - post- restoration. EA-Hor is included to illustrate the between-years response at the catchment outlet at the long-term EA macro-invertebrate monitoring site, however it was not included in the repeated-measure ANOVA to avoid confounding effects of different scale comparisons.

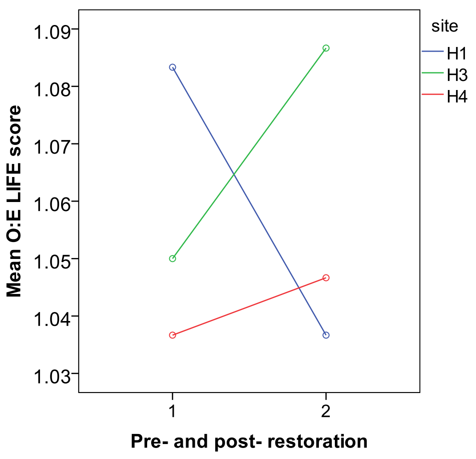


Fig. 6.26 Interaction plot elucidating the statistically near-significant difference in the response of O:E LIFE during pre- and post- restoration monitoring period at the three study sites H1, H3 and H4 ($P < 0.082$). While mean O:E LIFE increased at H3 and H4, it declined at H1 between the pre- and post-restoration period. The slope of the line illustrates the different rate and direction of response at the three sites.

V. DISCUSSION

A. Exporing the impact of land use mitigation measures in the Aller catchment on water quality determinands at a catchment scale.

a. Hydrological characterisation

Characterisation of the spatial distribution of total discharge, total water yield and flashiness within each sub-catchment informs the interpretation of the observed spatial variability of water quality determinands across the two study catchments (Soulsby et al., 2002). The spatial distribution of soil types and topography exert a first order control on the catchment hydrological response (Tetzlaff et al., 2007). With the exception of the steep H3 and A9 sub-catchments, the Q5:Q95 ratio of both Aller and Horner Water is at the low end of the range between 7.45 – 96 reported in literature (Jordan et al., 2005, Jordan et al., 2012b), indicating low flashiness. The prevailing HOST types 3 and 17 in the central parts of the Aller catchment (Chapter 3, Fig. 3.4, p. 203) indicate permeable soil types with no or limited contribution from groundwater at > 2 m depth, except for the Wigton Moor soil series in the riparian corridor (HOST 7-10) which may be subject to prolonged seasonal saturated sub-surface and overland flow, with an aquifer at < 2 m depth (Soil Survey of England and Wales, 1983, Boorman et al., 1995). The deep clay soils (Evesham 2 and Worcester) (Fig. 3.3, p. 202) on the north-eastern side of the catchment represent hydrologically more responsive HOST type 21 (Boorman et al., 1995) that may contribute to the saturation of soils in the riparian zone during high flow events as 'return flow' (Kirchner et al., 2000). However, the generally permeable nature of soils and lower rainfall-runoff coefficient (Chapter 4, Fig. 4.7c) in the Aller catchment indicates that the quicker hydrological response of the river Aller, identified in Chapter 4 and expressed as the lag between start of an event and peak discharge (Fig. 4. 7b) is likely to be related to intensive land use that has been shown to alter the soil physical properties and therefore hydrological response through reduced organic matter content, erosion, soil compaction and drainage (Batey and McKenzie, 2006, Price et al., 2010). Highest Q5:Q95 ratio and therefore greatest hydrological responsiveness, has been recorded in the middle reaches of the Aller catchment at A12 where infiltration excess overland flow was observed to occur along paved roads and unpaved tracks. Tetzlaff et al. (2007) also observed that road construction contributed to a rapid hydrological response of a medium-size upland catchment in Scotland by "intercepting flow paths and routing water more rapidly to streams, as well as generating infiltration-excess overland flow". Sub-surface drainage of the riparian grasslands is also known to occur in the A12 sub-catchment (Nigel Hester, pers. comm. 24th May 2013) and is likely to increase its hydrological responsiveness (Deasy, 2007).

b. Characterisation of water quality

i. Suspended sediment and particulate carbon

The altered hydrological connectivity described above is likely to be responsible for the high median SS concentrations observed in the A12 sub-catchment during high flow events through enhanced mobilisation of sediment and nutrients from intensively managed land (Deasy et al., 2009, Reaney et al., 2011). Field observations during rainfall events identified arable fields as major sources of suspended sediment, with a direct delivery pathway into the watercourse along paved roads (Fig. 6.2e-f). The comparison of SS loads between monitoring sites in the Aller catchment indicates that while SS loads in baseflow increase downstream with discharge, in stormflow this pattern is altered and anthropogenic SS sources and preferential pathways are likely to be more important controls of SS loads.

The negative correlation between increasing % of woodland within a 10 m buffer along the riparian corridor and SS stormflow concentrations suggests that bank erosion may also be an important source of SS in the Aller catchment (Stutter et al., 2012). The analysis of a chemograph (6.18, p. 240) for one event recorded simultaneously at the three monitoring locations in the Aller catchment (A11, A12, A7) indicates a rapid mobilisation of the accumulated pool of SS (flat hysteresis) and an easily mobilised and exhausted nearby source of TPC (clockwise hysteresis), possibly from the riparian zone (McDonnell, 2003). Conversely, during extreme events (Fig. 6.20, p. 244), SS source in the Aller catchment, but not in Horner Water, shows an exhaustion effect (clockwise hysteresis), while the TPC content declines in both catchments (clockwise hysteresis). Flat hysteresis has also been described as a 'single-valued' line (Williams, 1989) or no-hysteresis response (Asselman, 1999) and can indicate a continuous supply of sediment throughout the event (Williams, 1989), while the exhaustion effect has been attributed to the formation of an 'armoured layer' that reduced further soil erosion during high intensity rainfall events prior to the occurrence of peak discharge (Williams, 1989). The weak positive correlation between TPC stormflow concentrations and % moorland within a 10 m riparian buffer in the five stormflow monitoring sub-catchments perhaps reflects a difference in soil organic matter content between the two study catchments, as characterised in Chapter 3.

ii. DOC

Increasing DOC concentrations in baseflow within the Aller catchment suggest an increasing contribution of autochtonous nutrient sources along the river continuum (Vannote et al., 1980), such as increased net primary production and microbial breakdown of organic matter (Jarvie et al., 2008), although increasing downstream concentrations of DOC due to influx of terrestrially derived DOC from the riparian zone have also been reported (Dalzell 2011). Agricultural land use may also contribute to increased DOC concentrations through livestock poaching (Jarvie et al., 2008) and dunging, although such impacts have not been observed at a large scale in this study catchment. The positive correlation between DOC baseflow concentration and % grassland within a 10 m riparian buffer zone in the five stormflow monitoring sub-catchments suggests that pastoral land use in the Aller catchment may be a contributing factor to the elevated baseflow DOC concentrations in this catchment, possibly due to higher soil organic matter content commonly associated with grasslands (Bilotta, 2008, Roberts et al., 2012).

The comparison of ranking of DOC concentrations and loads supports the interpretation of different hydrological pathways operating within the two study catchments outlined in Chapter 4, that while in baseflow DOC concentrations within the Horner Water catchment are likely to be derived from deeper soil horizons with reduced DOC concentrations, in stormflow DOC is likely derived from the upper soil layers with a higher organic matter content. Conversely, shallower flow paths likely to occur on flatter topography on seasonally wet deep loam (Wigton Moor series) in the river corridor in the middle reaches of the Aller catchment may be contributing to the higher baseflow DOC concentrations as compared to Horner Water, with some possible contribution from groundwater. The negative correlation between DOC stomflow concentration and % clay in five sub-catchments with stormflow monitoring supports this interpretation of different soil types and hydrological pathways as DOC sources between the two study catchments.

DOC loads increased with discharge across all sites, except in stormflow when the upper reaches of the Aller at A11 exported more DOC than the middle reaches at A12, suggesting that discharge is an important control over DOC loads. The analysis of the chemograph indicates a slowly mobilised distant source of DOC in the Aller catchment during a medium size event (anti-clockwise hysteresis) (Figs. 6.18 – 6.19, pp. 240-242), probably originating in the carbon rich organic woodland and moorland soils at higher altitude, while in Horner Water the response of DOC during a medium size event is limited (Fig. 6.19, p. 242). Conversely, during an extreme event (Fig. 6.20, p. 244), DOC is rapidly mobilised from nearby sources in both study catchments. Clockwise hysteresis has been attributed to an initial flushing of determinands from the riparian zone (including in-channel sources), followed by hillslope water (anti-clockwise hysteresis), once a certain mobilisation threshold has been exceed (McDonnell, 2003). The seemingly reversed pattern observed in the Aller catchment suggests that extensive catchment saturation is necessary to mobilise DOC in the carbon-rich surface soil horizons of permeable soils in the lower reaches of the Aller catchment basin.

iii. Phosphorus

The highest DRP concentrations and loads in the uppermost reaches of the Aller in the A11 sub-catchment may be related to a number of factors. Wood et al. (2005a) suggested that dilution of DRP concentrations in a downstream direction suggests a dilution effect between plot, field and catchment scales. However, the Aller catchment is underlain by a secondary minor aquifer (Environment Agency, 2013) and significant dilution of DRP concentrations from groundwater is therefore unlikely. Secondly, this sub-catchment supports a greater density of rural dwellings, hence there is a potential for increased pollution from rural point sources, such as septic tanks (Withers et al., 2012), supported by the occurrence of highest baseflow DRP concentrations in the upper parts of the Aller catchment. Thirdly, while the land ownership within this sub-catchment is more fragmented and therefore the stocking density within the sub-catchment is difficult to quantify, many fields on steep slopes in close proximity to the riparian corridor in this sub-catchment show evidence of hard grazing and supplementary feeding, previously shown to contribute to enhanced export of TP from grasslands (Bilotta et al., 2008). Bilotta (2008) found TP yields from an intensively managed grazed grassland between 2.52-5.68 kg ha^{-1} yr^{-1} while Heathwaite et al. (1997) reported TP loss from grazed lisymeters of 2-3 kg ha^{-1} yr^{-1}. Although the estimated yields of DRP in the Aller catchment were between 0.09 and 1.1 kg ha^{-1}, it has to be noted that DRP constitutes only a proportion of the TP export (Heathwaite et al., 1997, Deasy, 2007, Bilotta, 2008, Roberts et al., 2012). Unfortunately, it was not possible to measure TP within the remit of this project, however evidence from the literature suggests that increasing export of SS during stormflow in the middle reaches of the Aller is likely to lead to an increased export of PP (Walling et al., 1997, Bilotta, 2008).

Therefore the TP exports from the Aller catchment are likely to be substantially higher.

Examination of the chemograph (Figs. 6.19, 6.20, pp. 242-244) in the Aller catchment suggests a rapid mobilisation of an accumulated resource (flat hysteresis) of DRP regardless of event magnitude, suggesting an excess supply of P in accumulated sediments and catchment soils. By comparison, in the Horner Water catchment examination of the hysteresis patterns (Figs. 6.19, 6.20, pp. 242-244) indicates a quick mobilisation of a limited resource of DRP (clockwise hysteresis), reflecting the reduced availability of DRP in this catchment. These findings are somewhat contrary to those of Bowes et al. (2005) who found that P hysteresis changed downstream from anti-clockwise in the upland sub-catchment to clockwise in the lowlands, due to intensifying land use and reducing sediment particle size. However, reviewing existing literature, Bowes et al. (2005) found that other studies 'almost always observed clockwise trajectories' due to within-channel mobilisation of P species.

iv. Nitrogen

The high concentrations of TON in the middle reaches of the Aller appear to be related to the % arable land in this study and reflect the regular applications of inorganic and organic fertilisers. A dilution effect apparent in stormflow indicates a groundwater contribution to baseflow TON concentrations from a secondary minor aquifer that underlies the Aller catchment. While the analysis of the chemograph indicates a stronger stormflow dilution effect and hence greater groundwater contribution in baseflow at A7, the lower median stormflow TON concentrations at A12 may indicate a proportionally greater dilution with surface water in this sub-catchment during stromflow, as reflected by the higher Q5:Q95 ratio. TON loads increased in a downstream direction both when baseflow and stormflow data were used for load estimation, indicating the important control of discharge over the solute loads (Walling and Webb 1986).

v. Determinand yields

Highest SS yields in the upper reaches of the Aller catchment are in line with the conceptual understanding of fluvial sediment export, whereby sediment yields are expected to decline with an increasing catchment area due to a lower sediment delivery ratio and increasing opportunities for sediment storage (Walling and Webb, 1986). While the estimated SS yields at A11 of 1.9 t ha^{-2} are in excess of the average soil formation estimates in Britain of 1 t ha^{-2} yr^{-1} (Morgan 1985 in Bilotta, 2008), Bilotta (2008) noted that the variability of soil formation rate between different soil types and land uses in Britain is poorly understood and even erosion rates below the 1 t ha^{-2} yr^{-1} threshold may be significant, if they selectively remove smaller soil particles and reduce soil fertility. Further, SS represents only a portion of the total sediment yield exported from the catchment, thus under-estimating actual soil erosion rate (Brazier, 2004).

Solutes are typically transported directly to the catchment outlet (Walling and Webb 1986), therefore a reduction of yields would only be expected where dilution with groundwater occurs downstream (Jordan et al., 2005). The high DRP and TON yields in the upper reaches of the Aller catchment are likely to indicate a proportionally greater diffuse water pollution risk due to greater hydrological connectivity on steeper slopes, less attenuation and dilution and therefore higher pollutant transport efficiency (Haygarth et al., 2005a). Further, greater connectivity to soils with higher organic matter content under semi-natural vegetation and in grasslands may also be responsible for the highest overall DOC yields in the upper reaches of the Aller in the A11 sub-catchment (Burt and Pinay, 2005, Bracken and Croke, 2007).

vi. Water quality status

The current standard for mean DRP concentration to achieve high ecological status in the Aller catchment is 50 µg L^{-1} and in the Horner catchment it is 20 µg L^{-1}, however current proposals suggest lowering this threshold to between 13 and 40 µg L^{-1}, depending on altitude (UK TAG, 2012). In the Aller, the median baseflow DRP concentration of 54 µg L^{-1} at A11 exceeds the current standard, while median stormflow DRP concentrations of 51 and 77 µg L^{-1} exceed the standard at both A11 and A12. It has to be noted that the stormflow concentrations are likely to be under-estimated by approximately 30 % due to the reduced accuracy of the analytical method. The current guideline mean SS concentration threshold of 25 mg L^{-1} (UK TAG, 2008) is exceeded in baseflow at the three monitoring sites A11, A12 and A7 within the Aller catchment and at all but one (Horner Water outlet H5) site in stormflow. However, it has to be noted that the analytical technique in the present study measured total SS concentration, including the organic sediment fraction and colloidal material. Therefore, while this method is likely to return higher concentration values than the usual gravimetric filtration through a 0.7 µm filter, it can be argued that it is more relevant for the determination of ecological impacts as the organic sediment fraction and colloidal material are important in the transport of contaminants (Bilotta, 2008). A small amount of solute material is also precipitated with this method, which may result in proportionally higher estimates of SS concentrations, particularly in baseflow conditions. There is currently no standard for TON concentrations in flowing waters in the UK, however the mean TON concentration standard for drinking water of 50 mg L^{-1} (Leeson et al., 2003) was not exceeded at any monitoring site within the study catchments in either baseflow or stormflow.

c. **Likely effectiveness of mitigation measures**

The loading of water quality and land use variables on the same PCA axis indicates that water quality is closely linked to land use in the study area. The understanding of the hydrological and land use controls on water quality in the Aller catchment discussed above suggests that the conversion of arable land to grassland is likely to reduce sediment concentrations and SS and PP yields in the middle reaches of the catchment (Roberts et al., 2012), as long as excessive stocking densities are avoided (Bilotta et al., 2007, Bilotta, 2008). However, conversion of arable land to intensive grassland may also result in an enhanced DRP export through microbial re-mobilisation of PP, as has been shown elsewhere in some arable conversion studies and evaluation of grassland buffer strips (Roberts et al., 2012, Stutter et al., 2012).

The planned wooded buffer strips are likely to be effective in reducing the delivery of suspended sediment and PP to the watercourse (Roberts et al., 2012) both from the adjacent arable land and from eroding banks in pasture. The introduction of further wooded buffers on arable and intensively grazed land across the A12 and A7 sub-catchments would help to mitigate sediment delivery into the watercourse through increased bank stability (Kronvang et al., 2012). While vegetated buffer strips have been shown to increase DRP exports through increased re-mobilisation of PP (Stutter et al., 2012), wooded buffers are less likely to suffer from these problems due to increased storage of P by trees in the below ground biomass (Sovik and Syversen 2008 cf Roberts et al., 2012). However, the buffers may need to be maintained through annual mowing in order to prevent their saturation with P and maintain their efficacy (Roberts et al., 2012, Stutter et al., 2012). The vegetated buffer strips may also be effective in reducing TON concentrations in the middle reaches of the Aller due to the propensity of seasonally wet deep loam of Wigton Moor series for seasonal saturation (Boorman et al., 1995, Soil Survey of England and Wales, 1983), which may allow sufficient residence time for denitrification to occur. However, the effectiveness of buffer strips to remove nutrients has not been conclusively established (Bergfur et al., 2012) and 5 m wide buffers were shown to be ineffective in delivering desired improvements to water quality on permeable soils (Noij et al., 2012). Therefore, buffer strips alone may not be sufficient to mitigate TON input into the watercourse and reduction of agricultural inputs may need to be required, if TON loading to the Aller was to be reduced.

The flood protection levées are likely to reduce sediment delivery into the Aller during high storm events, as dams and anthropogenic barriers are known to trap sediment (Ockenden et al., 2012, Fryirs, 2013) and floodplain restoration has been shown to be an effective way of reducing sediment, TP and nitrogen loads (Van der Lee et al., 2004, Scholz, 2007). Floodplains are most effective at trapping a greater % of annual load of sediment, N and P of smaller rivers (Noe and Hupp, 2009) and may trap between 26-47 % of sediment (Walling and Owens, 2003, Kronvang et al., 2007), 3 - 37 % of N (Van der Lee et al., 2004, Forshay and Stanley, 2005, Noe and Hupp, 2009) and 4 - 59 % of annual P load (Van der Lee et al., 2004, Kronvang et al., 2007, Noe and Hupp, 2009).

However, flooding of the land may lead to longer-term anaerobic conditions and enhanced solubilisation of DRP from the accumulated soil reserves in this part of the catchment (Jordan and Rippey, 2003, Loeb et al., 2008, Vidon, 2010, Roberts et al., 2012), although the extensive management of most of the flooded fields to date with minimal fertiliser input will help to minimise the risk of pollution swapping from this source.

The currently proposed mitigation measures will not address the extremely high soil erosion rates in the upper reaches of the Aller catchment, probably attributable just to one arable field immediately adjacent to the watercourse upstream of the monitoring site that was left deep ploughed and fallow throughout the winter of the sampling year. Equally, the proposed measures will not address the increased risk of DRP delivery from the same sub-catchment.

B. The response of physico-chemical water quality determinands and macro-invertebrate communities to upland ditch blocking in Horner Water catchment one year after habitat restoration.

The below average rainfall during the pre-restoration period coupled with an above average rainfall during the post-restoration period resulted in a significantly different discharge between these two periods. This in turn was likely to be responsible for the significantly higher instantaneous DOC loads at the three Horner Water tributaries during the post-restoration period, as annual runoff is an important control of solute loads (Walling and Webb, 1986). H3 supported a significantly smaller discharge than the other two tributaries, which was also reflected in lower SS and solute loads in this sub-catchment. There was no significant difference in the response of pollutant concentrations and instantaneous loads during the pre- post- restoration periods between the three sub-catchments. However the near-significant interaction effect of discharge and DOC load ($P < 0.101$ and $P < 0.06$, resp.) likely reflects the different hydrological characteristics of the H3 sub-catchment. In the less flashy sub-catchments H1 and H4 (Q5:Q95 = 16.87 and 6.76, resp.), discharge increased between the pre- and post- restoration period. However, in the flashy H3 sub-catchment (Q5:Q95 = 34.5), mean instantaneous discharge did not change between the pre- and post- restoration period. Therefore, the statistical analysis did not show any conclusive effects of restoration on instantaneous discharge, pollutant concentrations and loads during the 1 year of post-restoration monitoring, as both the control (H1) and the restored (H4) sub-catchments responded in the same way. The differentiated response of DOC load and mean discharge in the H3 sub-catchment, as compared to H1 and H4, can be attributed to the different runoff characteristics, i.e. the greater flashiness, of this sub-catchment.

Although there was no statistically significant difference in the response of macro-invertebrate indices during the pre- and post- restoration period between the three sub-catchments, the near-significant interaction effect of O:E LIFE index may signal a likely differentiated response of biota to antecedent flow conditions at H1 as compared to H3 and H4. The examination of the time-series plot in Fig. 6.25 shows reduced O:E LIFE between May 2011 and May 2012 at the long-term EA invertebrate monitoring site at the Horner Water catchment outlet, likely to be due to a period of below-average rainfall in 2010-2011. In the upland headwaters at H1, the response of biota to low flows seems to have been delayed by six months until November 2011, however at H3 and H4 the response of the biological index is delayed further by another six months until May 2012. Wilson (2011b) found reduced variability of discharge and more stable water tables that offer greater resilience to drought following peatland restoration. It could be hypothesised, that the upland restoration that took place in autum 2011 allowed the maintenance of baseflow and delayed the effects of 2010-11 drought on aquatic biota in the H3 and H4 sub-catchments.

The monthly water quality sampling frequency could be criticised as not adequate for picking up a signal from restoration. Whilst it was not feasible to implement flow integrated sampling within these three study sub-catchments in this study, several studies have successfully evaluated the effects of upland ditch blocking using a fortnightly (Wilson et al., 2011a), monthly (Clay et al., 2009) or less frequent spatially distributed sampling design (Yallop and Clutterbuck, 2009, Armstrong et al., 2010). A recent study examining the uncertainties associated with reduced sampling frequency on DOC load estimation (Buttner and Tittel, 2013) found that monthly sampling results in an underestimation between 13-19 %, which compares favourably with similar studies of P (Johnes, 2006, Cassidy and Jordan, 2011). Conversely, the presence of a sufficient pre-restoration baseline and a control catchment is considered critical for the unequivocal evaluation of treatment effects (Wilson et al., 2010, Turner et al., 2013). The experimental design in this study originally included sub-catchment H1 as a control as it is located above a reservoir which buffers the effects of land use change on downstream flood risk, making any such interventions meaningless in the context of the wider project objectives. Unfortunately, a limited amount of ditch blocking was nevertheless undertaken in this sub-catchment. However, as the works affected only 5 % of the sub-catchment area, for the purposes of this investigation H1 may still be considered as a limited control.

The lack of significant physico-chemical and biological response signal to the upland ditch blocking may therefore be due to a time lag in the response of hydrological and water quality variables to peatland restoration (Ramchunder et al., 2009). For example, Wilson et al. (2010) first detected changes in hydrological variables one year after ditch blocking, while Haapalehto et al. (2011) and Holden et al. (2011) found that hydrological, water quality and vegetation variables were still changing 6 -10 years after restoration. Therefore, several authors emphasise the need for long-term monitoring of restoration schemes (Holl et al., 2009, Armstrong et al., 2010, Wilson et al., 2010). Finally, the lack of significant response may be due to the already favourable condition of the upland moorland vegetation within this protected area. The stocking densities are low and burning regime is infrequent, mostly concentrated on controlling encroaching scrub vegetation on the slopes of the steep coombes on the moorland edge. Anthropogenic input of sediment and nutrients into the tributaries is modest and the macro-invertebrate communities are in near reference state (see Chapter 5). Therefore there may be limited scope for further improvement of water quality in Horner Water and the lack of negative impact of extensive ditch blocking may be taken as a positive sign of the benign ecological impact of these extensive works.

VI. CONCLUSIONS

This study provides a firm baseline for the evaluation of the impact of future land use change on water quality in the lowland agricultural Aller catchment. A significant hot-spot of high nutrient and sediment yields was identified in the upper reaches of the catchment, while high sediment and DRP concentrations and loads were found in the middle reaches of the catchment. The proposed conversion of arable land to pasture and the construction of flood alleviation levées are likely to lead to reduced sediment input into the river Aller, however, they may also enhance DRP fluxes, unless low input management of grassland is implemented in these areas. Additional wooded buffers in the riparian corridor within the A7 and A12 sub-catchments are likely to lead to further reductions of SS loads and yields through the stabilisation of stream and river banks, while flood retention measures in the floodplain will likely contribute to the removal N through denitrification. To date, this study has not found a conclusive signal of any positive or negative impact of the upland restoration measures on water quality at the sub-catchment scale. This may be due to a limited period of post-restoration monitoring to date but may also be interpreted as a positive sign of a benign impact of extensive land use alterations in this high quality environment.

Chapter 7

SYNTHESIS AND FUTURE RESEARCH NEEDS

This research contributes significantly to the current research agenda that examines the cumulative impact of land use mitigation measures on multiple pollutants in freshwater systems, using catchments as real world research platforms. In this chapter, a concise summary of the main research findings is presented together with suggestions for further research.

Chapter 3 research question: How does spatial variability of key soil properties vary between the two contrasting study catchments and what are the implications for mitigation of poor water quality?

In Chapter 3, the spatial variability of soil bulk density, total soil C, N, P and $\delta^{15}N$ in the two contrasting study catchments was characterised in order to provide a robust baseline for the monitoring of future land use changes and identify likely critical source areas of diffuse water pollution. A stronger degree of spatial dependence was found in the agricultural catchment (Aller) for all soil properties, except for $\delta^{15}N$. In addition, bulk density, TP, IP, OP, C:N ratio, $\delta^{15}N$ and carbon storage also showed a longer range of spatial auto-correlation in the agricultural catchment, indicating large-scale homogenisation of soil properties in this study catchment. The kriged surfaces of soil variables identified likely critical source areas for targeting of land management interventions to improve water quality and highlighted the large spatial extent of the alterations of soil properties, with implications for the rates of soil organic matter turnover, nutrient retention and prolonged restoration time-scales. While extensive alteration of soil properties is likely to have a direct impact on above- and below- ground terrestrial biodiversity, the links between these alterations and the ecological status of water bodies are less clear and deserve further attention.

Comparison of nutrient stock calculations (carbon and phosphorus) using the detailed geostatistical sampling and the national NSRI dataset showed comparable results, indicating that higher resolution soil sampling does not necessarily improve the estimation of nutrient stocks at the scale of these two study catchments. This finding supports the use of coarse-resolution national data sets for the estimation of soil nutrient stocks at a range of scales.

Chapter 4 research question: What are the current rates of fluvial carbon export in terms of dissolved organic and total particulate carbon from the two catchments and how do they relate to soils, prevailing land use and habitat mitigation?

This research quantified the total fluvial fluxes of dissolved organic and particulate carbon in two study catchments with contrasting land uses. The agricultural Aller catchment yielded proportionally greater fluxes of suspended sediment and particulate carbon than the semi-natural catchment, likely due to enhanced rates of soil erosion. The proportionally greater flux of dissolved organic carbon from the agricultural catchment may be due to a number of factors. Firstly, it is likely to reflect the faster turnover of soil organic matter as a result of anthropogenic nutrient addition. Secondly, addition of nutrients may promote autochtonous autotrophic DOC production and transformation of particulate carbon into DOC in the fluvial environment. Finally, alteration of hydrological pathways as a result of land drainage may also contribute to enhanced DOC fluxes along preferential pathways. The implications of enhanced fluvial carbon fluxes on the cycling of other nutrients in the aquatic environment are currently poorly understood, as are the implications of the enhanced fluvial DOC flux from agricultural catchments for the ecological status of freshwaters and the global carbon cycle. Further research in replicated catchments with contrasting land use but similar climatic and topographic controls would help to further constrain the significance of enhanced fluvial carbon fluxes in agricultural catchments for the global carbon cycle, while qualitative analysis of DOC and POC in catchments with contrasting land uses would elucidate the sources, pathways and ecological significance of the altered carbon cycling.

Chapter 5 research question: Can the new pressure-specific invertebrate index PSI act as a tool for determining ecologically relevant water quality sedimentation targets?

In this study the PSI index has been shown to relate to the % of fine bed sediment cover (silt and clay) across a narrow gradient of impact. PSI was not related to mean suspended sediment concentration. In addition, PSI was not related to the % of time for which the current guideline SS threshold of 25 mg L^{-1} has not been exceeded, although the sample size for this analysis was limited. Two existing macro-invertebrate metrics – LIFE and % EPT abundance, were also related to the % fine bed sediment cover, however this relationship was statistically less significant than for PSI. Further, while PSI was correlated with the existing macro-invertebrate LIFE metric, the relationship was weaker in the absence of hydrological stress. PSI and % EPT were not correlated, suggesting that they were responding differently to multiple environmental pressures. The present study indicates that PSI and % fine bed sediment cover have the potential to act as simple tools for the monitoring and setting of twin sedimentation targets, however further testing along a pronounced gradient of multiple stressors is recommended.

Chapter 6 research questions:

a) Are the proposed mitigation measures in the lowland Aller catchment likely to deliver water quality improvements at a catchment scale?

This research established a firm baseline against which the effects of future land use changes on water quality in the Aller catchment can be evaluated. Greatest concentrations of SS, DRP and TON were recorded in the middle reaches of the Aller catchment at sampling locations A12 and A7, reflecting the enhanced input of sediment and nutrients from the intensively farmed arable and grassland land uses. Field observations identified a number of direct preferential overland delivery pathways of sediment from arable fields along paved roads. The proposed conversion of arable land on steep slopes within the Aller catchment is likely to reduce this source of enhanced flux of sediment into the watercourse, as are the proposed flood management alleviation levées. However, while both of these measures are likely to reduce the sedimentation impact in the Aller, greater extent of intensively managed grassland and prolonged anaerobic conditions in the floodplain may lead to an enhanced flux of DRP, unless low-input management of these permanent grasslands can be secured. A number of suitable management prescriptions are outlined in the Higher Level Environmental Stewardship Scheme, including those relating to: Arable reversion to unfertilised grassland to prevent erosion or run-off (HJ3), Preventing erosion or runoff from intensively managed improved grassland (HJ6), Seasonal livestock removal on grassland with no input restriction (HJ7), Nil fertiliser supplement (HJ8), Restoration of species rich semi-natural grassland (HK7) and Restoration of wet grassland for wintering waders and wildfowl (HK12) (Natural England, 2013). Whilst some of the permanent grassland fields in the floodplain, managed in-hand by the National Trust or the tenant farmer, already receive no-input, this kind of management should be extended to all fields that will be subject to enhanced flooding due to the construction of flood alleviation levées in order to reduce the risk of phosphorus leaching.

Whilst the observed median TON concentrations in the Aller catchment between 6.5 – 10.4 mg TON L^{-1} are low, compared to the current freshwater drinking standard of 50 mg TON L^{-1}, they are above the perceived eutrophication level of 2.2 – 4.4 mg TON L^{-1} for running waters. The extended period of soil saturation in the floodplain and the introduction of wooded buffer strips will likely lead to enhanced denitrification and thus help to reduce TON concentrations in the middle reaches of the Aller catchment. The relationship between the % of woodland within a 10 m buffer and SS storm flow concentrations found in this study suggests that bank instability is an important source of sediment in the freshwater environment. Therefore, it is recommended that additional wooded buffers along the tributaries in the A7 and A12 sub-catchments would help to stabilise the river banks and reduce the sedimentation impact. Highest yields of SS, DRP, DOC, TPC and TON were recorded in the upper parts of the Aller catchment at the A11 monitoring site. Whilst for SS and TPC this may be related to increasing sediment storage with the increasing catchment size, this is not the case with solute loads. Therefore, high solute yields reflect proportionally greater nutrient input in the Aller headwaters in the A11 sub-catchment and will not be addressed by the currently proposed mitigation measures in the middle reaches of the catchment.

b) <u>How does upland ditch restoration impact on the chemical and biological indicators of water quality in three headwater tributaries of Horner Water?</u>

No clear positive or negative physico-chemical or biological signal can be detected as a result of the upland ditch blocking in the Horner Water catchment one year after restoration. Whilst this may in part be due to the limited period of post-restoration monitoring, it may also indicate that the extensive earth-moving works had no adverse effect on water quality in this high quality semi-natural environment. However, the statistically near-significant results indicate that macro-invertebrate monitoring could potentially act as a sensitive tool in detecting a signal from the upland ditch blocking in terms of maintenance of base flow and a delayed response to drought. Therefore, data collected in this study could be subjected to further analysis to understand the detailed macro-invertebrate community response and to examine whether bio-monitoring could provide a simpler time-integrated solution to the evaluation of restoration schemes, as compared to long-term hydrological and physico-chemical monitoring.

How effective can ecosystem management be in delivering water quality objectives?

Long-term monitoring of the national action plans in Denmark and the Netherlands has demonstrated that significant water quality improvements of a single contaminant (nitrate) are possible through large-scale implementation of a range of mitigation measures that target both sources and delivery pathways. Recent modelling of anticipated response times of Irish aquifers has also shown that improvements in the nitrate status of ground water bodies in response to extensive mitigation measures can be expected within two decades. Similarly, recent modelling has shown that depletion of soil P status can also be anticipated within similar timescales. These findings indicate that despite the complexity of the hydrological, physical, biological and land use controls within catchments, improvements in the ecological status of water bodies can be expected, albeit over longer timescales than originally envisaged by policy makers. Detailed baseline characterisation of water quality at nested scales in catchment-scale research platforms represents a transferable monitoring approach and a valuable resource that will help to inform the effectiveness of future land use changes and provide high quality empirical observations for modelling studies that could help to further the understanding of the complex interactions and controls on water quality at a catchment scale. The novel application of frequency exceedance curves, used in this study for the characterisation of water quality at nested observation sites, can be applied elsewhere to assess the impact of land use change on the ranking of sites pre- and post-restoration, and thus assess the direction of the mitigation impact.

The large scale alteration of soil physical and chemical properties at a catchment scale found in this study is further evidence of extensive anthropogenic impact on catchment processes from the most fundamental microbial level to large scale hydrological response. The enhanced fluvial carbon export from the agricultural catchment observed in this study is just one sign of an ecosystem-level response to these cumulative anthropogenic catchment-scale alterations. Restoration of such extensive anthropogenic impact to a more natural state will take time, while the detection of positive change will require commitment to collection of long-term observation time series. However, while long-term collection of high resolution data is resource intensive, testing of the PSI index in Chapter 5 shows that the development of simple effective indicator approaches to identification and monitoring of environmental pressures that utilise existing datasets and monitoring techniques represents a cost-effective solution, thus delivering a tool that "adequately represents small scale process complexity ... at a catchment scale" (Soulsby et al., 2006). Similarly, the near-significant signal from upland restoration detected by the macro-invertebrate LIFE index indicates that bio-monitoring may offer an ecologically meaningful, time-integrated solution to the monitoring of landscape-scale restoration schemes.

Collection of high-quality hydrological and physico-chemical water quality data is demanding due to technological and logistical challenges. A clear emerging learning point from catchment scale evaluation projects relates to the need for sufficient pre-restoration monitoring period, allowing for the installation and testing of field monitoring equipment and almost inevitable initial difficulties with collection of reliable data. Ongoing need for continuous data quality control, field equipment maintenance and high man-power input needed for the collection of flow rating data during high flow events also need to be acknowledged at the start of any monitoring scheme. Further challenges relate to the delays with obtaining of statutory consents and the feasibility of effecting actual land management change on farmed land that is subject to business considerations.

Whilst the extent of Nitrate Vulnerable Zones in England has recently been reduced, there is little evidence that the current restrictions within NVZs had a significant effect on the improvement of drinking water status, as compared to non-designated areas. Conversely, the initial evaluation of the effectiveness of the Catchment Sensitive Farming Initiative in England indicates that this approach may be successful in reducing the effects of diffuse water pollution by a number of contaminants on recipient water courses. Perhaps the whole-territory approach to the implementation of the Nitrates Directive in the Republic of Ireland, that also incorporates the objectives of the Water Framework Directive, could offer some insights into how different policy approaches (NVZs, CSFI, CBA) could be integrated. In the absence of a wider policy tool, an observed challenge in the lowland catchment in this study related to a ‘pollution swapping’ scenario, whereby whilst a voluntary agreement for arable conversion was secured from one landowner using an agri-environment scheme agreement, an unforeseen simultaneous conversion of permanent grassland to arable land occurred on a neighbouring holding on similarly ‘high-risk’ ground. This illustrates the challenge of securing lasting land management and land use change at a sufficient scale in a commercial environment.

A number of recent research initiatives, investigating the effects of land management and land use change on ecosystem services such as flood risk management, water resource management and management of diffuse water pollution have been instigated, including the Defra funded Demonstration Test Catchments platform and the Multi-objective Flood Management Demonstration Projects. From a policy-perspective, it would be efficient to assemble the learning outcomes from all of these schemes to inform further scheme implementation and secure continued scientific monitoring that is integrated between projects set-up with different policy objectives in mind.

In summary, a number of learning points emerge from this thesis:

- Agriculture results in an extensive alteration of soil physical and chemical properties, with implications for ecosystem functioning and restoration time-scales.
- Agricultural land use leads to enhanced fluvial export of sediment, particulate and dissolved organic carbon with poorly understood consequences for the health of the aquatic ecosystems and the global carbon cycle.
- The new macro-invertebrate bio-monitoring index PSI appears to be a promising simple integrated tool for the detection of sedimentation impacts and setting of twin sedimentation targets, in conjunction with the monitoring of % fine bed sediment cover.
- The potential of macro-invertebrate monitoring to act as a sensitive time-integrated tool for the monitoring of the effects of upland ditch blocking on base flow maintenance should be investigated further.
- The proposed mitigation measures in the lowland catchment may deliver water quality improvements, however there is likely to be a need for additional wooded buffers in the most extensively managed sub-catchments and implementation of no-input grassland management, especially on newly flooded areas. An ongoing challenge relates to unforeseen future land management changes driven by commercial considerations that may obscure the signal from the implementation of individual mitigation measures at a catchment scale.

- Integration of learning and coordination of research from different research platforms and demonstration projects set up to measure the impact of land management and land use change on different ecosystem services would be beneficial.

Appendices

Chapter 3

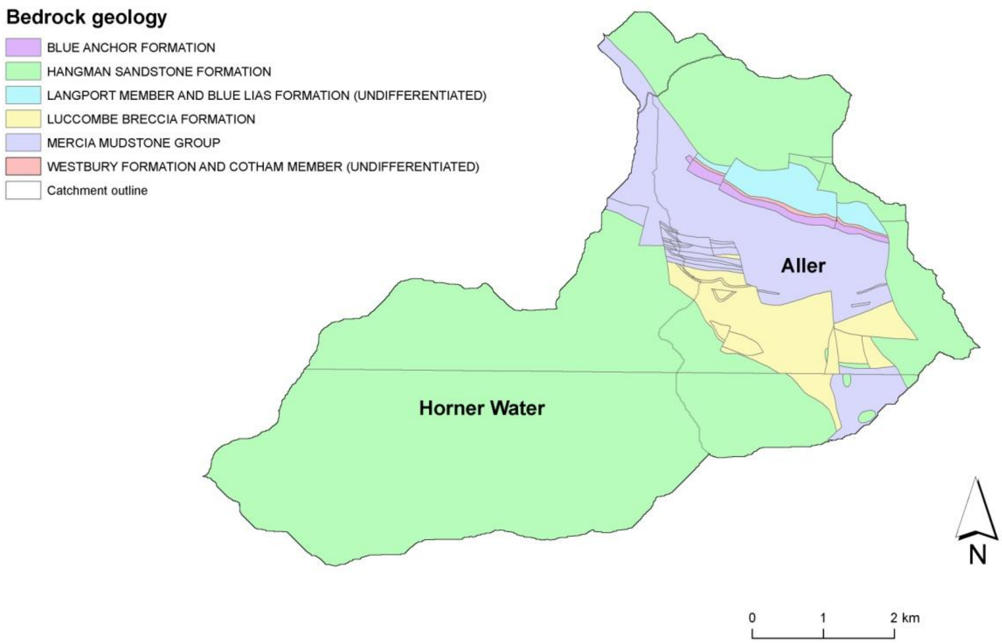


Fig. 3.2 Bedrock geology in the two study catchments. Source: OS Digimap

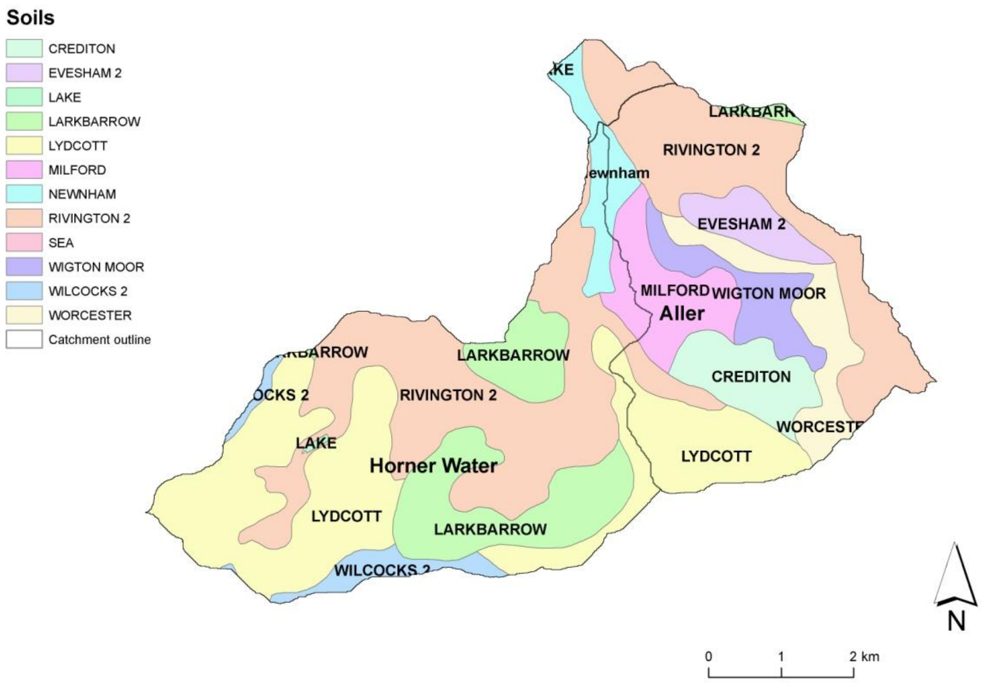


Fig. 3.3 National 1:250,000 soil map of the two study catchments. Source: NATMAP vector, Soils Data @ Cranfield University (NSRI) and for the Controller of HMSO 2013

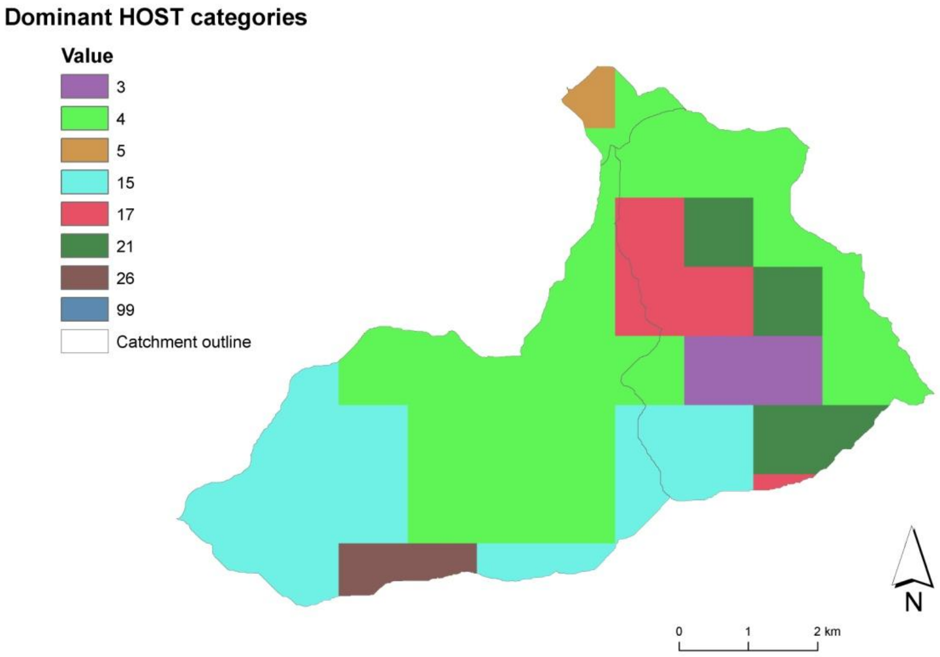


Fig. 3.4 Dominant HOST soil classification categories in the two study catchments. Categories 3-5 represent permeable well drained soils on permeable substrates with predominantly vertical water movement with an aquifer at > 2 m depth. Class 17 represents freely draining soil types up to a slowly permeable or an impermeable substrate at < 1 m depth and no significant groundwater contribution. Class 21 is a soil type with a propensity for short seasonal saturation on slowly permeable or impermeable substrates, with a predominantly lateral water movement and no significant groundwater contribution. Classes 15 and 26 are peaty soils with a propensity for saturation excess overland flow; 99 – sea. Source: CEH

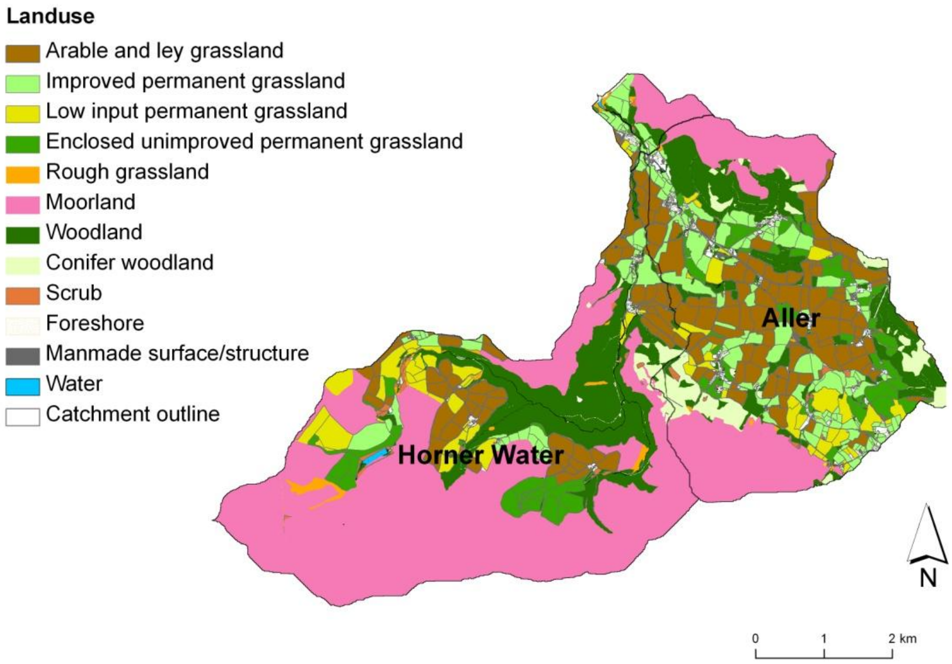


Fig. 3.5 Land use map of the study catchments compiled from Natural England agri-environment scheme information, OS Mastermap and farmer interviews.

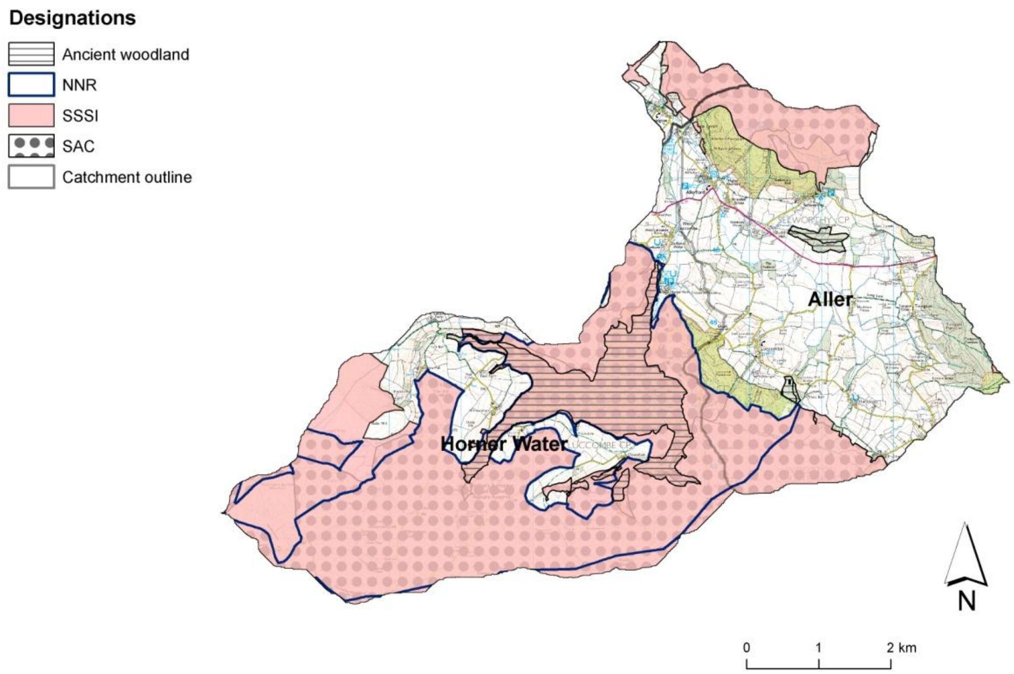
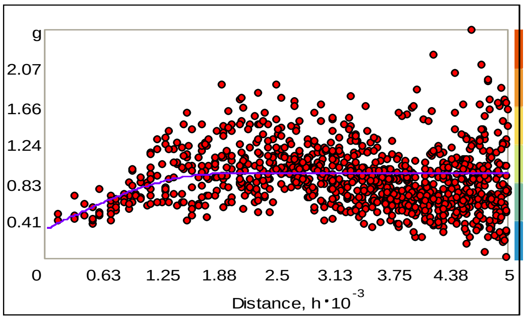
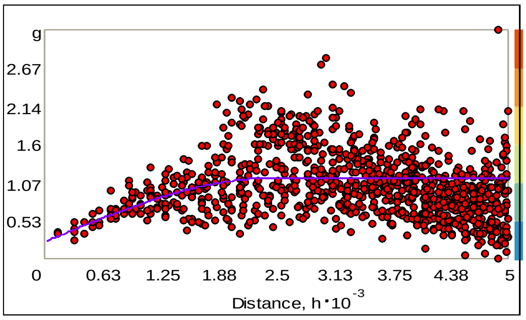


Fig. 3.6 Nature conservation designations on the Holnicote Estate. NNR – National Nature Reserve, SSSI – Site of Special Scientific Interest, SAC – Special Area of Conservation. The largest part of the Horner Water catchment is semi-natural and lies within designated sites, whist most of the Aller catchment is used for agriculture. Source: Natural England

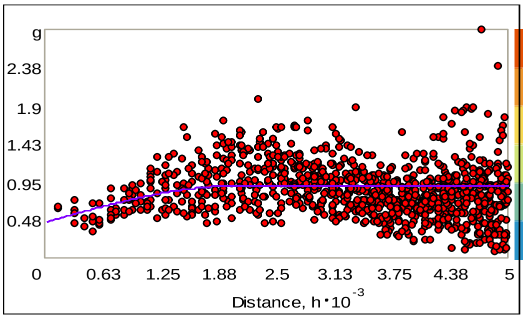
Bulk density g cm^{-3}



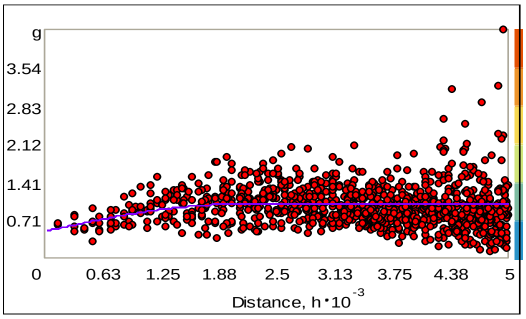
δ^{15}N



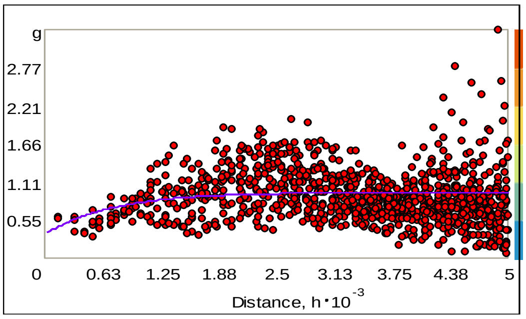
TN %



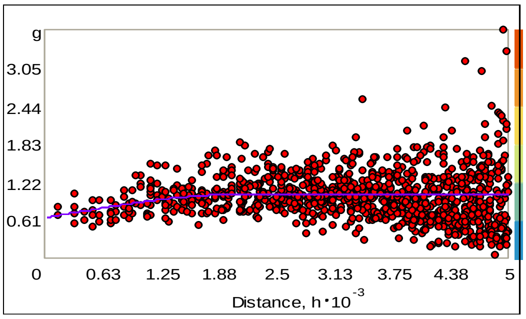
C storage g cm^{-2}



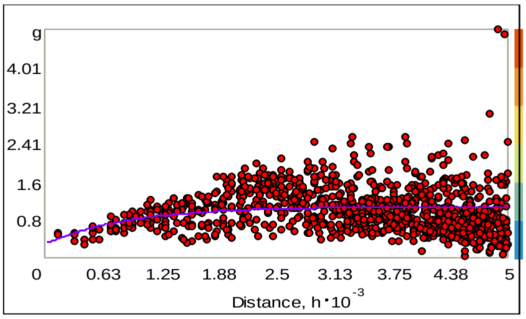
TC %



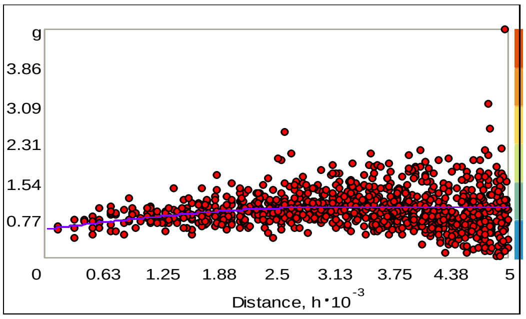
N storage g cm^{-2}



C:N ratio



TP g kg^{-1}



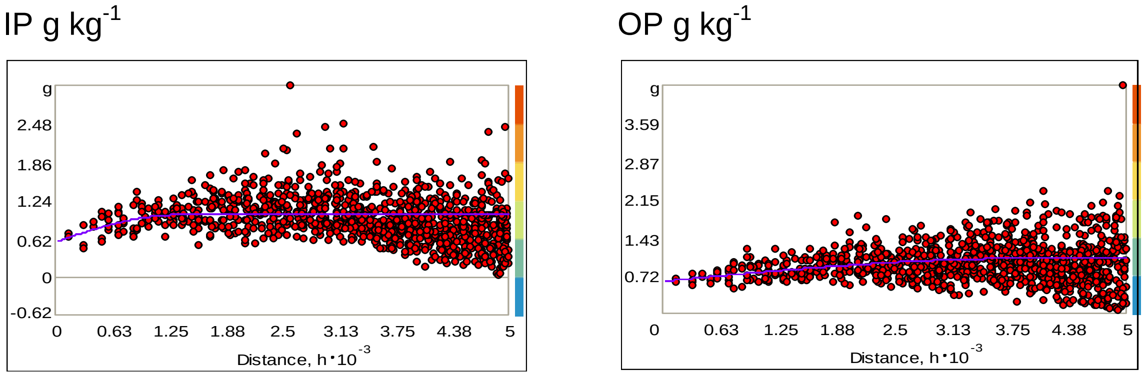
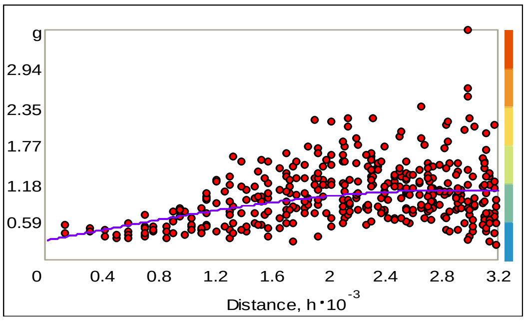
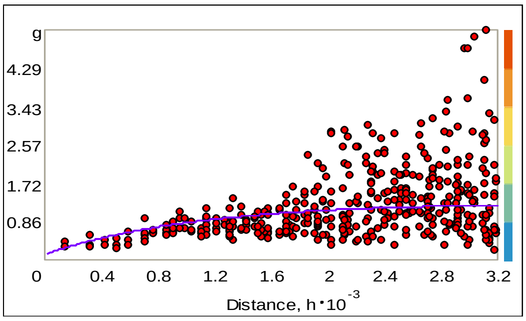


Fig. 3.10 Fitted theoretical semivariograms for measured soil properties for the two catchments combined, lag distance 200 m, number of lags 25. Distance on x-axis in km, y-axis denotes semivariance.

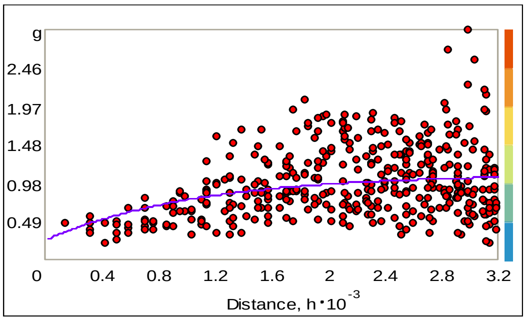
Bulk density g cm^{-3}



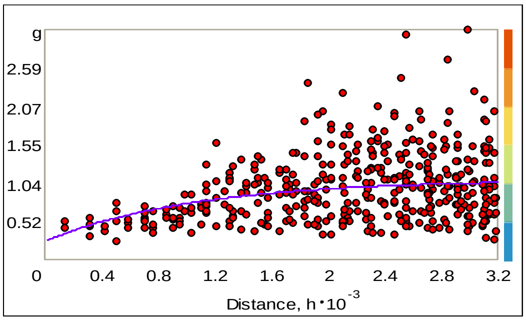
δ^{15}N



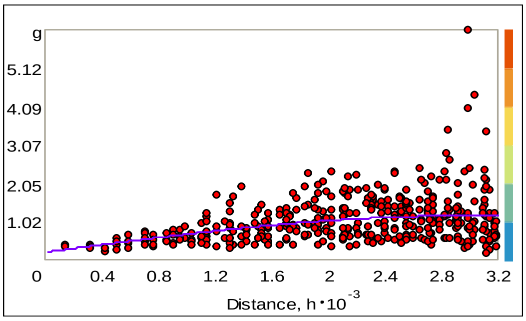
TN %



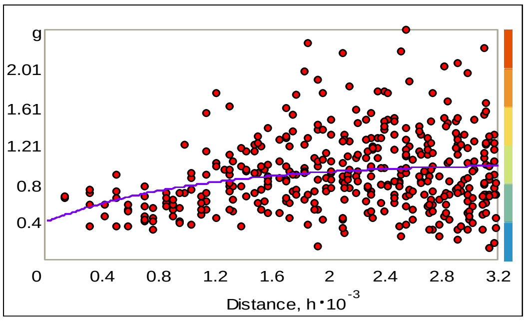
C storage g cm^{-2}



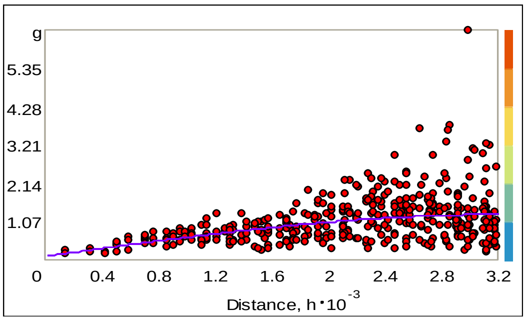
TC %



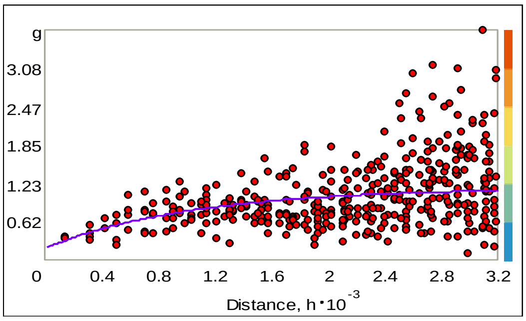
N storage g cm^{-2}



C:N ratio



TP mg kg^{-1}



IP g mkg^{-1} OP mg kg^{-1}

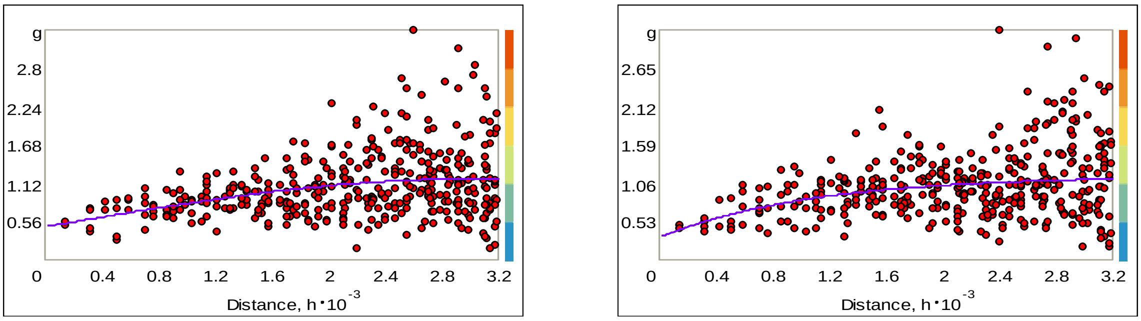
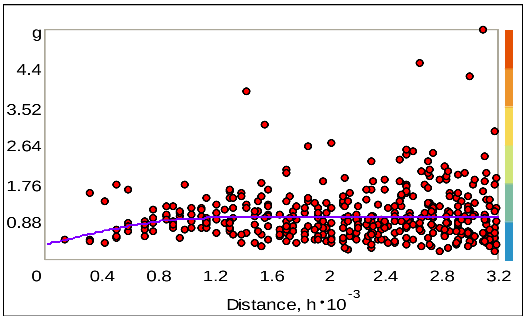
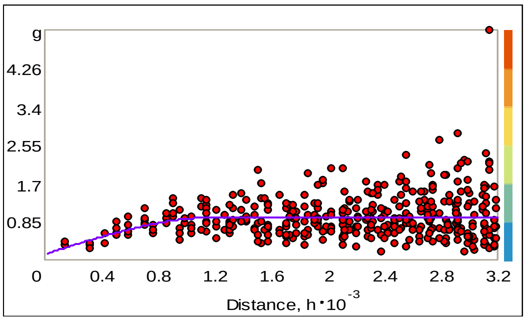


Fig. 3.11 Fitted theoretical semivariograms for measured soil properties for the Aller catchment, lag distance 200 m, number of lags 16. Distance on x-axis in km, y-axis denotes semivariance.

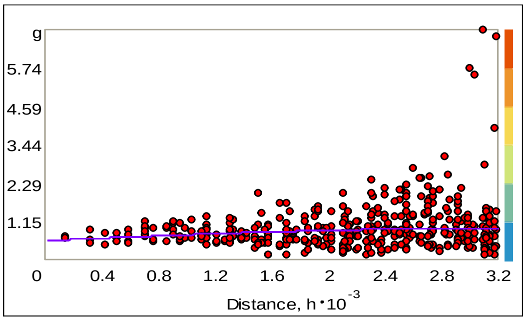
Bulk density g cm^{-3}



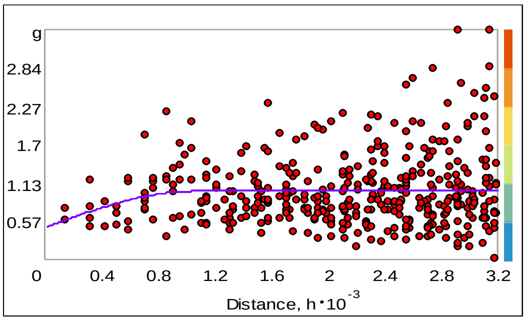
$\delta^{15}N$



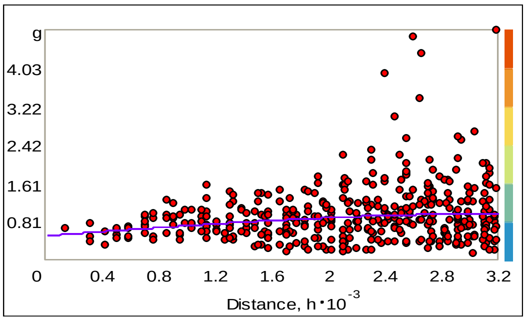
TN %



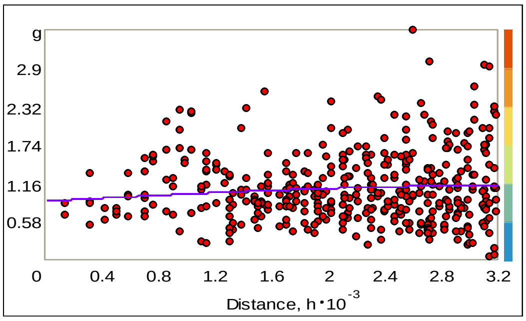
C storage g cm^{-2}



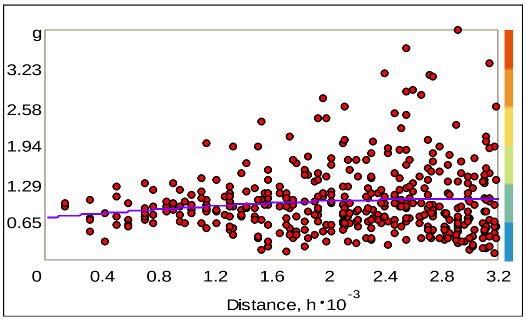
TC %



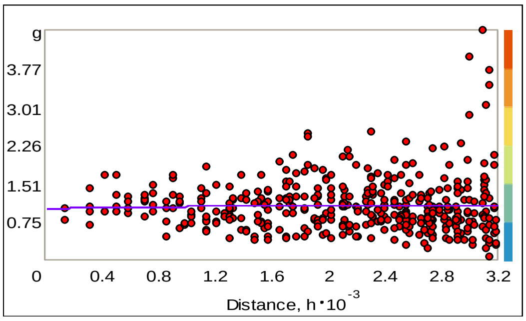
N storage g cm^{-2}



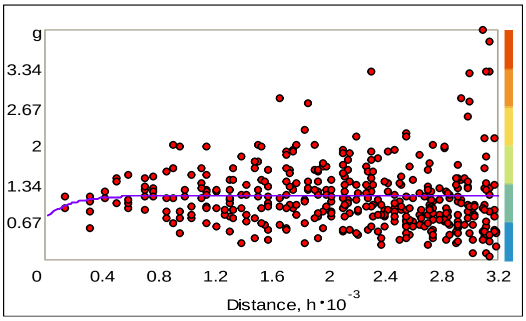
C:N ratio



TP mg kg^{-1}



IP mg kg^{-1}



OP mg kg^{-1}

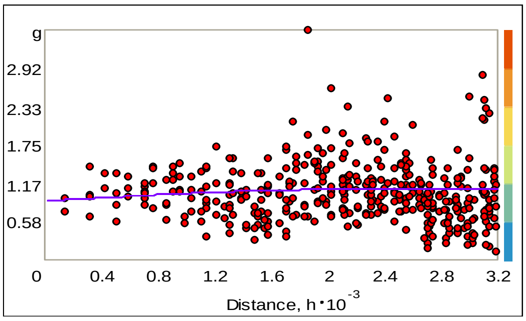


Fig. 3.12 Fitted theoretical semivariograms for measured soil properties for the Horner Water catchment, lag distance 200 m, number of lags 16. Distance on x-axis in km, y-axis denotes semivariance.

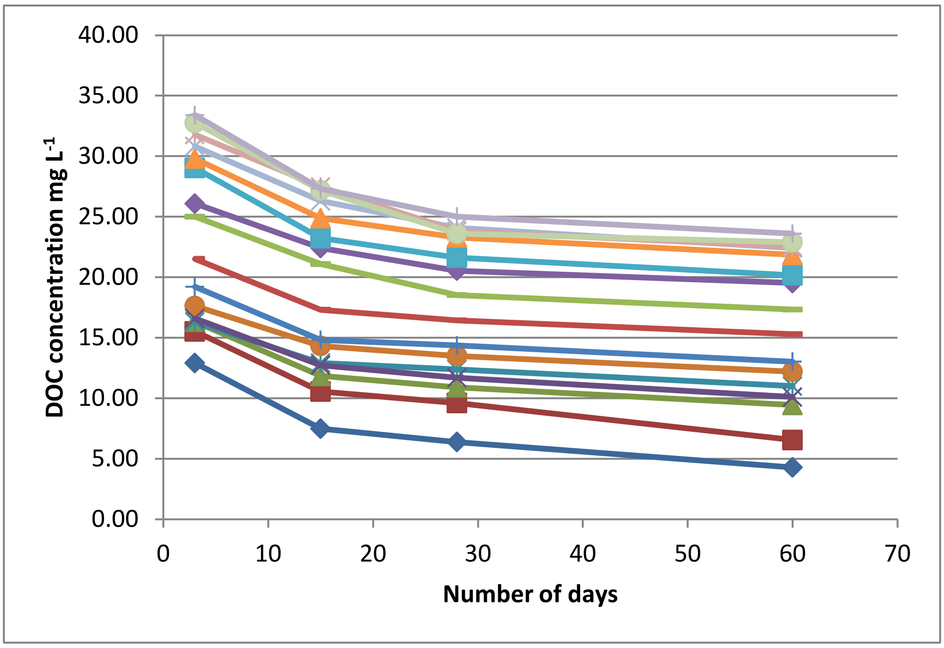


Fig. 4.2 DOC storage test on days 3, 15, 28 and 60 after the rainfall event shows a mean loss of DOC concentration of 0.38mg L^{-1} per day (SD=0.071) over the first 15 days of storage, across the range of concentrations.

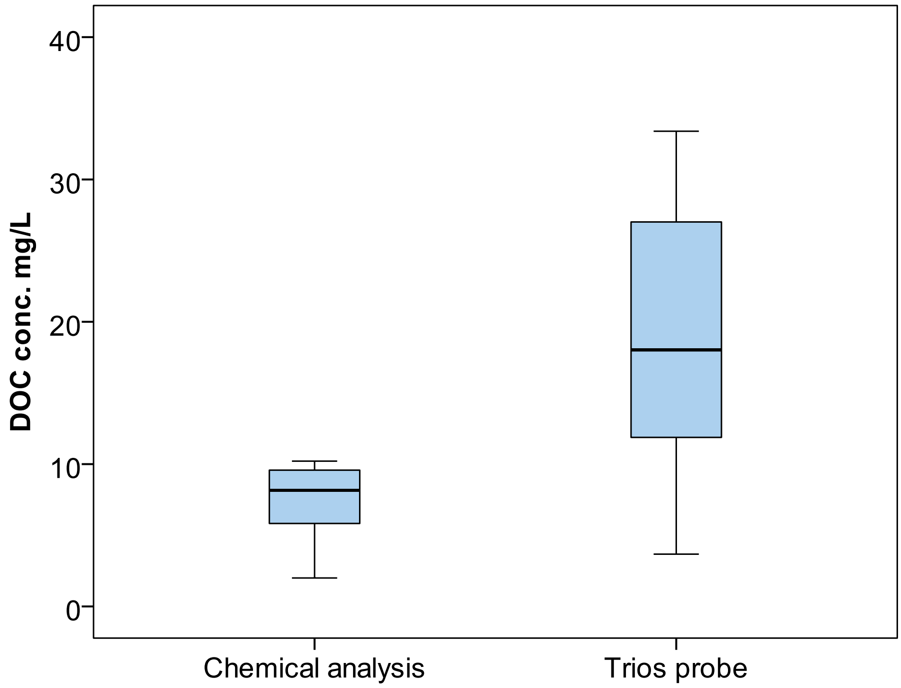


Fig. 4.3 Comparison of spectrometry and chemical analysis shows significantly higher DOC concentrations obtained on the Trios probe than those using Skalar Formacs^{HT} TOC Analyser (t-test, $P < 0.001$, $N = 30$). For Trios measurements mean = 18.88 mg L^{-1}, SD = 9.64; for chemical analysis mean = 7.42 mg L^{-1} with SD = 2.54.

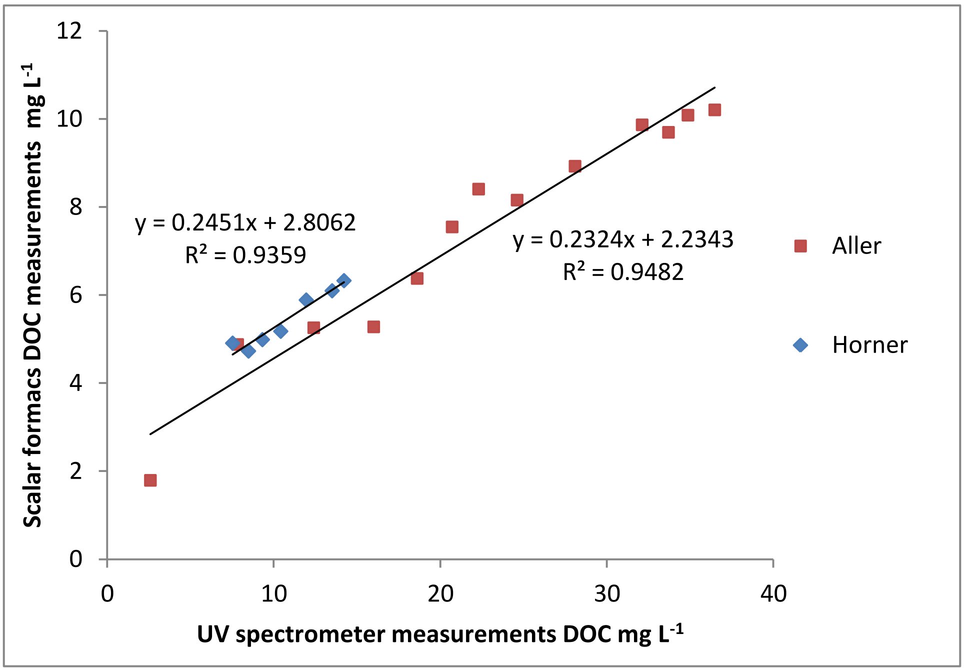


Fig. 4.4 Linear regression model applied to stormflow DOC measurements to allow pooling of data with baseflow samples analysed on the Skalar Formacs^{HT} TOC Analyser.

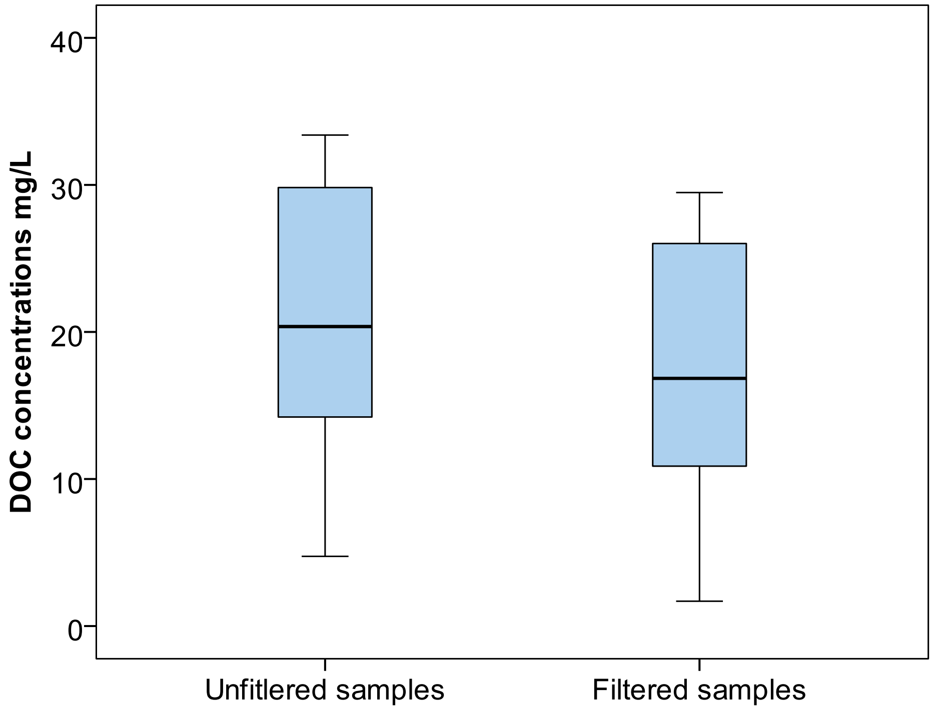


Fig. 4.5 Unfiltered samples analysed on the Trios spectrometer showed higher mean DOC concentrations, however this difference was not statistically significant (t-test, $P < 0.355$, $N=24$) and hence was not pursued further in the laboratory protocol. For unfiltered samples mean = 20.89 mg L^{-1}, SD = 9.31; for filtered samples mean = 17.35 mg L^{-1} with SD = 9.03.

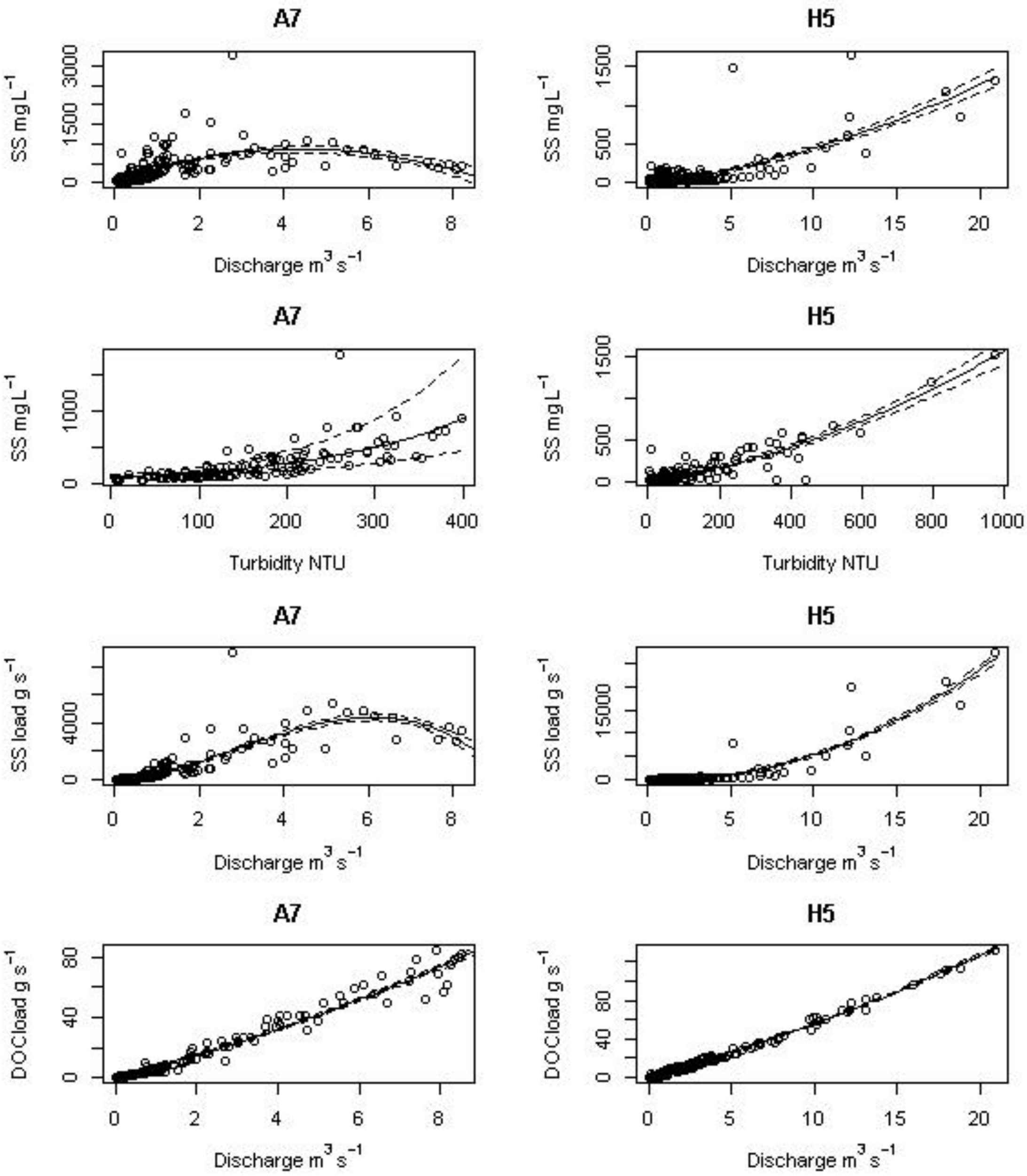


Fig. 4.6 Calibration relationships between discharge, turbidity and SS concentrations, SS loads and DOC loads at the Aller (A7) and Horner Water (H5) catchment outlets. Corresponding equations are presented in Table 4.2.

Determinand	Equation	R^2	Lower 95% coeff.	Upper 95% coeff.	N
Aller					
SS	$405.365*Q-49.453*Q^2+0.523*Q^3$	66.50	358.288 -72.363 -1.868	452.442 -26.544 2.915	479
SS	$82.63*\exp(0.006*NTU)$	74.08	61.01 0.005	107.89 0.007	133
SS load	$131.535*Q+311.929*Q^2*-35.181*Q^3$	78.66	22.400 258.820 -40.725	240.672 365.039 -29.637	479
DOC load	$6.762*Q+0.307*Q^2$	97.62	6.257 0.231	7.266 0.384	242
Horner Water					
SS	$26.04*Q+1.86*Q^2$	66.86	18.76 1.32	33.32 2.40	377
SS	$0.644*NTU+0.0009*NTU^2$	87.40	0.476 0.0006	0.811 0.0012	121
SS load	$-130.638*Q+65.988*Q^2$	87.33	-192.785 61.403	-68.491 70.573	377
DOC load	$4.910*Q+0.075*Q^2$	99.49	4.679 0.065	4.941 0.085	217

Table 4.2 Calibration equations for relationships between discharge, turbidity and SS concentrations, SS loads and DOC loads at the Aller (A7) and Horner Water (H5) catchment outlets. Q – discharge, NTU – Nephelometric turbidity units, N – number of samples.

Date	Catchment	Total rainfall (mm)	Peak rainfall intensity (mm hr^{-1})	Total event Q (m^3)	Peak Q (m^3 s^{-1})	Event duration (min)	Lag start event to peak Q (min)	Lag peak rainfall intensity to peak Q (min)	Rainfall/runoff coefficient
21/08/2010	A	8.00	26.40	6927.51	0.28	1350	30	150	0.04
25/08/2010	A	53.80	14.40	94679.73	1.36	6120	675	135	0.12
23/09/2010	H	18.20	11.20	28797.3	0.48	1515	360	255	0.08
01/10/2010	A	15.60	11.20	14468.56	0.36	2085	510	105	0.06
	H	24.00	16.80	89973.9	1.90	2340	1035	120	0.19
6/11/2010	A	16.00	5.60	13607.94	0.20	2460	1635	780	0.06
	H	24.00	4.00	113552.10	1.25	2640	1470	270	0.23
8/11/2010	A	16.40	4.80	55049.91	0.40	4080	615	210	0.23
	H	29.60	8.00	320826.60	2.15	4410	2115	1050	0.54
7/01/2011	A	27.40	8.80	137103.80	1.25	4665	120	165	0.34
	H	28.00	7.20	213093.00	1.39	4335	1695	1485	0.38
10/01/2011	A	11.40	4.80	66752.06	1.24	1905	510	480	0.40
11/01/2011	H	15.60	3.20	129760.20	1.75	1905	570	585	0.41
12/01/2011	H	38.60	4.00	611507.70	3.58	4500	1725	855	0.79
13/01/2011	A	7.80	1.60	64208.02	0.81	1695	1050	840	0.56
12/06/2011	A	11.60	3.20	9426.24	0.18	1860	885	195	0.06
	H	21.80	4.00	59181.30	0.81	3615	795	180	0.13
18/06/2011	A	6.20	3.20	3838.66	0.10	930	435	285	0.04
	H	14.80	8.00	34649.10	0.35	2640	885	450	0.17
26/08/2011	A	25.40	17.60	22693.43	0.83	2055	615	405	0.06

	H	29.20	11.20	39349.80	1.31	2370	1815	435	0.06
06/09/2011	H	20.60	4.80	84690.00	1.41	3420	450	270	0.20
18/09/2011	A	25.20	12.80	9463.64	0.28	1365	750	330.00	0.03
	H	40.40	19.20	102920.40	1.66	2970	1485	465	0.13
24/10/2011	A	25.40	18.40	11724.10	0.37	2415	1065	165	0.03
	H	22.80	18.40	79670.70	1.83	2235	1095	150	0.17
04/11/2011	A	16.40	20.80	28747.34	0.45	4245	210	180	0.12
11/11/2011	A	14.60	7.20	12756.02	0.94	6480	240	165	0.26
	H	13.40	8.00	134283.60	1.23	3660	420	225	0.50
11/12/2011	A	15.20	7.20	64000.78	0.67	1590	810	750	0.20
8/12/2011	A	8.40	4.80	45328.70	0.96	2685	420	165	0.52
	H	14.20	6.40	104166.90	2.39	1470	690	195	0.36
12/12/2011	H	53.60	7.20	704691.90	13.15	3240	375	75	0.65
3/01/2012	H	41.40	8.80	753847.20	21.53	2355	705	165	0.90
3/01/2012	A	28.20	6.40	317278.34	8.18	2565	735	120	0.77

Table 4.3 Hydrological characteristics of 35 hydrological events examined in the Aller (A) and Horner Water (H) catchments between 21st August 2010 and 3rd January 2012. Q- discharge, min - minutes.

Date	Catchment	Peak SS conc. (mg L^{-1})	Peak SS flux (g s^{-1})	Peak DOC conc. (mg L^{-1})	Peak DOC flux (g s^{-1})	Peak TPC (%)	Peak TPC conc. (mg L^{-1})	Peak TPC flux (g s^{-1})
21/08/2010	A	132.99	37.55			15.17	18.15	5.13
25/08/2010	A	1161.11	1581.54			15.45	152.78	208.10
23/09/2010	H	32.89	15.72			24.01	6.73	3.22
01/10/2010	A	184.61	66.71			15.20	26.04	9.41
	H	164.99	308.71			23.72	29.97	56.08
06/11/2010	A	90.02	16.46			11.94	10.57	1.93
	H	29.79	33.84			20.80	6.20	7.04
08/11/2010	A	147.65	54.82			11.64	15.70	5.85
	H	16.09	22.78			16.13	2.60	3.68
07/01/2011	A	1001.01	1255.60	14.03	9.94	14.22	100.79	122.49
	H	71.34	64.42	5.78	7.81	30.76	12.93	11.67
10/01/2011	A	414.89	514.18	6.97	8.47	10.19	35.70	44.24
11/01/2011	H	55.97	97.66	5.56	9.55	19.53	10.40	18.15
12/01/2011	H	107.57	361.02	6.19	22.03	17.97	11.36	39.47
13/01/2011	A	319.63	238.66	5.26	4.14	9.52	19.57	15.77
12/06/2011	A	86.63	14.75			14.73	12.52	2.08
	H	170.65	124.70			19.59	28.75	21.01
18/06/2011	A	57.84	5.00			12.78	7.39	0.64
	H	27.97	9.11			17.54	4.31	1.40
26/08/2011	A	305.35	233.96	4.41	3.51	17.63	46.58	35.69
	H	218.77	220.40	5.16	6.02	23.71	50.44	48.45
06/09/2011	H	143.71	195.16	7.59	10.37	25.09	31.76	43.13
18/09/2011	A	88.99	22.13	5.23	1.44	15.29	12.10	3.32
	H	151.34	251.23	6.99	11.61	22.05	25.45	42.25
24/10/2011	A	367.66	134.86	5.25	1.55	16.52	53.24	19.53
	H	169.63	288.40	6.10	10.42	23.05	38.01	64.16
04/11/2011	A	370.90	162.49			14.48	48.19	21.11
11/11/2011	A	1183.67	1121.97	5.60	4.73	13.42	153.80	145.26
	H	68.34	83.10	6.31	6.86	22.60	14.72	18.00
08/12/2011	A	431.12	408.65	4.66	4.13	11.50	47.25	44.63

Date	Catchment	Peak SS conc. (mg L^{-1})	Peak SS flux (g s^{-1})	Peak DOC conc. (mg L^{-1})	Peak DOC flux (g s^{-1})	Peak TPC (%)	Peak TPC conc. (mg L^{-1})	Peak TPC flux (g s^{-1})
	H	129.57	309.02	4.67	10.56	17.18	20.86	49.76
11/12/2011	A	148.41	77.37	3.98	2.69	10.67	14.37	8.92
12/12/2011	H	1642.54	20183.59	6.27	78.45	16.49	199.49	2451.39
03/01/2012	A	1078.60	5273.67	10.71	84.62	7.97	62.95	323.18
	H	1321.33	27588.06	6.31	132.53	14.07	114.53	2057.24

Table 4.5 Water quality characteristics of 35 rainfall events examined in the Aller and Horner Water catchments between 21st August 2010 and 3rd January 2012. SS – suspended sediment, DOC – dissolved organic carbon, TPC – total particulate carbon. Flux refers to instantaneous flux.

Water quality parameter	Catchment	Hydrological control	P <	R^2	Standard error of estimate	Constant	Unstandardised coefficients	Standardised coefficients
Log SS maximum concentration (mg L^{-1})	Horner	Log peak Q m3/s	0.0001	0.736	0.294	2.942	1.111	0.653
		Log lag peak rainfall intensity to peak Q (min)					-0.575	-0.373
	Aller	Log peak Q m3/s	0.0001	0.840	0.180	1.724	1.210	0.572
		Event duration (min)					0.0001	0.593
Log SS max instantaneous flux (g s^{-1})	Horner	Log peak Q m3/s	0.0001	0.902	0.308	2.654	2.455	0.840
		Log lag peak rainfall intensity to peak Q (min)					-0.634	-0.239
	Aller	Log peak Q m3/s	0.0001	0.932	0.307	0.900	2.855	0.742
		Event duration					0.0001	0.416
Log TPC maximum concentration (mg L^{-1})	Horner	Log peak Q m3/s	0.0001	0.644	0.312	2.544	0.788	0.508
		Log peak rainfall intensity to peak Q (min)					-0.661	-0.470
	Aller	Event duration (min)	0.0001	0.875	0.205	0.829	0.0001	0.685
		Log peak Q m3/s					0.785	0.407
TPC (%)	Horner	Runoff coefficient	0.025	0.292	3.603	23.882	-8.842	-0.541
	Aller	Runoff coefficient	0.0001	0.864	1.402	13.368	-7.260	-0.609
		Rainfall intensity					0.146	0.390

Water quality parameter	Catchment	Hydrological control	P <	R^2	Standard error of estimate	Constant	Unstandardised coefficients	Standardised coefficients
Log TPC maximum instantaneous flux (g s^{-1})	Horner	Log peak Q m3/s	0.0001	0.881	0.298	2.268	2.037	0.793
		Log peak rainfall intensity to peak Q (min)					-0.694	-0.298
	Aller	Log peak Q m3/s	0.0001	0.932	0.263	0.174	2.276	0.694
		Event duration (min)					0.0001	0.479
Log DOC maximum concentration (mg L^{-1})	Horner	-						
	Aller	Log peak Q m3/s	0.038	0.435	0.110	0.661	0.392	0.660
Log DOC max instantaneous flux (g s^{-1})	Horner	Log peak Q m3/s	0.0001	0.979	0.063	0.502	1.211	0.990
	Aller	Log peak Q m3/s	0.0001	0.969	0.116	0.196	1.860	0.969

Table 4.7 Stepwise multiple regression models of sediment and carbon peak event concentrations and instantaneous fluxes with extreme events. N = 35 (18 for Aller and 17 for Horner). SS – suspended sediment, TPC – particulate organic carbon, DOC – dissolved organic carbon. Non-normally distributed parameters were $Log_{10}(x+1)$ transformed.

Water quality parameter	Catchment	Hydrological control	P <	R^2	Standard error of estimate	Constant	Unstandardised coefficients	Standardised coefficients
Log SS maximum concentration (mg L^{-1})	Horner	-						
	Aller	Log peak Q m3/s	0.0001	0.938	0.111	1.568	2.635	0.686
		Event duration (min)					0.0001	0.418
Log SS max instantaneous flux (g s^{-1})	Horner	Log peak Q m3/s	0.0001	0.653	0.324	2.638	2.918	0.775
		Log lag peak rainfall intensity to peak Q (min)					-0.695	-0.437
	Aller	Log peak Q m3/s	0.0001	0.967	0.141	0.610	5.544	0.819
		Event duration					0.0001	0.269
Log TPC maximum concentration (mg L^{-1})	Horner	-						
	Aller	Log peak Q m3/s	0.0001	0.865	0.163	0.674	2.108	0.550
		Event duration (min)					0.0001	0.521
TPC (%)	Horner	-						
	Aller	Rainfall intensity	0.0001	0.620	1.437	13.042	0.157	0.483
		Runoff coefficient					-5.999	-0.457
Log TPC maximum instantaneous flux (g s^{-1})	Horner	Log peak Q m3/s	0.001	0.614	0.311	2.206	2.450	0.712
		Log peak rainfall intensity to peak Q (min)					-0.731	-0.503
	Aller	Log peak Q m3/s	0.0001	0.957	0.142	-0.066	4.477	0.759
		Event duration					0.0001	0.342

Water quality parameter	Catchment	Hydrological control	P <	R^2	Standard error of estimate	Constant	Unstandardised coefficients	Standardised coefficients
Log DOC maximum concentration (mg L^{-1})	Horner	-						
	Aller	-						
Log DOC max instantaneous flux (g s^{-1})	Horner	Log peak Q m3/s	0.001	0.804	0.070	0.445	1.342	0.896
	Aller	Log peak Q m3/s	0.001	0.818	0.102	-0.024	2.718	0.904

Table 4.8 Stepwise multiple regression models of sediment and carbon peak event concentrations and instantaneous fluxes without extreme events. N = 32 (17 for Aller and 15 for Horner). SS – suspended sediment, TPC – particulate organic carbon, DOC – dissolved organic carbon. Non-normally distributed parameters were log-transformed.

Chapter 5

a) PSI:

Fixed effects	Estimate	SE	c.P-value*
Intercept	66.864	5.094	<0.001
Log. % bed sed. cover	-6.806	2.087	<0.002
Log. altitude	7.343	2.738	<0.010

Random effects (site level)	SD[†]
Intercept	4.128
Residual	7.348
No. of samples	51
No. of sites	13
k[+]	5

b) O:E PSI:

Fixed effects	Estimate	SE	c.P-value*
Intercept	1.312	0.042	<0.001
Log. % bed sed. cover	-0.096	0.038	<0.014

Random effects (site level)	SD[†]
Intercept	0.093
Residual	0.122
No. of samples	51
No. of sites	13
k[+]	4

c) LIFE

Fixed effects	Estimate	SE	c.P-value*
Intercept	8.108	0.099	<0.001
Log. % bed sed. cover	-0.228	0.089	<0.014

Random effects (site level)	SD[†]
Intercept	0.221
Residual	0.291
No. of samples	51
No. of sites	13
k[+]	4

d) O:E LIFE

Fixed effects	Estimate	SE	c.P-value*
Intercept	1.057	0.013	<0.001
Log. % bed sed. cover	-0.026	0.012	<0.034

Random effects (site level)	SD†
Intercept	0.031
Residual	0.038
No. of samples	51
No. of sites	13
k+	4

e) EPT % richness

Fixed effects	Estimate	SE	c.P-value*
Intercept	23.331	3.336	<0.001
Log. % bed sed. cover	-7.335	2.887	<0.014

Random effects (site level)	SD†
Intercept	8.008
Residual	9.079
No. of samples	51
No. of sites	13
k+	4

*based on 10,000 Markov chain Monte Carlo simulations

†Expressed as SD, i.e. in response variable score units

+ total number of model parameters (k), including the intercept, fixed effects, random effect and residual variance

Table 5.4 Parameters for the mixed effect hierarchical generalised linear models showing the functional relationship between a) PSI, % fine bed sediment cover and altitude b) O:E PSI and % fine bed sediment cover c) LIFE and % fine bed sediment cover d) O:E LIFE and % fine bed sediment cover and e) EPT % abundance and fine bed sediment cover.

Site	Equation	R^2	Lower 95% coeff.	Upper 95% coeff.
H3	$0.00028*e^{29.45*S}$	99.09	0.00016	0.00049
			27.43	31.65
H4	$-5.4138*S^2+4.3584*S-0.2605$	99.75	-7.3589	-3.4687
			3.4823	5.2344
			-0.3351	-0.1859
A7	$5.0232*S^2-0.2384*S$	98.6	3.4038	6.6427
			-0.9972	0.5203
A8	$29.061*S^2+1.825*S$	95.38	5.2843	52.8379
			-7.8504	11.4997
A9	$1.1133*S^2+0.1984*S$	99.41	0.4516	1.7750
			-0.0218	0.4185
A10	$0.7358*S$	99.43	0.5665	0.9051
A11	$7.1048*S^2-0.2904*S$	99.00	5.7906	8.4189
			-0.5291	-0.0517
A12	$12.5557*S^2+0.1363*S$	99.24	9.4848	15.6266
			-0.7163	0.9889
A13	$1.5889*S-0.0349$	99.91	0.9851	2.1928
			-0.0665	-0.0032

Table 6.1 Stage/discharge equations for nine monitoring sites with 95% confidence intervals used to calculate a continuous discharge record from 15' stage data. S – stage in m.

Site		Discharge ($m^3 s^{-1}$)	SS conc. ($mg L^{-1}$)	DOC (conc. $mg L^{-1}$)	TON conc. ($mg L^{-1}$)	DRP conc. ($\mu g L^{-1}$)	Alkalinity ($mg L^{-1}$)	SS inst. load ($g s^{-1}$)	DOC inst. load ($g s^{-1}$)	TON inst. load ($g s^{-1}$)	pH	Temp ^oC
A10	Median	0.03	18.98	3.93	6.17	57	61.20	0.93	0.10	0.24	8.07	13.10
	Minimum	0.01	4.47	1.66	1.89	20	21.60	0.01	0.01	0.00	7.21	10.10
	Maximum	0.09	60.28	8.83	16.25	75	311.70	1.93	0.67	0.63	8.22	16.00
	N	18	14	21	21	5	19	14	18	18	10	9
A11	Median	0.02	36.58	2.76	6.58	54	134.45	0.76	0.05	0.11	8.19	14.20
	Minimum	0.01	14.94	0.98	3.93	36	105.80	0.19	0.02	0.05	7.26	10.10
	Maximum	0.06	51.66	21.29	8.05	76	202.40	2.30	0.30	0.42	8.32	15.30
	N	20	15	21	22	5	20	15	19	20	11	10
A12	Median	0.06	31.35	3.00	10.41	23	135.15	1.99	0.17	0.56	8.11	14.00
	Minimum	0.03	17.32	1.32	9.70	9	98.70	0.81	0.06	0.31	7.08	11.80
	Maximum	0.24	56.10	7.88	11.65	57	219.60	6.68	1.11	2.41	8.26	15.40
	N	19	15	22	22	5	20	15	19	19	11	10
A13	Median	0.05	42.13	2.70	7.62	24	128.85	2.17	0.15	0.39	8.28	14.70
	Minimum	0.04	6.42	1.23	5.46	6	100.50	0.22	0.05	0.21	7.23	10.70
	Maximum	0.13	64.62	13.78	9.47	56	202.10	6.47	0.70	1.21	8.46	15.40
	N	21	15	22	22	5	20	15	21	21	11	10
A7	Median	0.10	32.95	4.07	9.88	37	131.10	4.29	0.31	0.98	7.78	13.30
	Minimum	0.03	24.70	1.70	8.06	9	87.80	0.92	0.10	0.28	6.79	9.70
	Maximum	1.11	69.81	10.56	11.68	71	217.50	70.76	6.71	10.38	8.42	16.40
	N	32	27	34	34	9	31	27	32	32	22	22
A8	Median	0.07	13.46	2.14	5.68	13	43.90	0.84	0.16	0.34	7.71	12.90
	Minimum	0.01	1.41	0.49	2.49	0	16.50	0.04	0.01	0.06	6.41	8.50
	Maximum	0.70	29.40	19.44	8.44	82	77.70	14.46	0.91	3.14	8.65	15.80
	N	34	27	34	34	9	31	26	33	33	22	22
A9	Median	0.01	33.82	3.02	6.51	41	82.95	0.17	0.02	0.04	8.11	16.45
	Minimum	0.01	24.94	0.01	1.74	24	60.20	0.06	0.01	0.00	7.20	11.30
	Maximum	0.02	92.19	9.16	8.14	79	106.30	0.91	0.16	0.18	8.24	17.70
	N	19	15	22	22	5	20	15	19	19	11	10
H1	Median	0.13	9.20	2.33	2.12	11	11.20	0.93	0.29	0.24	7.00	11.10
	Minimum	0.02	0.01	0.84	0.57	0	1.20	0.01	0.02	0.03	6.40	7.20

Site		Discharge ($m^3 s^{-1}$)	SS conc. (mg L^{-1})	DOC (conc. mg L^{-1})	TON conc. (mg L^{-1})	DRP conc. (µg L^{-1})	Alkalinity (mg L^{-1})	SS inst. load (g s^{-1})	DOC inst. load (g s^{-1})	TON inst. load (g s^{-1})	pH	Temp ^{o}C
	Maximum	0.65	25.46	8.75	4.18	20	30.00	6.56	2.47	1.14	7.62	14.20
	N	34	27	34	34	9	31	27	34	34	22	22
H3	Median	0.01	8.61	1.39	3.75	9	20.20	0.04	0.01	0.02	7.31	11.20
	Minimum	0.01	0.01	0.27	2.31	0	9.00	0.01	0.01	0.01	6.55	7.80
	Maximum	0.07	22.38	7.01	13.24	22	47.00	0.63	0.20	0.33	7.64	13.60
	N	31	27	34	34	9	31	27	31	31	22	22
H4	Median	0.19	8.46	1.21	3.08	10	14.30	1.98	0.22	0.64	7.44	11.90
	Minimum	0.02	2.62	0.13	1.36	0	6.70	0.29	0.01	0.06	6.43	8.60
	Maximum	0.57	67.94	8.67	5.74	23	35.80	12.98	1.60	1.76	7.79	15.70
	N	31	27	33	33	9	30	27	31	31	22	22
H5	Median	0.31	9.42	2.00	4.49	6	19.00	3.01	0.56	1.20	7.60	12.35
	Minimum	0.07	3.88	0.41	2.65	0	9.00	0.82	0.03	0.26	6.40	8.70
	Maximum	3.14	33.58	19.94	5.90	49	40.90	38.31	5.28	10.98	8.35	15.10
	N	31	27	34	34	9	31	27	30	30	22	22

Table 6.4 Summary statistics of the monthly measurements of physico-chemical water quality determinands and discharge across all monitoring sites that were related to land use, soil type and soil properties within each sub-catchment. SS at 6 sites (H1, H3, H4, H5, A7, A8) was sampled between 21st September 2010 and 26th November 2012, while at the remaining 5 sites (A9, A10, A11, A12, A13) it was sampled between 21st September 2010 and 3rd November 2011. DOC and TON were sampled at the 6 sites between 25th February 2010 and 26th November 2012, while at the remaining 5 sites they were sampled between 25th February 2010 and 3rd November 2011. DRP was sampled at six sites on the following occasions: 30th June, 27th July, 23rd September 2010; 10th February, 3rd November, 8th December 2011; 12th January, 22nd February, 20th March 2012, while on the remaining 5 locations it was sampled on 30th June, 27th July, 23rd September 2010, 10th February and 3rd November 2011. A variable number of discharge values is due to the gradual installation of continuous discharge monitoring across the two study catchments between 27th April and 28th July 2010. Temperature and pH were monitored from 27th January and 10th February 2011 until the end of monitoring on 26th November 2012 and 3rd November 2011 at the two groups of sites.

site	Arable (%)	Grass-land (%)	Moor-land (%)	Wood-land (%)	Peat (%)	Clay (%)	BD (g cm^{-3})	TC (%)	TN (%)	C:N	$\delta^{15}N$	Loam (%)	C storage (g cm^{-2})	N storage (g cm^{-2})
A10	8.91	20.25	33.48	31.34	43.73	0.00	0.56	21.12	1.01	19.75	0.74	56.27	0.41	0.02
A11	10.05	51.56	13.04	21.18	17.88	26.24	0.92	9.20	0.65	11.82	3.39	55.87	0.28	0.02
A12	25.57	24.92	22.55	21.29	18.22	21.87	0.93	10.34	0.69	12.12	3.52	59.04	0.31	0.02
A13	14.79	36.25	27.13	18.67	31.02	0.00	0.86	10.89	0.72	12.62	2.89	52.75	0.31	0.02
A7	26.60	28.35	20.32	20.91	16.62	21.05	0.95	9.26	0.65	11.66	3.88	62.33	0.29	0.02
A8	16.74	19.85	40.84	19.88	28.00	7.95	0.78	16.76	0.94	14.65	2.91	63.97	0.39	0.03
A9	9.70	19.13	40.49	27.45	0.00	27.35	0.83	14.66	0.90	14.37	2.80	72.65	0.43	0.03
H1	0.00	5.42	93.82	0.41	87.08	0.00	0.44	15.94	1.42	18.67	1.64	12.92	0.44	0.02
H3	5.75	4.55	82.15	7.32	55.49	0.00	0.42	30.28	1.25	19.38	2.16	44.51	0.38	0.02
H4	2.58	12.31	72.89	11.28	25.26	0.00	0.59	24.45	1.20	18.43	1.30	74.74	0.44	0.03
H5	7.52	14.01	59.81	17.46	41.03	0.00	0.65	21.93	1.12	16.90	2.06	58.81	0.42	0.03

Table 6.5 Summary of soil and land use characteristics that were related to water quality parameters collected in baseflow and stormflow.

Sampling Location	Date Sampled	No. of samples taken	TPC %	DRP ug L^{-1}	TON mg L^{-1}	SS mg L^{-1}	DOC mg L^{-1}
A8	23/09/2010	24	1		1	1	
	01/10/2010	24	1	1	1	1	
	29/10/2010	2		1	1	1	
	05/11/2010	24		1	1		
	08/11/2010	22	1	1	1	1	
	17/11/2010	1		1	1	1	
	07/01/2011	24	1	1	1	1	
	10/01/2011	23	1			1	1
	12/01/2011	24	1	1	1	1	1
	08/05/2011	2				1	
	12/06/2011	24	1	1	1	1	
	18/06/2011	14	1			1	
	06/09/2011	15	1	1	1	1	1
	18/09/2011	20	1			1	1
	24/10/2011	9	1		1	1	1
	11/11/2011	8				1	1
	08/12/2011	5		1	1	1	1
	12/12/2011	19		1	1	1	1
	23/12/2011	4				1	
	03/01/2012	2		1	1	1	
	21/11/2012	18		1	1	1	
Total	**21**	**308**	**11**	**13**	**15**	**20**	**8**
H5	08/06/2010	2			1		
	04/07/2010	5			1		
	14/07/2010	3			1	1	
	17/07/2010	13			1	1	
	18/07/2010	5				1	
	20/07/2010	6				1	
	26/08/2010	5		1	1	1	
	14/09/2010	23		1	1	1	
	23/09/2010	24	1		1	1	
	01/10/2010	24	1	1	1	1	
	29/10/2010	1		1	1	1	
	05/11/2010	24		1	1	1	1
	08/11/2010	24		1	1	1	1
	17/11/2010	6		1	1	1	
	07/01/2011	24	1	1	1	1	1
	11/01/2011	6	1			1	1
	12/01/2011	24	1	1	1	1	1
	08/05/2011	5	1			1	
	12/06/2011	24	1	1	1	1	
	18/06/2011	14	1	1			
	22/07/2011	12				1	
	26/08/2011	10	1	1	1	1	1

Sampling Location	Date Sampled	No. of samples taken	TPC %	DRP ug L^{-1}	TON mg L^{-1}	SS mg L^{-1}	DOC mg L^{-1}
	06/09/2011	9	1	1	1	1	1
	18/09/2011	24				1	1
	20/09/2011	3				1	
	24/10/2011	13	1		1	1	1
	27/10/2011	1	1		1	1	1
	11/11/2011	4				1	1
	07/12/2011	12			1	1	
	08/12/2011	5		1	1	1	1
	12/12/2011	18		1	1	1	1
	03/01/2012	24		1	1	1	1
	09/04/2012	17		1	1	1	1
	07/07/2012	2				1	
	11/07/2012	7				1	
	22/11/2012	24		1	1	1	1
	22/12/2012	15		1	1	1	1
	26/01/2013	14				1	
	29/01/2013	18				1	
Total	**39**	**494**	**27**	**19**	**26**	**36**	**17**
A7	15/07/2010	15			1	1	
	17/07/2010	22			1	1	
	21/08/2010	13	1	1	1	1	
	23/08/2010	24		1	1	1	
	25/08/2010	24	1	1	1	1	
	26/08/2010	24		1	1	1	
	06/09/2010	24		1	1	1	
	23/09/2010	10		1	1	1	
	01/10/2010	24	1	1	1	1	
	06/11/2010	24		1	1	1	1
	08/11/2010	24		1	1	1	1
	17/11/2010	24		1	1	1	
	07/01/2011	24	1	1	1	1	1
	10/01/2011	24	1	1	1	1	1
	13/01/2011	24	1	1	1	1	1
	07/05/2011	6	1		1	1	
	12/06/2011	24	1	1	1	1	
	18/06/2011	8	1			1	
	26/08/2011	24	1	1	1	1	1
	18/09/2011	3	1			1	1
	24/10/2011	8	1		1	1	1
	27/10/2011	4	1		1	1	1
	04/11/2011	10				1	1
	11/11/2011	14				1	1
	02/12/2011	6				1	
	04/12/2011	4				1	
	06/12/2011	14		1	1	1	
	07/12/2011	24		1	1	1	

Sampling Location	Date Sampled	No. of samples taken	TPC %	DRP ug L^{-1}	TON mg L^{-1}	SS mg L^{-1}	DOC mg L^{-1}
	08/12/2011	16		1	1	1	1
	11/12/2011	8		1	1	1	1
	03/01/2012	24		1	1	1	1
	24/09/2012	8				1	
	05/10/2012	13				1	
	22/11/2012	19		1	1	1	1
Total	**34**	**561**	**13**	**21**	**26**	**34**	**15**
A11	16/07/2010	7				1	
	10/08/2010	4	1	1	1	1	
	21/08/2010	5	1	1	1	1	
	25/08/2010	24	1	1	1	1	
	26/08/2010	24		1	1	1	
	06/09/2010	3		1	1	1	
	14/09/2010	6		1	1	1	
	23/09/2010	11	1	1	1	1	
	01/10/2010	12		1	1	1	
	03/10/2010	12	1	1	1	1	
	29/10/2010	2		1	1		
	05/11/2010	24		1	1	1	
	08/11/2010	24		1	1	1	
	17/11/2010	20		1	1	1	
	07/01/2011	24	1	1	1	1	1
	27/12/2010	4	1			1	
	10/01/2011	22	1	1	1	1	1
	13/01/2011	24	1	1	1	1	1
	17/01/2011	22	1	1	1	1	1
	13/02/2011	5	1	1	1	1	1
	15/02/2011	12	1	1	1	1	1
	25/02/2011	7	1			1	
	19/02/2011	3	1			1	
	21/04/2011	24	1			1	
	07/05/2011	24	1			1	
	21/05/2011	24	1			1	
	04/11/2011	8				1	1
	11/11/2011	12				1	1
Total	**28**	**393**	**17**	**19**	**19**	**27**	**8**
A12	21/08/2010	6	1	1	1	1	
	23/08/2010	10	1	1	1	1	
	25/08/2010	20	1	1	1	1	
	06/09/2010	3	1	1	1	1	
	23/09/2010	6	1	1	1	1	
	01/10/2010	12	1	1	1	1	
	03/10/2010	12	1	1	1	1	
	06/11/2010	22	1	1	1	1	
	08/11/2010	24	1	1	1	1	
	06/05/2011	3	1			1	

Sampling Location	Date Sampled	No. of samples taken	TPC %	DRP ug L^{-1}	TON mg L^{-1}	SS mg L^{-1}	DOC mg L^{-1}
	12/06/2011	5	1		1	1	
	26/08/2011	21	1	1	1	1	1
	18/09/2011	6	1			1	1
	24/10/2011	24				1	1
	04/11/2011	4				1	1
	11/11/2011	13				1	1
	02/12/2011	12				1	
	04/12/2011	8				1	
	06/12/2011	4				1	
Total	**19**	**215**	**13**	**10**	**11**	**19**	**5**
Total	**141**	**1971**	**81**	**82**	**97**	**136**	**53**

Table 6.8 List of all events captured at the five stormflow monitoring sites with date, total number of events and total number of samples captured at each site. Number 1 denotes an event that was analysed for a given determinand.

Site		SS load (t)	DOC load (t)	TPC load (t)	TON load (t)	DRP load (kg)	SS yield (t km^2)	DOC yield (t km^{-2})	TPC yield (t km^{-2})	TON yield (t km^{-2})	DRP yield (kg km^{-2})
A10	Baseflow	-	-	-	-	-	-	-	-	-	-
	Stormflow	-	-	-	-	-	-	-	-	-	-
A11	Baseflow	78.89	8.28	-	15.59	-	23.27	2.44	-	4.60	-
	Stormflow	651.10	15.90	103.68	24.27	386.61	192.06	4.69	30.58	7.16	114.05
A12	Baseflow	76.19	8.44	-	24.61	-	5.98	0.66	-	1.93	-
	Stormflow	937.58	11.39	103.83	20.88	200.34	73.54	0.89	8.14	1.64	15.71
A13	Baseflow	-	-	-	-	-	-	-	-	-	-
	Stormflow	-	-	-	-	-	-	-	-	-	-
A7	Baseflow	108.29	10.81	-	28.37	-	7.40	0.74	-	1.94	-
	Stormflow	857.05	20.35	111.86	36.51	324.66	58.54	1.39	7.64	2.49	22.18
A8	Baseflow	517.19	92.26	-	173.33	-	13.32	2.38	-	4.46	-
	Stormflow	4178.73	182.77	602.91	159.09	364.11	107.64	4.71	15.53	4.1	9.38
A9	Baseflow	15.98	1.43	-	2.91	-	7.84	0.70	-	1.43	-
	Stormflow	-	-	-	-	-	-	-	-	-	-
H1	Baseflow	59.39	18.63	-	12.71	-	12.83	4.02	-	2.75	-
	Stormflow	-	-	-	-	-	-	-	-	-	-
H3	Baseflow	7.46	1.82	-	4.50	-	2.69	0.66	-	1.62	-
	Stormflow	-	-	-	-	-	-	-	-	-	-
H4	Baseflow	112.83	14.50	-	14.43	-	22.39	2.88	-	2.86	-
	Stormflow	-	-	-	-	-	-	-	-	-	-
H5	Baseflow	171.76	34.84	-	52.00	-	8.49	1.72	-	2.57	
	Stormflow	483.14	73.4	110.43	51.61	49.04	23.89	3.63	5.46	2.55	2.42

Table 6.9 Determinand loads and yields calculated for the baseline pre-restoration period between 29th July 2010 and 18th November 2011 for all sites using the Walling formula 5 (Walling and Webb, 1985) using just monthly baseflow samples (for all sites) and both baseflow and stormflow samples (stormflow monitoring sites) to give the best available estimate. Only stormflow data was available for TPC and DRP calculations. Calculations of SS loads and yields based on monthly baseflow data alone show proportionally greatest underestimation, as compared to stormflow estimates.

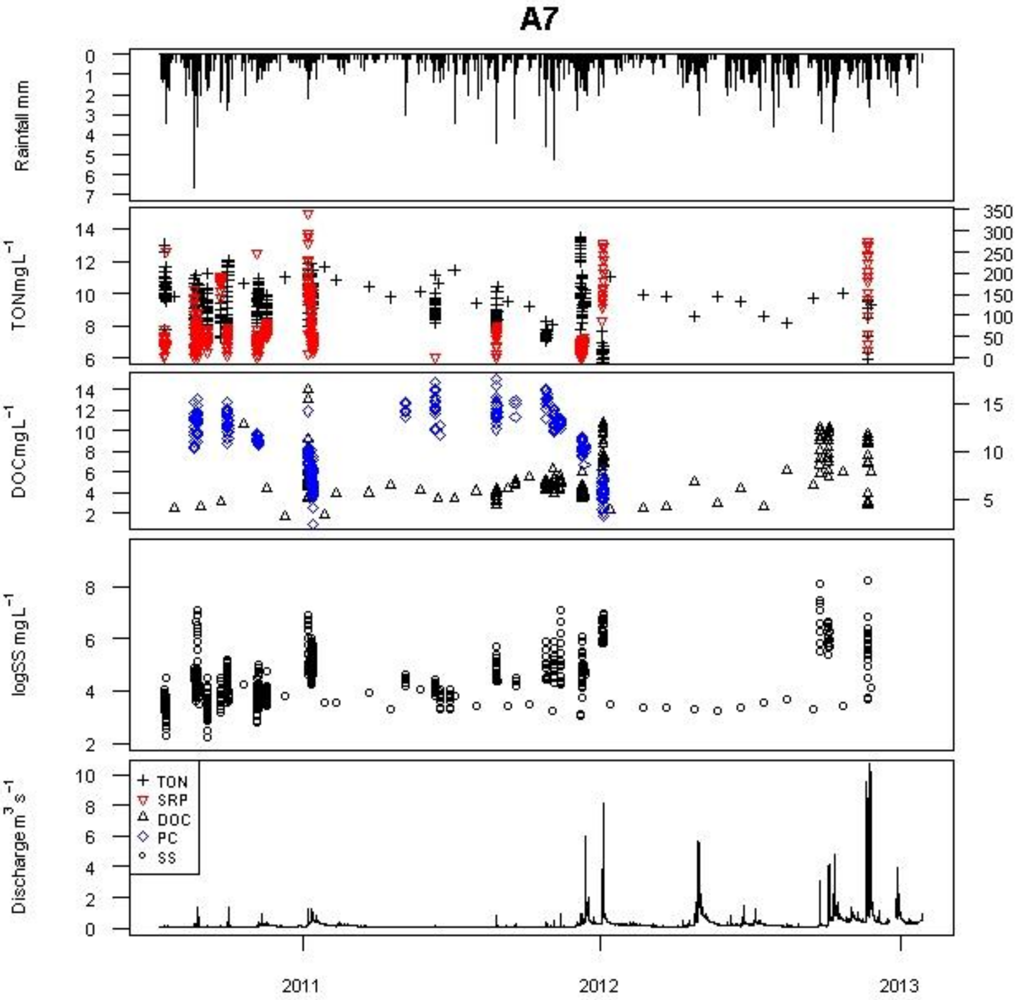


Fig. 6.9 Chemograph showing all monthly and stormflow monitoring data collected at A7 between 10th July 2010 and 28th January 2013.

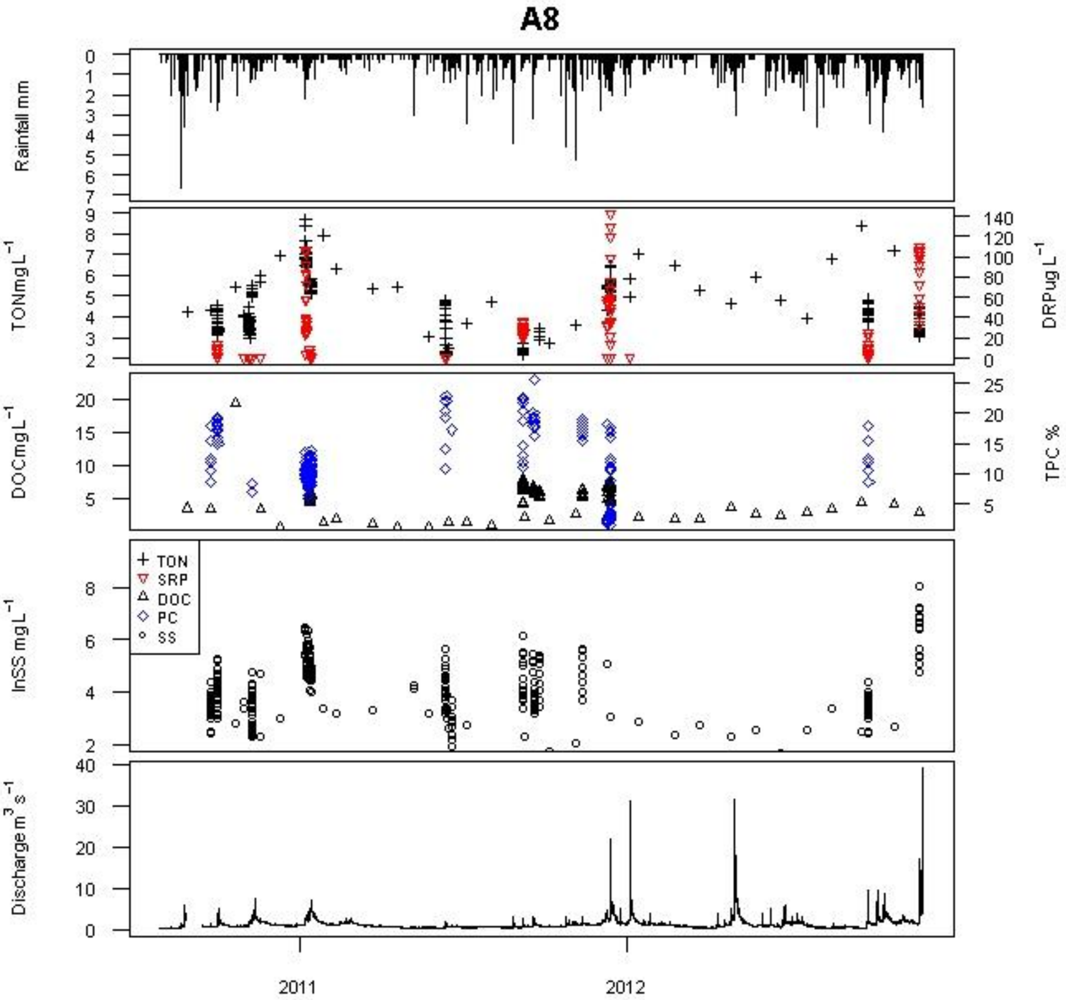


Fig. 6.10 Chemograph showing all monthly and stormflow monitoring data collected at A8 between 28th July 2010 and 25th November 2012.

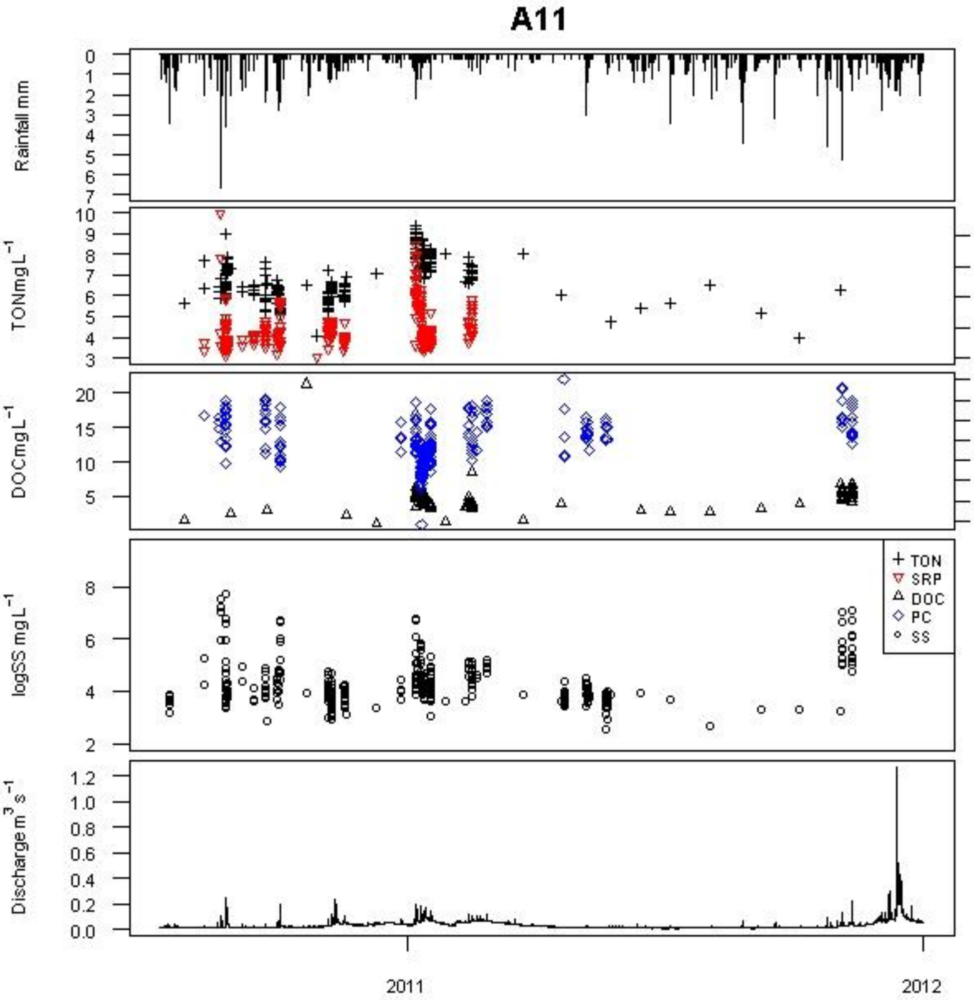


Fig. 6.11 Chemograph showing all monthly and stormflow monitoring data collected at A11 between 10th July 2010 and 31st December 2011.

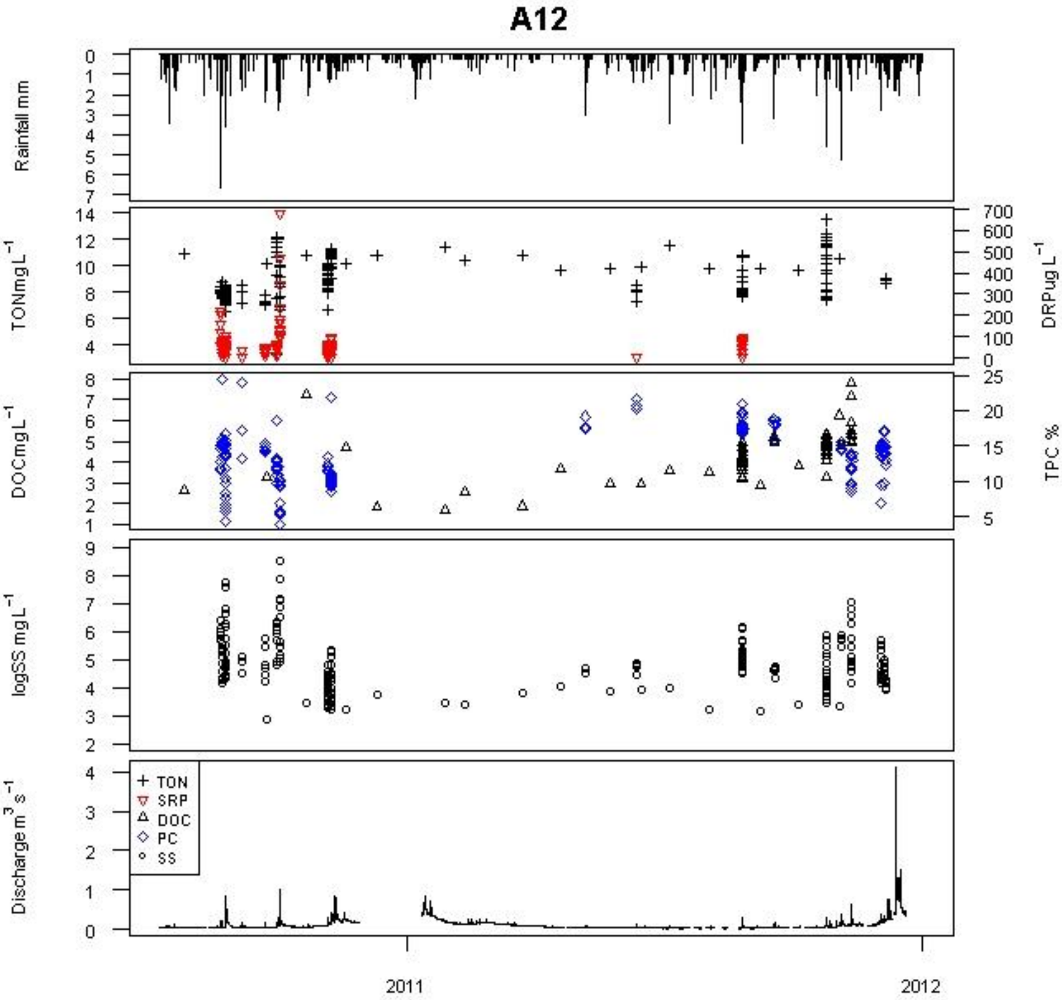


Fig. 6.12 Chemograph showing all monthly and stormflow monitoring data collected at A12 between 10th July 2010 and 31st December 2011.

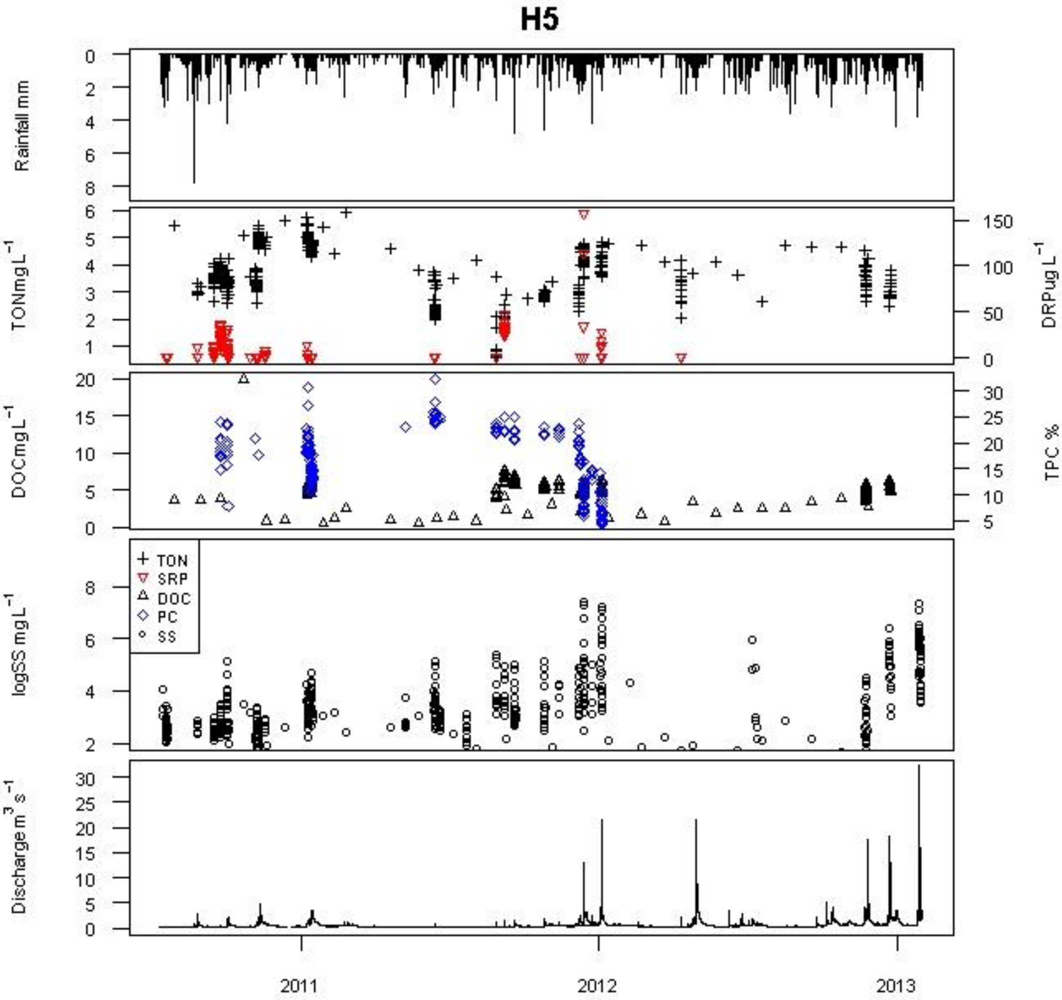
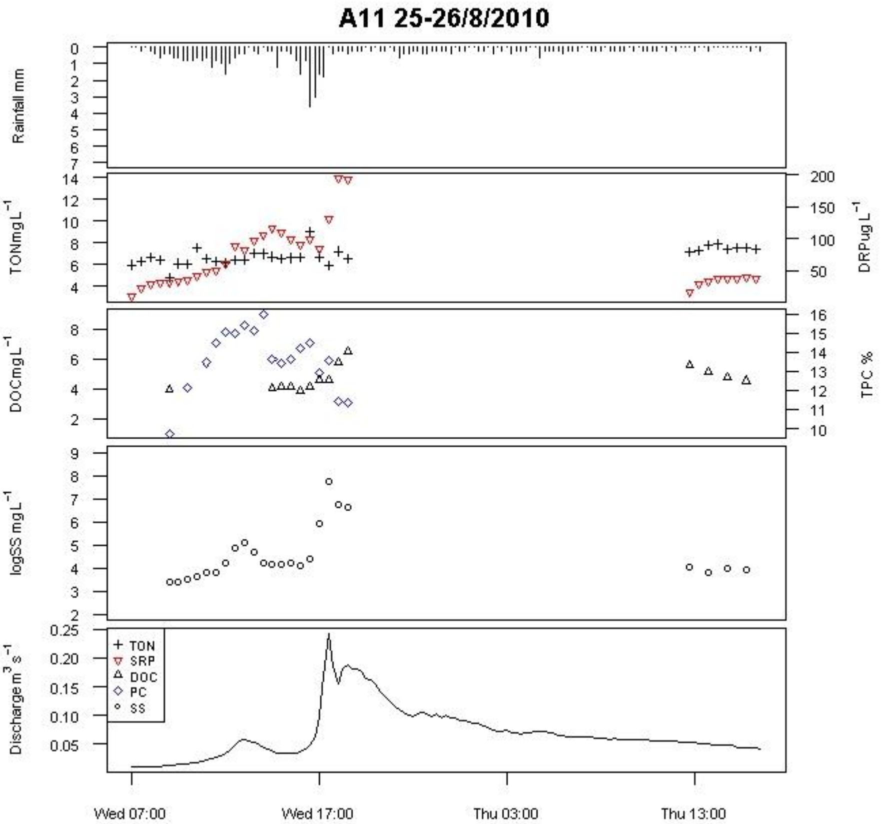
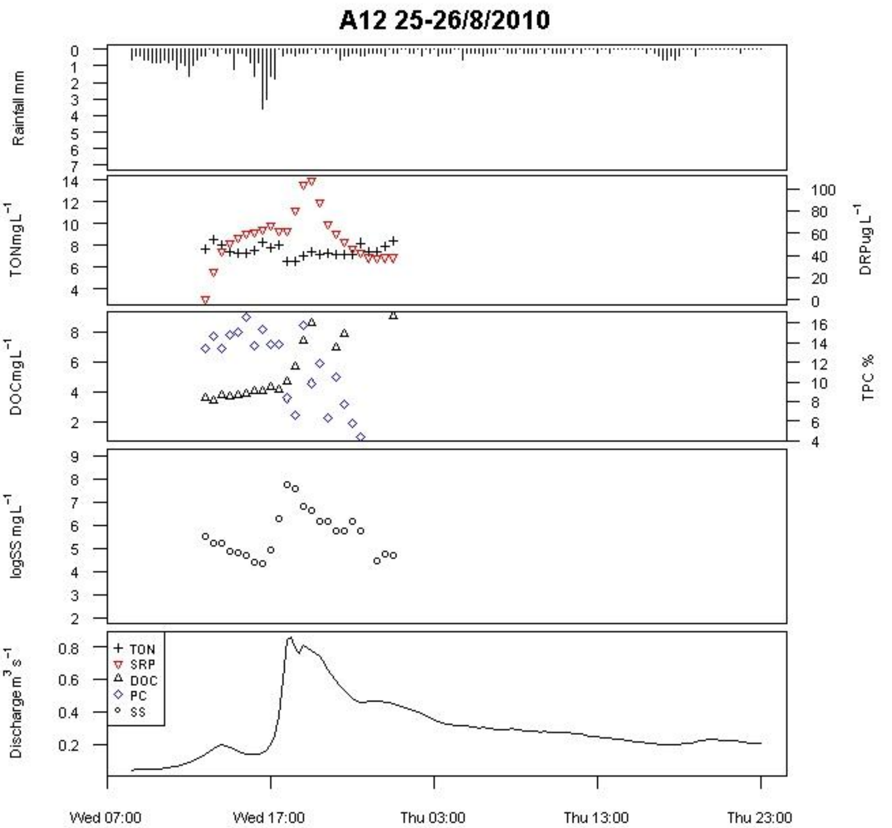


Fig. 6.13 Chemographs showing all monthly and stormflow monitoring data collected at H5 between 10th July 2010 and 31st January 2013.


A11 25-26/8/2010
Rainfall mm
TONmg L^{-1}
DRPug L^{-1}
DOCmg L^{-1}
TPC %
logSS mg L^{-1}
Discharge m^3 s^{-1}
TON
SRP
DOC
PC
SS
Wed 07:00
Wed 17:00
Thu 03:00
Thu 13:00


A12 25-26/8/2010
Rainfall mm
TONmg L^{-1}
DRPug L^{-1}
DOCmg L^{-1}
TPC %
logSS mg L^{-1}
Discharge m^3 s^{-1}
TON
SRP
DOC
PC
SS
Wed 07:00
Wed 17:00
Thu 03:00
Thu 13:00
Thu 23:00

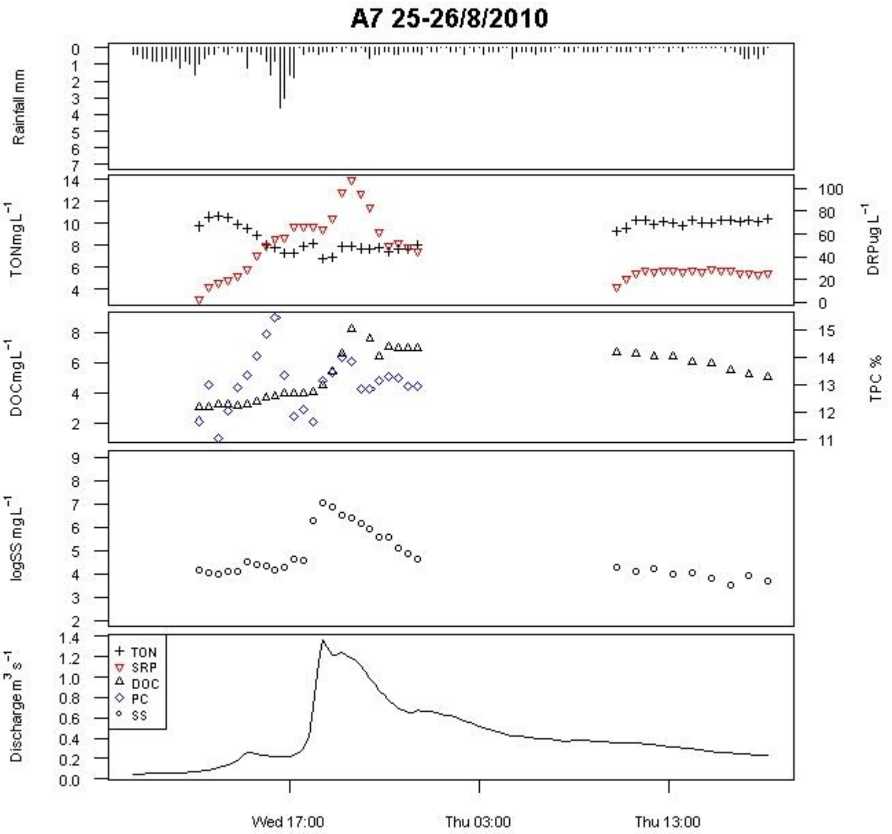
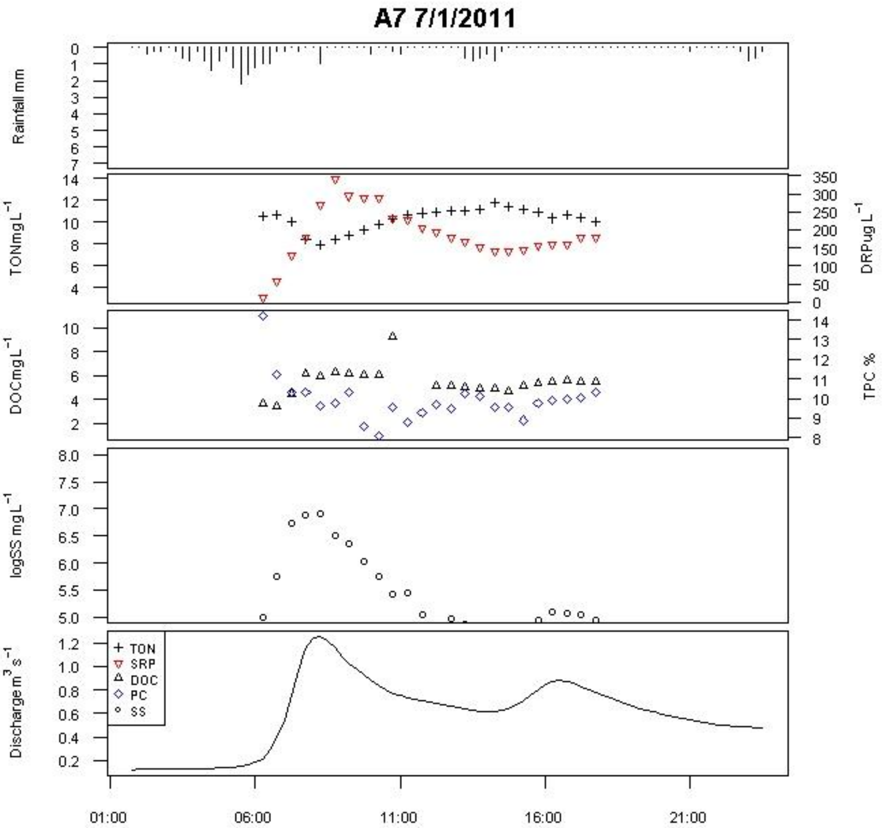


Fig. 6.18 Chemographs of a medium size event captured simultaneously at three monitoring sites in the Aller catchment show a clockwise hysteresis for TON and PC, anti-clockwise hysteresist for DOC and DRP and flat hysteresis for SS at the catchment outlet. At A11 and A12 DRP exhibits a slightly delayed anti-clockwise hysteresis.


A7 7/1/2011
Rainfall mm
TONmg L^{-1}
DRPug L^{-1}
DOCmg L^{-1}
TPC %
logSS mg L^{-1}
Discharge m^3 s^{-1}
TON
SRP
DOC
PC
SS
01:00
06:00
11:00
16:00
21:00

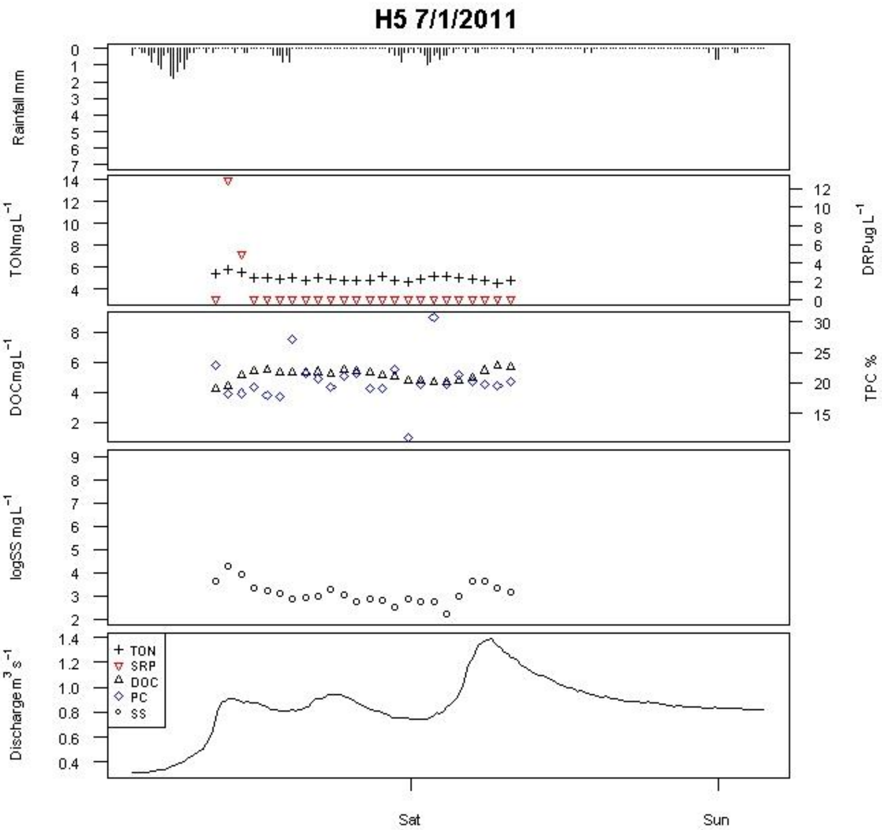
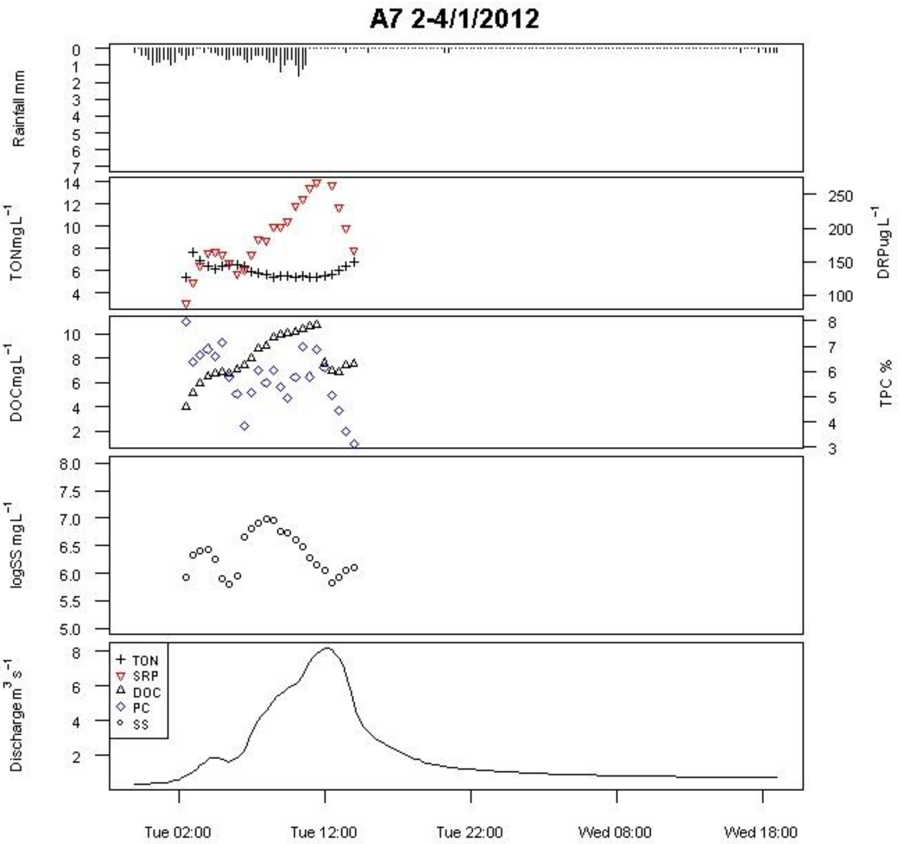

H5 7/1/2011
Rainfall mm
TONmg L^{-1}
DRPug L^{-1}
DOCmg L^{-1}
TPC %
logSS mg L^{-1}
Discharge m^3 s^{-1}
TON
SRP
DOC
PC
SS
Sat
Sun

Fig. 6.19 Chemographs of a medium size event recorded simultaneously at both catchment outlets (A7 1:45 am – 23:30 pm and H5 2:15 am – 9th January 2011 3:30 pm) illustrate the limited response of most water quality determinands to discharge in the Horner Water catchment, with only SS concentrations displaying flat hysteresis and DRP concentrations clock-wise hysteresis. The Aller catchment responds in a consistent manner as described in Fig. 6.14.


A7 2-4/1/2012
Rainfall mm
TONmg L^{-1}
DRPug L^{-1}
DOCmg L^{-1}
TPC %
logSS mg L^{-1}
Discharge m^3 s^{-1}
TON
SRP
DOC
PC
SS
Tue 02:00
Tue 12:00
Tue 22:00
Wed 08:00
Wed 18:00

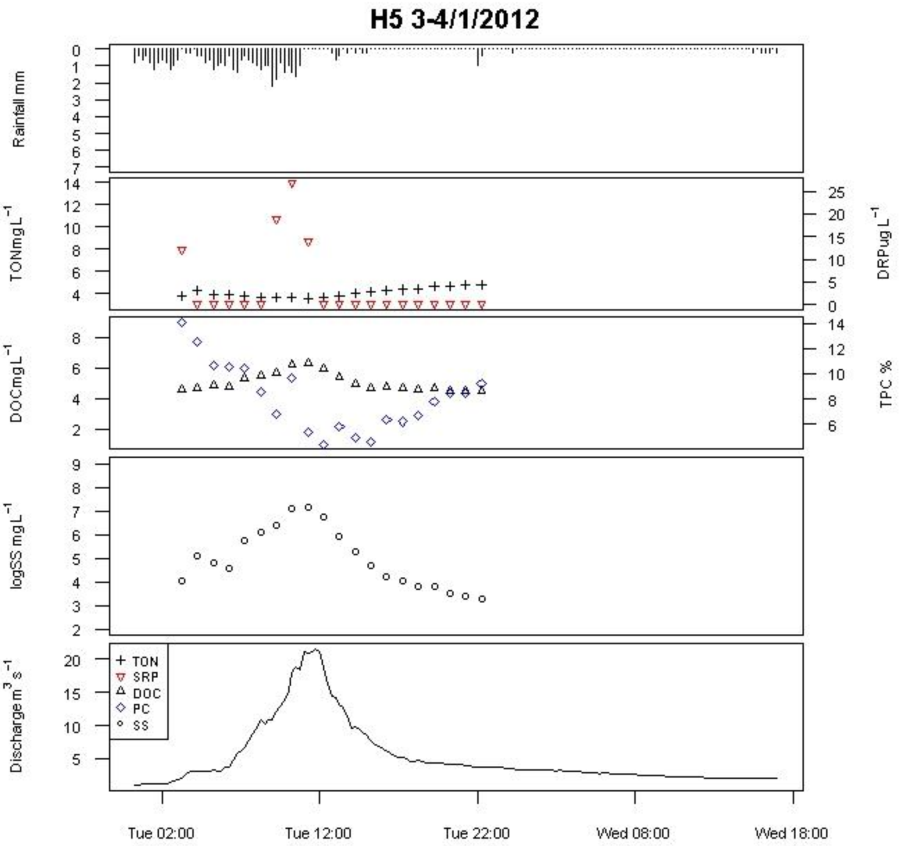

H5 3-4/1/2012
Rainfall mm
TONmg L^{-1}
DRPug L^{-1}
DOCmg L^{-1}
TPC %
logSS mg L^{-1}
Discharge m^3 s^{-1}
TON
SRP
DOC
PC
SS
Tue 02:00
Tue 12:00
Tue 22:00
Wed 08:00
Wed 18:00

Fig. 6.20 Chemographs of an extremely large event recorded simultaneously at both catchment outlets (A7 2nd January 2012 23:00 pm – 4/1/2012 19:00 pm and H5 3/1/2012 0:15 am – 4th January 2012 17:00 pm) shows a clockwise hysteresis for PC and flat hysteresis for DOC in both study catchments. DRP exhibited a clockwise hysteresis in the Horner catchment while SS showed a clockwise hysteresis in the Aller catchment. TON shows a typical dilution effect.

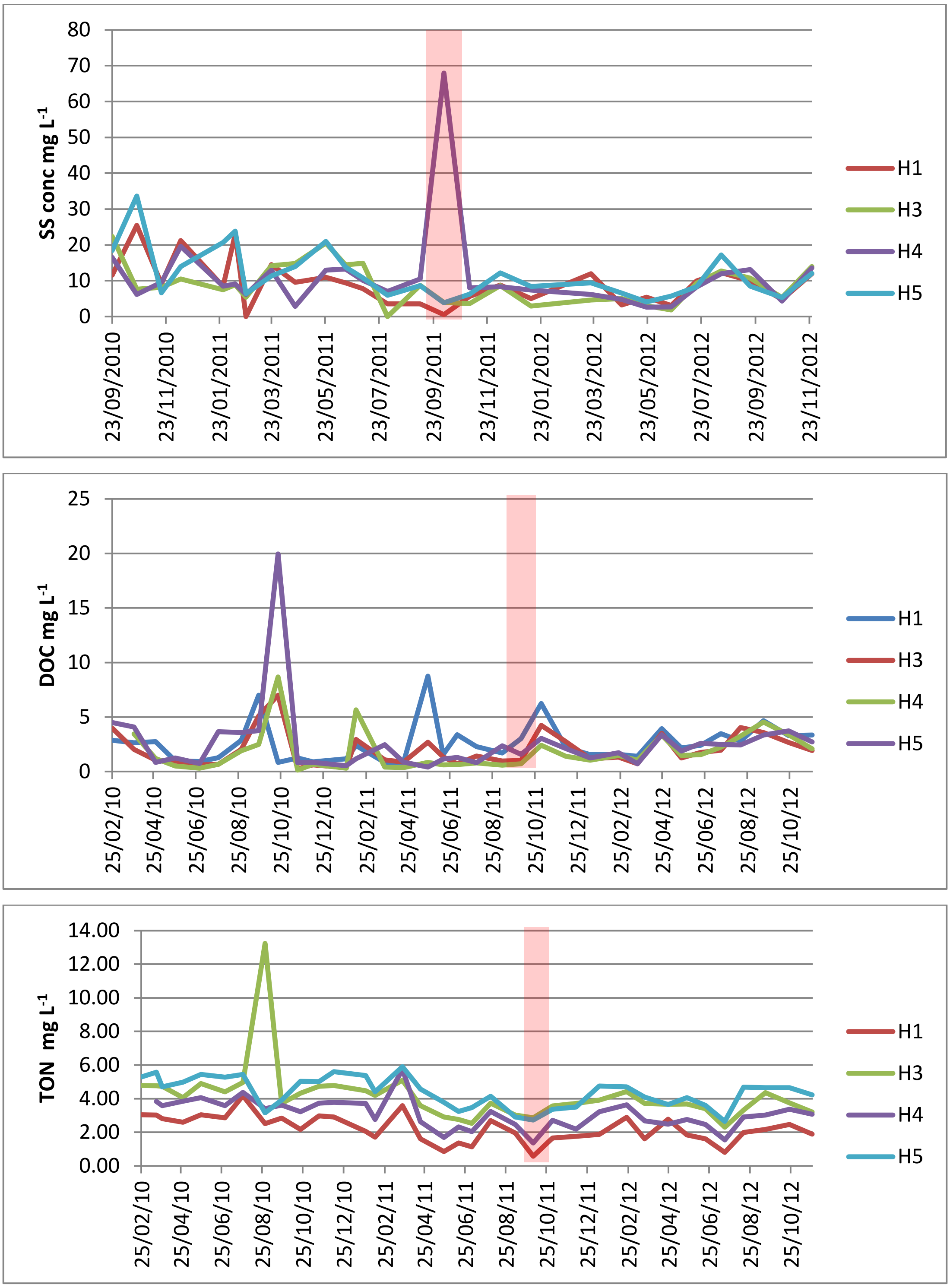


Fig. 6.22 Time series plots of water quality determinands pre- and post- habitat restoration in the Horner Water catchment. The pink rectangle marks the period of restoration works.

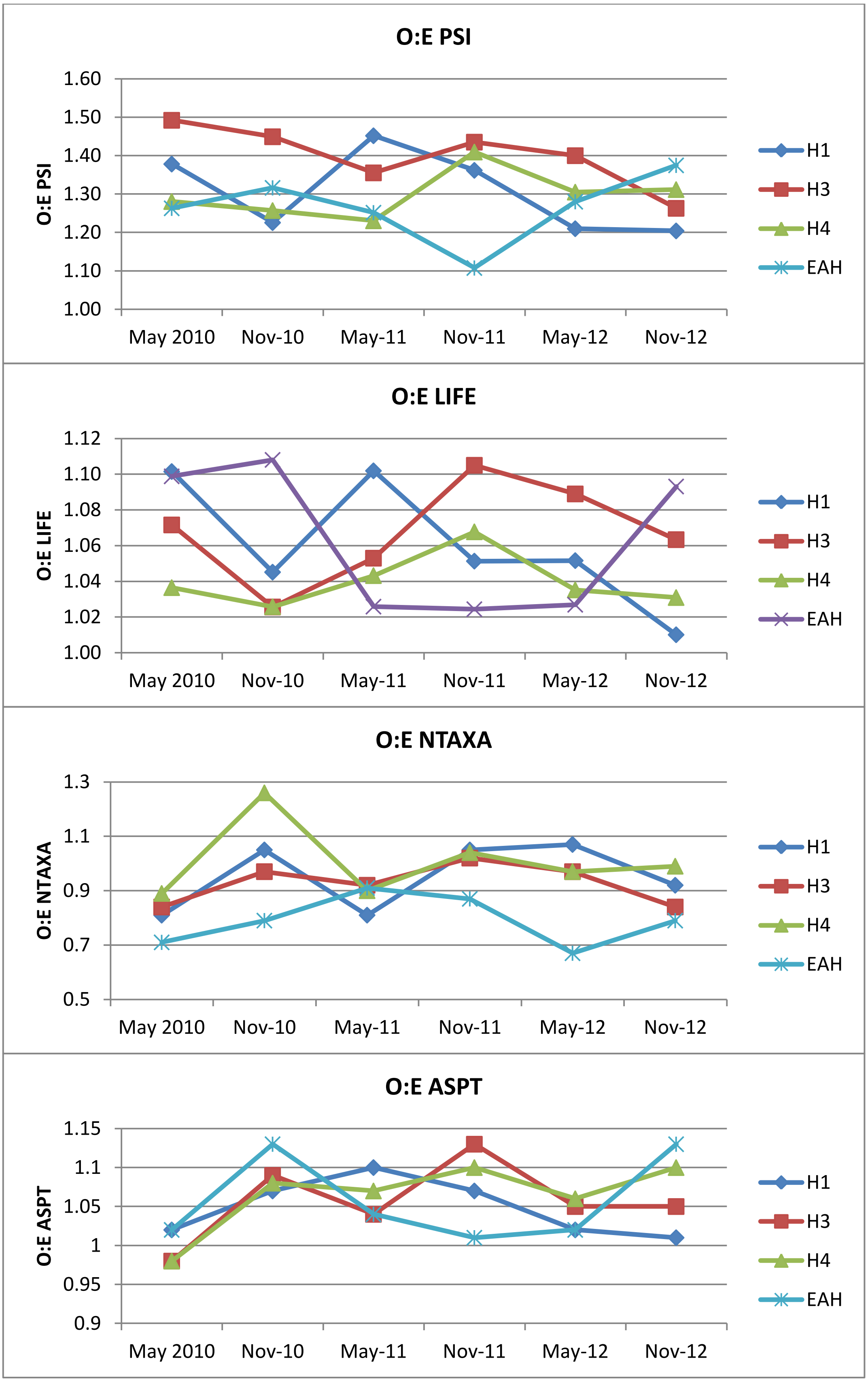


Fig. 6.25 Time series plots of invertebrate indexes pre- and post- habitat restoration in the Horner catchment. Pre-restoration: May 2010-May 2011, post-restoration November 2011-November 2012.

References

AITKENHEAD, J. A., HOPE, D. & BILLETT, M. F. (1999) The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales. *Hydrological Processes,* 13**,** 1289-1302.

AITKENHEAD, J. A. & MCDOWELL, W. H. (2000) Soil C : N ratio as a predictor of annual riverine DOC flux at local and global scales. *Global Biogeochemical Cycles,* 14**,** 127-138.

ÁLVAREZ-CABRIA, M., BARQUÍN, J. & ANTONIO JUANES, J. (2010) Spatial and seasonal variability of macroinvertebrate metrics: Do macroinvertebrate communities track river health? *Ecological Indicators,* 10**,** 370-379.

ANDERSON, K. & KUHN, N. J. (2008) Variations in soil structure and reflectance during a controlled crusting experiment. *International Journal of Remote Sensing,* 29**,** 3457-3475.

ANGRADI, T. R. (1999) Fine sediment and macroinvertebrate assemblages in Appalachian streams: a field experiment with biomonitoring applications. *Journal of the North American Benthological Society,* 18**,** 49-66.

ARMITAGE, P. D., MOSS, D., WRIGHT, J. F. & FURSE, M. T. (1983) The performance of a new biological water-quality score system based on macroinvertebrates over a wide-range of unpolluted running-water sites. *Water Research,* 17**,** 333-347.

ARMSTRONG, A., HOLDEN, J., KAY, P., FRANCIS, B., FOULGER, M., GLEDHILL, S., MCDONALD, A. T. & WALKER, A. (2010) The impact of peatland drain-blocking on dissolved organic carbon loss and discolouration of water; results from a national survey. *Journal of Hydrology,* 381**,** 112-120.

ASSELMAN, N. E. M. (1999) Suspended sediment dynamics in a large drainage basin: the River Rhine. *Hydrological Processes,* 13**,** 1437-1450.

AVERY, B. W. (1980) *Soil classification for England and Wales (higher categories)*, Soil Survey, Harpenden, UK.

BALANA, B. B., VINTEN, A. & SLEE, B. (2011) A review on cost-effectiveness analysis of agri-environmental measures related to the EU WFD: Key issues, methods, and applications. *Ecological Economics,* 70**,** 1021-1031.

BATEY, T. & MCKENZIE, D. (2006) Soil compaction: identification directly in the field. *Soil Use and Management,* 22**,** 123-131.

BATTIN, T. J., KAPLAN, L. A., FINDLAY, S., HOPKINSON, C. S., MARTI, E., PACKMAN, A. I., NEWBOLD, J. D. & SABATER, F. (2008) Biophysical controls on organic carbon fluxes in fluvial networks. *Nature Geoscience,* 1**,** 95-100.

BELL, M. J., WORRALL, F., SMITH, P., BHOGAL, A., BLACK, H., LILLY, A., BARRACLOUGH, D. & MERRINGTON, G. (2011) UK land-use change and its impact on SOC: 1925-2007. *Global Biogeochemical Cycles,* 25.

BERGFUR, J., DEMARS, B. O. L., STUTTER, M. I., LANGAN, S. J. & FRIBERG, N. (2012) The Tarland Catchment Initiative and Its Effect on Stream Water Quality and Macroinvertebrate Indices. *J. Environ. Qual.,* 41**,** 314-321.

BILLETT, M. F., CHARMAN, D. J., CLARK, J. M., EVANS, C. D., EVANS, M. G., OSTLE, N. J., WORRALL, F., BURDEN, A., DINSMORE, K. J., JONES, T., MCNAMARA, N. P., PARRY, L., ROWSON, J. G. & ROSE,

R. (2012) Carbon balance of UK peatlands: current state of knowledge and future research challenges. *Climate Research,* 45**,** 13-29.

BILOTTA, G. S. (2008) The mobilisation and transport of sediments, colloids and phosphorus from improved temperate grasslands. Unpublished PhD Thesis, pp. 340. *Geography.* University of Exeter, Exeter.

BILOTTA, G. S. & BRAZIER, R. E. (2008) Understanding the influence of suspended solids on water quality and aquatic biota. *Water Research,* 42**,** 2849-2861.

BILOTTA, G. S., BRAZIER, R. E. & HAYGARTH, P. M. (2007) The Impact of Grazing Animals on the Quality of Soils, Vegetation, and Surface Waters in Intensively Managed Grasslands. *Advances in Agronomy,* 94**,** 237-280.

BILOTTA, G. S., BRAZIER, R. E., HAYGARTH, P. M., MACLEOD, C. J. A., BUTLER, P. & GRANGER, S. (2008) Rethinking the Contribution of Drained and Undrained Grasslands to Sediment-Related Water Quality Problems. *Journal of Environmental Quality,* 37**,** 906-914.

BILOTTA, G. S., BURNSIDE, N. G., CHEEK, L., DUNBAR, M. J., GROVE, M. K., HARRISON, C., JOYCE, C., PEACOCK, C. & DAVY-BOWKER, J. (2012) Developing environment-specific water quality guidelines for suspended particulate matter. *Water Research,* 46**,** 2324-2332.

BILOTTA, G. S., KRUEGER, T., BRAZIER, R. E., BUTLER, P., FREER, J., HAWKINS, J. M. B., HAYGARTH, P. M., MACLEOD, C. J. A. & QUINTON, J. N. (2010) Assessing catchment-scale erosion and yields of suspended solids from improved temperate grassland. *Journal of Environmental Monitoring,* 12, 731-739.

BLACKWELL, M. S. A. & PILGRIM, E. S. (2011) Ecosystem services delivered by small-scale wetlands. *Hydrological Sciences Journal-Journal Des Sciences Hydrologiques,* 56**,** 1467-1484.

BOERNER, R. E. J., SCHERZER, A. J. & BRINKMAN, J. A. (1998) Spatial patterns of inorganic N, P availability, and organic C in relation to soil disturbance: a chronosequence analysis. *Applied Soil Ecology,* 7**,** 159-177.

BOL, R., OSTLE, N. J., PETZKE, K. J., CHENU, C. & BALESDENT, J. (2008) Amino acid (15)N in long-term bare fallow soils: influence of annual N fertilizer and manure applications. *European Journal of Soil Science,* 59**,** 617-629.

BONADA, N., PRAT, N., RESH, V. H. & STATZNER, B. (2006) Developments in aquatic insect biomonitoring: A comparative analysis of recent approaches. *Annual Review of Entomology*, 51, 495-523.

BOORMAN, D. B., HOLLIS, J. M. & LILLY, A. (1995) *Hydrology of soil types: a hydrologically-based classification of the soils of the United Kingdom*, Institute of Hydrology, Wallingford, pp. 137.

BOWES, M. J., HOUSE, W. A., HODGKINSON, R. A. & LEACH, D. V. (2005) Phosphorus-discharge hysteresis during storm events along a river catchment: the River Swale, UK. *Water Research,* 39**,** 751-762.

BRACKEN, L. J. & CROKE, J. (2007) The concept of hydrological connectivity and its contribution to understanding runoff-dominated geomorphic systems. *Hydrological Processes,* 21**,** 1749-1763.

BRADFORD, M. A., FIERER, N. & REYNOLDS, J. F. (2008) Soil carbon stocks in experimental mesocosms are dependent on the rate of labile carbon, nitrogen and phosphorus inputs to soils. *Functional Ecology,* 22**,** 964-974.

BRADY, N. C. & WEIL, R. R. (1999) *The Nature and Properties of Soils*, Pentice Hall, Upper Saddle River, New Jersey, pp. 881.
BRAZIER, R. E. (2004) Quantifying soil erosion by water in the UK: a review of monitoring and modelling approaches. *Progress in Physical Geography,* 28**,** 340-365.
BRAZIER, R. E., BILOTTA, G. S. & HAYGARTH, P. M. (2007) A perspective on the role of lowland, agricultural grasslands in contributing to erosion and water quality problems in the UK. *Earth Surface Processes and Landforms*, 32, 964-967.
BRULAND, G. L., GRUNWALD, S., OSBORNE, T. Z., REDDY, K. R. & NEWMAN, S. (2006) Spatial distribution of soil properties in Water Conservation Area 3 of the Everglades. *Soil Science Society of America Journal,* 70**,** 1662-1676.
BRYCE, S. A., LOMNICKY, G. A. & KAUFMANN, P. R. (2010) Protecting sediment-sensitive aquatic species in mountain streams through the application of biologically based streambed sediment criteria. *Journal of the North American Benthological Society,* 29**,** 657-672.
BRYMAN, A. & CRAMER, D. (2011) *Quantitative Data Analysis with IBM SPSS 17, 18 & 19*, Routledge, pp. 377.
BUCKINGHAM, S., TIPPING, E. & HAMILTON-TAYLOR, J. (2008) Concentrations and fluxes of dissolved organic carbon in UK topsoils. *Science of the Total Environment,* 407**,** 460-470.
BUCKLEY, C. (2012) Implementation of the EU Nitrates Directive in the Republic of Ireland - A view from the farm. *Ecological Economics,* 78**,** 29-36.
BUCKLEY, C. & CARNEY, P. (2013) The potential to reduce the risk of diffuse pollution from agriculture while improving economic performance at farm level. *Environmental Science & Policy,* 25**,** 118-126.
BUCKLEY, C., HYNES, S. & MECHAN, S. (2012) Supply of an ecosystem service-Farmers' willingness to adopt riparian buffer zones in agricultural catchments. *Environmental Science & Policy,* 24**,** 101-109.
BURT, T. P. (2006) Linking hydrology and biogeochemistry in complex landscapes: implications for diffuse nitrate pollution. *BHS 9th National Hydrology Symposium.* Durham, British Hydrological Society, pp. 15-20.
BURT, T. P. & PINAY, G. (2005) Linking hydrology and biogeochemistry in complex landscapes. *Progress in Physical Geography,* 29**,** 297-316.
BUTTNER, O. & TITTEL, J. (2013) Uncertainties in dissolved organic carbon estimation in a small stream. *Journal of Hydrology and Hydromechanics,* 61**,** 81-83.
CAMBARDELLA, C. A., MOORMAN, T. B., NOVAK, J. M., PARKIN, T. B., KARLEN, D. L., TURCO, R. F. & KONOPKA, A. E. (1994) Field-Scale Variability of Soil Properties in Central Iowa Soils. *Soil Science Society of America Journal,* 58**,** 1501-1511.
CARDENAS, L. M., CUTTLE, S. P., CRABTREE, B., HOPKINS, A., SHEPHERD, A., SCHOLEFIELD, D. & DEL PRADO, A. (2011) Cost effectiveness of nitrate leaching mitigation measures for grassland livestock systems at locations in England and Wales. *Science of the Total Environment,* 409**,** 1104-1115.
CAREY, P. D., SHORT, C., MORRIS, C., HUNT, J., PRISCOTT, A., DAVIS, M., FINCH, C., CURRY, N., LITTLE, W., WINTER, M., PARKIN, A. & FIRBANK, L. G. (2003) The multi-disciplinary evaluation of a national

agri-environment scheme. *Journal of Environmental Management,* 69**,** 71-91.

CASSIDY, R. & JORDAN, P. (2011) Limitations of instantaneous water quality sampling in surface-water catchments: Comparison with near-continuous phosphorus time-series data. *Journal of Hydrology,* 405**,** 182-193.

CHADD, R. & EXTENCE, C. (2004) The conservation of freshwater macroin vertebrate populations: a community-based classification scheme. *Aquatic Conservation-Marine and Freshwater Ecosystems,* 14**,** 597-624.

CHANTIGNY, M. H. (2003) Dissolved and water-extractable organic matter in soils: a review on the influence of land use and management practices. *Geoderma,* 113**,** 357-380.

CHERRY, K. A., SHEPHERD, M., WITHERS, P. J. A. & MOONEY, S. J. (2008) Assessing the effectiveness of actions to mitigate nutrient loss from agriculture: A review of methods. *Science of the Total Environment,* 406**,** 1-23.

CLARK, J. M., LANE, S. N., CHAPMAN, P. J. & ADAMSON, J. K. (2007) Export of dissolved organic carbon from an upland peatland during storm events: Implications for flux estimates. *Journal of Hydrology,* 347**,** 438-447.

CLARKE, R., DAVY-BOWKER, J., DUNBAR, M. J., LAIZE, C., SCARLETT, P. & MURPHY, J. (2011) Enhancement of the River Invertebrate Classification Tool. SNIFFER, Edinburgh, UK, pp. 83.

CLAY, G. D., WORRALL, F. & FRASER, E. D. G. (2009) Effects of managed burning upon dissolved organic carbon (DOC) in soil water and runoff water following a managed burn of a UK blanket bog. *Journal of Hydrology,* 367**,** 41-51.

CLEWS, E. & ORMEROD, S. J. (2009) IMPROVING BIO-DIAGNOSTIC MONITORING USING SIMPLE COMBINATIONS OF STANDARD BIOTIC INDICES. *River Research and Applications,* 25**,** 348-361.

COLLINS, A. L. & ANTHONY, S. G. (2008) Assessing the likelihood of catchments across England and Wales meeting 'good ecological status' due to sediment contributions from agricultural sources. *Environmental Science & Policy,* 11**,** 163-170.

COLLINS, A. L. & MCGONIGLE, D. F. (2008) Monitoring and modelling diffuse pollution from agriculture for policy support: UK and European experience. *Environmental Science & Policy,* 11**,** 97-101.

COLLINS, A. L., NADEN, P. S., SEAR, D. A., JONES, J. I., FOSTER, I. D. L. & MORROW, K. (2011) Sediment targets for informing river catchment management: international experience and prospects. *Hydrological Processes,* 25**,** 2112-2129.

COOPER, D., NADEN, P., OLD, G. & LAIZE, C. (2008) Development of guideline sediment targets to support management of sediment inputs into aquatic systems. *Natural England Research Information Note.* www.naturalengland.org.uk, pp. 3. Last accessed on 24th July 2013.

CORRELL, D. L., JORDAN, T. E. & WELLER, D. E. (2001) Effects of precipitation, air temperature, and land use on organic carbon discharges from rhode river watersheds. *Water Air and Soil Pollution,* 128**,** 139-159.

CSF EVIDENCE TEAM, C. E. (2011) Catchment Sensitive Farming. ECSFI Phase I & 2 Full Evaluation Report. Environment Agency, Bristol, pp. 52.

CUTTLE, S. P., MACLEOD, C. J. A., CHADWICK, D. R., SCHOLEFIELD, D., HAYGARTH, P. M., NEWELL-PRICE, P., HARRIS, D., SHEPHERD, M. A., CHAMBERS, B. J. & HUMPHREY, R. (2007) An Inventory of

Methods to Control Diffuse Water Pollution from Agriculture (DWPA). *Prepared as part of Defra Project ES0203*, pp. 115.
CZERNIAWSKA-KUSZA, I. (2005) Comparing modified biological monitoring working party score system and several biological indices based on macroinvertebrates for water-quality assessment. *Limnologica,* 35**,** 169-176.
DALZELL, B. J., FILLEY, T. R. & HARBOR, J. M. (2007) The role of hydrology in annual organic carbon loads and terrestrial organic matter export from a midwestern agricultural watershed. *Geochimica Et Cosmochimica Acta,* 71**,** 1448-1462.
DALZELL, B. J., KING, J. Y., MULLA, D. J., FINLAY, J. C. & SANDS, G. R. (2011) Influence of subsurface drainage on quantity and quality of dissolved organic matter export from agricultural landscapes. *Journal of Geophysical Research-Biogeosciences,* 116.
DAVIES, O. L. (Ed.) (1967) *Statistical Methods in Research and Production with special reference to the chemical industry,* London and Endinburgh, Oliver and Boyd, pp. 383.
DAVY-BOWKER, J., CLARKE, R., CORBIN, T., VINCENT, H., PRETTY, J., HAWCZAK, A., BLACKBURN, J., MURPHY, J. & JONES, I. (2008) River Invertebrate Classification Tool. Final Report, Project WFD72C. SNIFER, Edinburgh, pp. 276.
DAVY-BOWKER, J., MURPHY, J. F., RUTT, G. R., STEEL, J. E. C. & FURSE, M. T. (2005) The development and testing of a macroinvertebrate biotic index for detecting the impact of acidity on streams. *Archiv Fur Hydrobiologie,* 163**,** 383-403.
DAWSON, J. J. C., ADHIKARI, Y. R., SOULSBY, C. & STUTTER, M. I. (2012) The biogeochemical reactivity of suspended particulate matter at nested sites in the Dee basin, NE Scotland. *Science of the Total Environment,* 434**,** 159-170.
DAWSON, J. J. C., BILLETT, M. F., NEAL, C. & HILL, S. (2002) A comparison of particulate, dissolved and gaseous carbon in two contrasting upland streams in the UK. *Journal of Hydrology,* 257**,** 226-246.
DAWSON, J. J. C. & SMITH, P. (2007) Carbon losses from soil and its consequences for land-use management. *Science of the Total Environment,* 382**,** 165-190.
DEASY, C. (2007) Effects of Scale on Phosphorus Transfer in Small Agricultural Catchments. Unpublished PhD Thesis, *Department of Geography.* University of Sheffield, pp. 369.
DEASY, C., BRAZIER, R. E., HEATHWAITE, A. L. & HODGKINSON, R. A. (2009) Pathways of runoff and sediment transfer in small agricultural catchments. *Hydrological Processes,* 23**,** 1349-1358.
DEASY, C., HEATHWAITE, A. L. & BRAZIER, R. E. (2008) A field methodology for quantifying phosphorus transfer and delivery to streams in first order agricultural catchments. *Journal of Hydrology,* 350**,** 329-338.
DEASY, C., QUINTON, J. N., SILGRAM, M., BAILEY, A. P., JACKSON, B. & STEVENS, C. J. (2010) Contributing understanding of mitigation options for phosphorus and sediment to a review of the efficacy of contemporary agricultural stewardship measures. *Agricultural Systems,* 103**,** 105-109.
DEFRA (2012) Catchment Based Approach. www.defra.gov.uk/environment/quality/water/legislation/catchment-approach. Last accessed on 22nd April 2013.

DOODY, D. G., FOY, R. H. & BARRY, C. D. (2012) Accounting for the role of uncertainty in declining water quality in an extensively farmed grassland catchment. *Environmental Science & Policy,* 24**,** 15-23.
DTC (2013) Demonstrating Catchment Management. Learning from the Demonstration Test Catchment projects. www.demonstratingcatchmentmanagement.net Last accessed on 24th July 2013.
DUNBAR, M. J., MURPHY, J., CLARKE, R., BAKER, R., DAVIES, C. & SCARLETT, P. (2010) Countryside Survey: Headwater Streams Report from 2007. *CS Technical Report No. 8/07.* Centre for Ecology and Hydrology, Wallingford, pp. 69.
DUNBAR, M. J., PEDERSEN, M. L., CADMAN, D., EXTENCE, C. A., WADDINGHAM, J., CHADD, R. P. & LARSEN, S. E. (2009a) River discharge and local-scale physical habitat influence macroinvertebrate LIFE scores. *Freshwater Biology,* 55**,** 226-242.
DUNBAR, M. J., WARREN, M., EXTENCE, C. A., BAKER, L., CADMAN, D., MOULD, D. J., HALL, J. & CHADD, R. P. (2009b) Interaction between macroinvertebrates, discharge and physical habitat in upland rivers. *Aquatic Conservation: Marine and Freshwater Ecosystems,* 20**,** S31-S44.
DUNGAIT, J. A. J., CARDENAS, L. M., BLACKWELL, M. S. A., WU, L., WITHERS, P. J. A., CHADWICK, D. R., BOL, R., MURRAY, P. J., MACDONALD, A. J., WHITMORE, A. P. & GOULDING, K. W. T. (2012) Advances in the understanding of nutrient dynamics and management in UK agriculture. *Science of the Total Environment,* 434**,** 39-50.
EKHOLM, P., TURTOLA, E., GRONGROOS, J., SEURI, P. & YLIVAINIO, K. (2005) Phosphorus loss from different farming systems estimated from soil surface phosphorus balance. *Agriculture, Ecosystems and Environment,* 110**,** 266-278.
ELLIS, M. M. (1936) Erosion silt as a factor in aquatic environments. *Ecology,* 17**,** 29-42.
ENVIRONMENT AGENCY (2009) Freshwater macro-invertebrate sampling in Rivers. *Operational instruction 018_08*, pp. 55.
ENVIRONMENT AGENCY (2012) Nitrate Vulnerable Zones. www.gov.uk/nitrate-vulnerable-zones. Last accessed on 22nd April 2013.
ENVIRONMENT AGENCY (2013) Aquifers. www.environment-agency.gov.uk/homeandleisure/117020.aspx. Last accessed on 24th July 2013.
ETTEMA, C. H. & WARDLE, D. A. (2002) Spatial soil ecology. *Trends in Ecology & Evolution,* 17**,** 177-183.
EVANS, C. D., MONTEITH, D. T. & COOPER, D. M. (2005) Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution,* 137**,** 55-71.
EVANS, D. J., GIBSON, C. E. & ROSSELL, R. S. (2006) Sediment loads and sources in heavily modified Irish catchments: A move towards informed management strategies. *Geomorphology,* 79**,** 93-113.
EVANS, M., QUINE, T. & KUHN, N. (2012) Geomorphology and terrestrial carbon cycling. *Earth Surface Processes and Landforms,* 38**,** 103-105.
EVANS, R. (1990) Soils at risk of accelerated erosion in England and Wales. *Soil Use and Management,* 6**,** 125-130.
EXTENCE, C. A., BALBI, D. M. & CHADD, R. P. (1999) River Flow Indexing Using British Benthic Macroinvertebrates: A Framework for Setting

Hydroecological Objectives. *Regulated Rivers: Research & Management,* 15**,** 543-574.
EXTENCE, C. A., CHADD, R. P., ENGLAND, J., DUNBAR, M. J., WOOD, P. J. & TAYLOR, E. D. (2013) The assessment of fine sediment accumulation in rivers using macro-invertebrate community response. *River Research and Applications*, 29, 17-55.
FAO (1993) World Soil Resources, An explanatory note on the FAO World Soil Resources Map at 1:25 000 000 scale, World Soil Resources Report 66 Rev. 1. FAO, Rome.
FAO, U. (2011) The state of the world's land and water resources for food and agriculture. Managing systems at risk. UN FAO, Rome, pp. 50.
FELD, C. K. (2013) Response of three lotic assemblages to riparian and catchment-scale land use: implications for designing catchment monitoring programmes. *Freshwater Biology,* 58**,** 715-729.
FENTON, O., SCHULTE, R. P. O., JORDAN, P., LALOR, S. T. J. & RICHARDS, K. G. (2011) Time lag: a methodology for the estimation of vertical and horizontal travel and flushing timescales to nitrate threshold concentrations in Irish aquifers. *Environmental Science & Policy,* 14**,** 419-431.
FINDLAY, D. C., COLBORNE, G. J. N., COPE, D. W., HARROD, T. R., HOGAN, D. V. & STAINES, S. J. (1984) *Soils and their use in South-west England.*, Bulletin No. 14. Soil Survey of Great Britain, pp. 419.
FORSHAY, K. J. & STANLEY, E. H. (2005) Rapid nitrate loss and denitrification in a temperate river floodplain. *Biogeochemistry,* 75**,** 43-64.
FRATERRIGO, J. M., TURNER, M. G., PEARSON, S. M. & DIXON, P. (2005) Effects of past land use on spatial heterogeneity of soil nutrients in southern appalachian forests. *Ecological Monographs,* 75**,** 215-230.
FRIBERG, N., BAATTRUP-PEDERSEN, A., PEDERSEN, M. & SKRIVER, J. (2005) The new Danish stream monitoring programme (NOVANA) - Preparing monitoring activities for the water framework directive era. *Environmental Monitoring and Assessment,* 111**,** 27-42.
FROMM, H., WINTER, K., FILSER, J., HANTSCHEL, R. & BEESE, F. (1993) The influence of soil type and cultivation system on the spatial distributions of the soil fauna and microorganisms and their interactions. *Geoderma,* 60**,** 109-118.
FRYIRS, K. (2013) (Dis)Connectivity in catchment sediment cascades: a fresh look at the sediment delivery problem. *Earth Surface Processes and Landforms,* 38**,** 30-46.
GELMAN, A. & HILL, J. (2007) *Data Analysis Using Regression and Multilevel/Hierarchical Models.*, Cambridge University Press, pp. 625.
GILLIAM, F. S. & DICK, D. A. (2010) Spatial heterogeneity of soil nutrients and plant species in herb-dominated communities of contrasting land use. *Plant Ecology,* 209**,** 83-94.
GOOVAERTS, P. (1998) Geostatistical tools for characterizing the spatial variability of microbiological and physico-chemical soil properties. *Biology and Fertility Soils,* 27**,** 315-334.
GRAEBER, D., GELBRECHT, J., PUSCH, M. T., ANLANGER, C. & VON SCHILLER, D. (2012) Agriculture has changed the amount and composition of dissolved organic matter in Central European headwater streams. *Science of the Total Environment,* 438**,** 435-446.
GRAND-CLEMENT, E., ANDERSON, K., SMITH, D., LUSCOMBE, D., GATIS, N., ROSS, M. & BRAZIER, R. E. (2013) Evaluating ecosystem goods

and services after restoration of marginal upland peatlands in South-West England. *Journal of Applied Ecology*. DOI: 10.1111/1365-2664.12039
GRAYSON, R. & HOLDEN, J. (2012) Continuous measurement of spectrophotometric absorbance in peatland streamwater in northern England: implications for understanding fluvial carbon fluxes. *Hydrological Processes,* 26**,** 27-39.
HAAPALEHTO, T. O., VASANDER, H., JAUHIAINEN, S., THAVANAINEN, T. & KOTIAHO, J. (2011) The Effect of Peatland Restoration on Water-Table Depth, Elemental Concentrations, and Vegetation: 10 Years of Changes. *Restoration Ecology,* 19**,** 587-598.
HAMILTON, S. K. (2012) Biogeochemical time lags may delay responses of streams to ecological restoration. *Freshwater Biology,* 57**,** 43-57.
HARMEL, D. & HAGGARD, B. E. (2007) Small Watershed Data Collection to Support Phosphorus Modeling. In: RADCLIFFE, D. E. & CABRERA, M. L. (Eds.) *Modeling Phosphorus in the Environment.* Crc Press-Taylor & Francis Group, 383-401.
HARRIS, G. & HEATHWAITE, A. L. (2005) Inadmissible evidence: knowledge and prediction in land and riverscapes. *Journal of Hydrology,* 304**,** 3-19.
HARRIS, G. P. & HEATHWAITE, A. L. (2012) Why is achieving good ecological outcomes in rivers so difficult? *Freshwater Biology,* 57**,** 91-107.
HAWKES, H. A. (1997) Origin and development of the biological monitoring working party score system. *Water Research,* 32**,** 964-968.
HAYGARTH, P. M., APSIMON, H., BETSON, M., HARRIS, D., HODGKINSON, R. & WITHERS, P. J. A. (2009) Mitigating Diffuse Phosphorus Transfer from Agriculture According to Cost and Efficiency. *Journal of Environmental Quality,* 38**,** 2012-2022.
HAYGARTH, P. M., CONDRON, L. M., HEATHWAITE, A. L., TURNER, B. L. & HARRIS, G. P. (2005a) The phosphorus transfer continuum: Linking source to impact with an interdisciplinary and multi-scaled approach. *Science of the Total Environment,* 344**,** 5-14.
HAYGARTH, P. M., DELGADO, A., CHARDON, W. J., LITAOR, M. I., GIL-SOTRES, F. & TORRENT, J. (2013) Phosphorus in soils and its transfer to water: from fine-scale soil processes to models and solutions in landscapes and catchments. *Soil Use and Management,* 29**,** 1-5.
HAYGARTH, P. M., WOOD, F. L., HEATHWAITE, A. L. & BUTLER, P. J. (2005b) Phosphorus dynamics observed through increasing scales in a nested headwater-to-river channel study. *Science of the Total Environment,* 344**,** 83-106.
HEATHWAITE, A. L., GRIFFITHS, P., HAYGARTH, P., JARVIS, S. C. & PARKINSON, R. (1997) Phosphorus loss from grassland soils: implications of land management for the quality of receiving waters. In: WEBB, B. W. (Ed.) *Proceeding of the 5th Scientific Assembly of the IAHS 23rd April – 3rd May 1997.* Rabat, Morocco, IAHS, 177-186 .
HEITKAMP, F., RAUPP, J. & LUDWIG, B. (2009) Impact of fertilizer type and rate on carbon and nitrogen pools in a sandy Cambisol. *Plant and Soil,* 319**,** 259-275.
HELMS, J. R., STUBBINS, A., RITCHIE, J. D. & MINOR, E. C. (2008) Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography,* 53**,** 955-969.

HERING, D., BORJA, A., CARSTENSEN, J., CARVALHO, L., ELLIOTT, M., FELD, C. K., HEISKANEN, A.-S., JOHNSON, R. K., MOE, J., PONT, D., SOLHEIM, A. L. & VAN DE BUND, W. (2010) The European Water Framework Directive at the age of 10: A critical review of the achievements with recommendations for the future. *Science of the Total Environment,* 408**,** 4007-4019.

HERNES, P. J., SPENCER, R. G. M., DYDA, R. Y., PELLERIN, B. A., BACHAND, P. A. M. & BERGAMASCHI, B. A. (2008) The role of hydrologic regimes on dissolved organic carbon composition in an agricultural watershed. *Geochimica Et Cosmochimica Acta,* 72**,** 5266-5277.

HILTON, J., O'HARE, M., BOWES, M. J. & JONES, J. I., (2006). How green is my river? A new paradigm of eutrophication in rivers. *Science of the Total Environment*, 365, 66-83.

HOLDEN, J., CHAPMAN, P. J. & LABADZ, J. C. (2004) Artificial drainage of peatlands: hydrological and hydrochemical process and wetland restoration. *Progress in Physical Geography,* 28**,** 95-123.

HOLDEN, J., WALLAGE, Z. E., LANE, S. N. & MCDONALD, A. T. (2011) Water table dynamics in undisturbed, drained and restored blanket peat. *Journal of Hydrology,* 402**,** 103-114.

HOLL, B. S., FIEDLER, S., JUNGKUNST, H. F., KALBITZ, K. & FREIBAUER, A. (2009) Characteristics of dissolved organic matter following 20 years of peatland restoration. *Science of the Total Environment,* 408**,** 78-83.

HOLMAN, I. P., WHELAN, M. J., HOWDEN, N. J. K., BELLAMY, P. H., WILLBY, N. J., RIVAS-CASADO, M. & MCCONVEY, P. (2008) Phosphorus in groundwater - an overlooked contributor to eutrophication? *Hydrological Processes,* 22**,** 5121-5127.

HOPE, D., BILLETT, M. F. & CRESSER, M. S. (1994) A review of the export of carbon in river water: fluxes and processes. *Environmental Pollution,* 84**,** 301-324.

HOPE, D., BILLETT, M. F. & CRESSER, M. S. (1997a) Exports of organic carbon in two river systems in NE Scotland. *Journal of Hydrology,* 193**,** 61-82.

HOPE, D., BILLETT, M. F., MILNE, R. & BROWN, T. A. W. (1997b) EXPORTS OF ORGANIC CARBON IN BRITISH RIVERS. *Hydrological Processes,* 11**,** 325-344.

HOROWITZ, A. J., STEPHENS, V. C., ELRICK, K. A. & SMITH, J. J. (2012) Concentrations and annual fluxes of sediment-associated chemical constituents from conterminous US coastal rivers using bed sediment data. *Hydrological Processes,* 26**,** 1090-1114.

HOUSER, J. N. & RICHARDSON, W. B. (2010) Nitrogen and phosphorus in the Upper Mississippi River: transport, processing, and effects on the river ecosystem. *Hydrobiologia,* 640**,** 71-88.

HOWARD-WILLIAMS, C., DAVIES-COLLEY, R., RUTHERFORD, K. & WILCOCK, R. (2010) Diffuse pollution and freshwater degradation: New Zealand Perspectives. IN VAN BOCHOVE, E., VANROLLEGHEM, P. A., CHAMBERS, P. A., THERIAULT, G., NOVOTNA, B. & BURKART, M. R. (Eds.) *Proceedings of the 14th International Conference of the IWA Diffuse Pollution Specialist Group, DIPCON 2010.* Quebec, Canada, IWA, 126-140.

HUTCHINS, M., FEZZI, C., BATEMAN, I., POSEN, P. & DEFLANDRE-VLANDAS, A. (2009) Cost-Effective Mitigation of Diffuse Pollution:

Setting Criteria for River Basin Management at Multiple Locations. *Environmental Management,* 44**,** 256-267.

JARVIE, H. P., HAYGARTH, P. M., NEAL, C., BUTLER, P., SMITH, B., NADEN, P. S., JOYNES, A., NEAL, M., WICKHAM, H., ARMSTRONG, L., HARMAN, S. & PALMER-FELGATE, E. J. (2008) Stream water chemistry and quality along an upland-lowland rural land-use continuum, south west England. *Journal of Hydrology,* 350**,** 215-231.

JARVIE, H. P., JICKELLS, T. D., SKEFFINGTON, R. A. & WITHERS, P. J. A. (2012) Climate change and coupling of macronutrient cycles along the atmospheric, terrestrial, freshwater and estuarine continuum. *Science of the Total Environment,* 434**,** 252-258.

JNCC, J. N. C. C. (2006) Special Areas of Conservation UK0030040 and UK0030148. www.jncc.defra.gov.uk/protectedsites/sacselection. Last accessed on 27th June 2012.

JOHNES, P. J. (2006) Uncertainties in annual riverine phosphorus load estimation: Impact of load estimation methodology, sampling frequency, baseflow index and catchment population density. *Journal of Hydrology,* 332**,** 241-258.

JOHNES, P. J., FOY, R., BUTTERFIELD, D. & HAYGARTH, P. M. (2007) Land use scenarios for England and Wales: evaluation of management options to support 'good ecological status' in surface freshwaters. *Soil Use and Management,* 23**,** 176-194.

JOHNSON, D., HODGKINSON, R. A., LORD, E., SILGRAM, M., COTTRILL, B., GOODAY, R., MORROW, K., SMITH, S. & HULIN, A. (2011) Nitrates Directive Consultation Document. The evidence base for assessing the impacts of the NVZ Action Programme on water quality across England and Wales. ADAS, Woolverhampton, UK, pp. 65.

JOHNSON, L. T., ROYER, T. V., EDGERTON, J. M. & LEFF, L. G. (2012) Manipulation of the Dissolved Organic Carbon Pool in an Agricultural Stream: Responses in Microbial Community Structure, Denitrification, and Assimilatory Nitrogen Uptake. *Ecosystems,* 15**,** 1027-1038.

JOHNSON, L. T., TANK, J. L. & ARANGO, C. P. (2009) The effect of land use on dissolved organic carbon and nitrogen uptake in streams. *Freshwater Biology,* 54**,** 2335-2350.

JONES, J. I., MURPHY, J. F., COLLINS, A. L., SEAR, D. A., NADEN, P. S. & ARMITAGE, P. D. (2012) The impact of fine sediment on macro-invertebrates. *River Research and Applications*, 28, 1055-1071.

JORDAN, P., ARNSCHEIDT, A., MCGROGAN, H. & MCCORMICK, S. (2007) Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser. *Hydrology and Earth System Sciences,* 11**,** 372-381.

JORDAN, P. & CASSIDY, R. (2011) Technical Note: Assessing a 24/7 solution for monitoring water quality loads in small river catchments. *Hydrology and Earth System Sciences,* 15**,** 3093-3100.

JORDAN, P., CASSIDY, R., MACINTOSH, K. A. & ARNSCHEIDT, J. (2013) Field and Laboratory Tests of Flow-Proportional Passive Samplers for Determining Average Phosphorus and Nitrogen Concentration in Rivers. *Environmental Science & Technology,* 47**,** 2331-2338.

JORDAN, P., HAYGARTH, P. M., SHORTLE, G. & HARRIS, R. C. (2012a) Catchment science and policy for agriculture and water quality. *Environmental Science & Policy,* 24**,** 1-3.

JORDAN, P., MELLAND, A. R., MELLANDER, P. E., SHORTLE, G. & WALL, D. (2012b) The seasonality of phosphorus transfers from land to water: Implications for trophic impacts and policy evaluation. *Science of the Total Environment,* 434**,** 101-109.

JORDAN, P., MENARY, W., DALY, K., KIELY, G., MORGAN, G., BYRNE, P. & MOLES, R. (2005) Patterns and processes of phosphorus transfer from Irish grassland soils to rivers - integration of laboratory and catchment studies. *Journal of Hydrology,* 304**,** 20-34.

JORDAN, P. & RIPPEY, B. (2003) Lake sedimentary evidence of phosphorus, iron and manganese mobilisation from intensively fertilised soils. *Water Research,* 37**,** 1426-1432.

KALLER, M. D. & HARTMAN, K. J. (2004) Evidence of a threshold level of fine sediment accumulation for altering benthic macroinvertebrate communities. *Hydrobiologia,* 518**,** 95-104.

KAPLAN, L. A., WIEGNER, T. N., NEWBOLD, J. D., OSTROM, P. H. & GANDHI, H. (2008) Untangling the complex issue of dissolved organic carbon uptake: a stable isotope approach. *Freshwater Biology,* 53**,** 855-864.

KAY, P., EDWARDS, A. C. & FOULGER, M. (2009) A review of the efficacy of contemporary agricultural stewardship measures for ameliorating water pollution problems of key concern to the UK water industry. *Agricultural Systems,* 99**,** 67-75.

KECHAVARZI, C., DAWSON, Q. & LEEDS-HARRISON, P. B. (2010) Physical properties of low-lying agricultural peat soils in England. *Geoderma,* 154**,** 196-202.

KEFFORD, B. J., ZALIZNIAK, L., DUNLOP, J. E., NUGEGODA, D. & CHOY, S. C. (2010) How are macroinvertebrates of slow flowing lotic systems directly affected by suspended and deposited sediment? *Environmental Pollution,* 158**,** 543-550.

KEMP, P., SEAR, D., COLLINS, A., NADEN, P. & JONES, I. (2011) The impacts of fine sediment on riverine fish. *Hydrological Processes,* 25**,** 1800-1821.

KIRCHNER, J. W., XIAHONG, F. & NEAL, C. (2000) Fractal stram chemistry and its implications for contaminant transport in catchments. *Nature,* 403**,** 524-527.

KLAUS, V. H., SINTERMANN, J., KLEINEBECKER, T. & HOELZEL, N. (2011) Sedimentation-induced eutrophication in large river floodplains - An obstacle to restoration? *Biological Conservation,* 144**,** 451-458.

KNIGHTON, D. (1998) *Fluvial forms and processes. A new perspective.*, Hodder Arnold, pp. 383.

KRONHOLM, S. & CAPEL, P. (2012) Concentrations, Loads, and Yields of Organic Carbon in Streams of Agricultural Watersheds. *Journal of Environmental Quality,* 41**,** 1874-1883.

KRONVANG, B., ANDERSEN, I. K., HOFFMANN, C. C., PEDERSEN, M. L., OVESEN, N. B. & ANDERSEN, H. E. (2007) Water exchange and deposition of sediment and phosphorus during inundation of natural and restored lowland floodplains. *Water Air and Soil Pollution,* 181**,** 115-121.

KRONVANG, B., AUDET, J., BAATTRUP-PEDERSEN, A., JENSEN, H. S. & LARSEN, S. R. E. (2012) Phosphorus Load to Surface Water from Bank Erosion in a Danish Lowland River Basin. *J. Environ. Qual.,* 41**,** 304-313.

KUZYAKOV, Y., FRIEDEL, J. K. & STAHR, K. (2000) Review of mechanisms and quantification of priming effects. *Soil Biology & Biochemistry,* 32**,** 1485-1498.
LAL, R. (2002) Agricultural activities and the global carbon cycle. *Proceedings of a Seminar of the Nordic-Agricultural-Researchers-Union.* Reykholt, ICELAND, 103-116.
LAL, R., APT, J., LAVE, L. & MORGAN, M. G. (2004a) Response to Comments on "Managing Soil Carbon". *Science,* 305**,** 1567d.
LAL, R., GRIFFIN, M., APT, J., LAVE, L. & MORGAN, M. G. (2004b) Managing Soil Carbon. *Science,* 304**,** 393.
LAMBERT, C. P. & WALLING, D. E. (1988) Measurement of channel storage of suspended sediment in a gravel-bed river. *CATENA,* 15**,** 65-80.
LARSEN, S. & ORMEROD, S. J. (2010a) Combined effects of habitat modification on trait composition and species nestedness in river invertebrates. *Biological Conservation,* 143**,** 2638-2646.
LARSEN, S. & ORMEROD, S. J. (2010b) Low-level effects of inert sediments on temperate stream invertebrates. *Freshwater Biology,* 55**,** 476-486.
LARSEN, S., PACE, G. & ORMEROD, S. J. (2011) Experimental effects of sediment deposition on the structure and function of macroinvertebrate assemblages in temperate streams. *River Research and Applications,* 27**,** 257-267.
LARSEN, S., VAUGHAN, I. P. & ORMEROD, S. J. (2009) Scale-dependent effects of fine sediments on temperate headwater invertebrates. *Freshwater Biology,* 54**,** 203-219.
LAWTON, J. H., BROTHERTON, P. N. M., BROWN, V. K., ELPHICK, C., FITTER, A. H., FORSHAW, J., HADDOW, R. W., HILBORNE, S., LEAFE, R. N., MACE, G. M., SOUTHGATE, M. P., SUTHERLAND, W. J., TEW, T. E., VARLEY, J. & WYNNE, G. R. (2010) Making Space for Nature: a review of England's wildlife sites and ecological network. Report to Defra. Defra, UK, pp. 119.
LEESON, J., EDWARDS, A., SMITH, J. W. N. & POTTER, H. A. B. (2003) Hydrogeological risk assessments for landfills and the derivation of groundwater control and trigger levels. LFTGNO1, pp. 81. Environment Agency, Bristol, UK.
LEIRA, M., JORDAN, P., TAYLOR, D., DALTON, C., BENNION, H., ROSE, N. & IRVINE, K. (2006) Assessing the ecological status of candidate reference lakes in Ireland using palaeolimnology. *Journal of Applied Ecology,* 43**,** 816-827.
LENAT, D. R., PENROSE, D. L. & EAGLESON, K. W. (1981) Variable effects of sediment addition on stream biota. *Hydrobiologia,* 79**,** 187-194.
LEXARTZA-ARTZA, I. & WAINWRIGHT, J. (2009) Hydrological connectivity: Linking concepts with practical implications. *CATENA,* 79**,** 146-152.
LI, J., RICHTER, D. D., MENDOZA, A. & HEINE, P. (2010) Effects of land-use history on soil spatial heterogeneity of macro- and trace elements in the Southern Piedmont USA. *Geoderma,* 156**,** 60-73.
LITTLEWOOD, I. G. (1992) Estimating Contaminant Loads in Rivers; A Review. *Report No. 117.* Institute of Hydrology, Wallingford, UK, pp. 81.
LIU, S., LI, Y., WU, J., HUANG, D., SU, Y. & WEI, W. (2012) Spatial variability of soil microbial biomass carbon, nitrogen and phosphorus in a hilly red soil landscape in subtropical China. *Soil Science and Plant Nutrition,* 56**,** 693-704.

LOEB, R., LAMERS, L. P. M. & ROELOFS, J. G. M. (2008) Prediction of phosphorus mobilisation in inundated floodplain soils. *Environmental Pollution,* 156**,** 325-331.

MACDONALD, D. H., CONNOR, J. & MORRISON, M. (2004) Economic Instruments for Managing Water Quality in New Zealand. CSIRO, Wellington, pp. 73.

MAINSTONE, C. P., DILS, R. M. & WITHERS, P. J. A. (2008) Controlling sediment and phosphorus transfer to receiving waters - A strategic management perspective for England and Wales. *Journal of Hydrology,* 350**,** 131-143.

MAINSTONE, C. P. & PARR, W. (2002) Phosphorus in rivers -- ecology and management. *The Science of the Total Environment,* 282-283**,** 25-47.

MARRIOTT, C. A., HUDSON, G., HAMILTON, D., NEILSON, R., BOAG, B., HANDLEY, L. L., WISHART, J., SCRIMGEOUR, C. M. & ROBINSON, D. (1997) Spatial variability of soil total C and N and their stable isotopes in an upland Scottish grassland. *Plant and Soil,* 196**,** 151-162.

MARSH, T. J. & HANNAFORD, J. (2008) UK Hydrometric Register. Hydrological data UK series. Centre for Ecology and Hydrology, Wallingford, UK, pp. 210.

MARTIN-ORTEGA, J. (2012) Economic prescriptions and policy applications in the implementation of the European Water Framework Directive. *Environmental Science & Policy,* 24**,** 83-91.

MATLACK, G. R. (2009) Long-term changes in soils of second-growth forest following abandonment from agriculture. *Journal of Biogeography,* 36**,** 2066-2075.

MATTHAEI, C. D., PIGGOTT, J. J. & TOWNSEND, C. R. (2010) Multiple stressors in agricultural streams: interactions among sediment addition, nutrient enrichment and water abstraction. *Journal of Applied Ecology,* 47**,** 639-649.

MATTHAEI, C. D., WELLER, F., KELLY, D. W. & TOWNSEND, C. R. (2006) Impacts of fine sediment addition to tussock, pasture, dairy and deer farming streams in New Zealand. *Freshwater Biology,* 51**,** 2154-2172.

MATTSSON, T., KORTELAINEN, P., LAUBEL, A., EVANS, D., PUJO-PAY, M., RAIKE, A. & CONAN, P. (2009) Export of dissolved organic matter in relation to land use along a European climatic gradient. *Science of the Total Environment,* 407**,** 1967-1976.

McDONNELL, J. J. (2003) Where does water go when it rains? Moving beyond the variable source area concept of rainfall-runoff response. *Hydrological Processes,* 17**,** 1869-1875.

McGONIGLE, D. F., HARRIS, R. C., MCCAMPHILL, C., KIRK, S., DILS, R., MACDONALD, J. & BAILEY, S. (2012) Towards a more strategic approach to research to support catchment-based policy approaches to mitigate agricultural water pollution: A UK case-study. *Environmental Science & Policy,* 24**,** 4-14.

MELLAND, A. R., MELLANDER, P. E., MURPHY, P. N. C., WALL, D. P., MECHAN, S., SHINE, O., SHORTLE, G. & JORDAN, P. (2012) Stream water quality in intensive cereal cropping catchments with regulated nutrient management. *Environmental Science & Policy,* 24**,** 58-70.

MELLANDER, P.-E., MELLAND, A. R., JORDAN, P., WALL, D. P., MURPHY, P. N. C. & SHORTLE, G. (2012) Quantifying nutrient transfer pathways in agricultural catchments using high temporal resolution data. *Environmental Science & Policy,* 24**,** 44-57.

MET OFFICE (2011) Fact Sheet No. 7 - Climate of southwest England. National Meteorological Library and Archive. Met Office UK, pp. 20.
MILLEDGE, D. G., LANE, S. N., HEATHWAITE, A. L. & REANEY, S. M. (2013) A Monte Carlo approach to the inverse problem of diffuse pollution risk in agricultural catchments. *Science of the Total Environment,* 433**,** 434-449.
MILLENIUM ECOSYSTEM ASSESSMENT (2005) Ecosystems and human wellbeing: synthesis. Island Press, Washington DC, pp. 155.
MILNE, R. & BROWN, T. A. (1997) Carbon in the vegetation and soils of Great Britain. *Journal of Environmental Management,* 49**,** 413-433.
MINEAU, M. M., RIGSBY, C. M., DAMON, T. E., FERNANDEZ, I. J., NORTON, S. A., TSUTOMU, O., VALETT, H. M. & SIMON, K. S. (2012) Chronic catchment nitrogen enrichment and stoichiometric constraints on the bioavailability of dissolved organic matter from leaf leachate. *Freshwater Biology,* 58**,** 10.1111/fwb.12054.
MOLINERO, J. & BURKE, R. A. (2009) Effects of land use on dissolved organic matter biogeochemistry in piedmont headwater streams of the Southeastern United States. *Hydrobiologia,* 635**,** 289-308.
MONAGHAN, R. M., CAREY, P. L., WILCOCK, R. J., DREWRY, J. J., HOULBROOKE, D. J., QUINN, J. M. & THORROLD, B. S. (2009) Linkages between land management activities and stream water quality in a border dyke-irrigated pastoral catchment. *Agriculture Ecosystems & Environment,* 129**,** 201-211.
MONAGHAN, R. M., DE KLEIN, C. A. M. & MUIRHEAD, R. W. (2008) Prioritisation of farm scale remediation efforts for reducing losses of nutrients and faecal indicator organisms to waterways: A case study of New Zealand dairy farming. *Journal of Environmental Management,* 87**,** 609-622.
MONK, W. A., WOOD, P. J., HANNAH, D. M., EXTENCE, C. A., CHADD, R. P. & DUNBAR, M. J. (2012) How does macroinvertebrate taxonomic resolution influence ecohydrological relationships in riverine ecosystems. *Ecohydrology,* 5**,** 36-45.
MONTGOMERY, D. R. (2007a) *Dirt: The Erosion of Civilizations*, University of California Press, Berkeley, CA.
MONTGOMERY, D. R. (2007b) Soil erosion and agricultural sustainability. *Proceedings of the National Academy of Sciences of the United States of America,* 104**,** 13268-13272.
MOOSHAMMER, M., WANEK, W., SCHNECKER, J., WILD, B., LEITNER, S., HOFHANSL, F., BLOECHL, A., HAEMMERLE, I., FRANK, A. H., FUCHSLUEGER, L., KEIBLINGER, K. M., ZECHMEISTER-BOLTENSTERN, S. & RICHTER, A. (2012) Stoichiometric controls of nitrogen and phosphorus cycling in decomposing beech leaf litter. *Ecology,* 93**,** 770-782.
NATURAL ENGLAND (2013) *Higher Level Stewardship. Environmental Stewardship Handbook.* Fourth edition - January 2013, pp. 120.
NEAL, C. & HEATHWAITE, A. L. (2005) Nutrient mobility within river basins: a European perspective. *Journal of Hydrology,* 304**,** 477-490.
NEWCOMBE, C. P. & MACDONALD, D. D. (1991) Effects of suspended sediments on aquatic ecosystems. *North American Journal of Fisheries Management,* 11**,** 72-82.
NEWELL-PRICE, P., HARRIS, D., TAYLOR, D., WILLIAMS, J. R., ANTHONY, S. G., DUETHMANN, D., GOODAY, R. D., LORD, E. I., CHAMBERS, B. J., CHADWICK, D. R. & MISSELBROOK, R. D. (2011) An Inventory of

Mitigation Methods and Guide to their Effects on Diffuse Water Pollution, Greenhouse Gas Emissions and Ammonia Emissions from Agriculture. Prepared as part of Defra Project WQ0106, pp. 162.
NEWSON, M. D. & LARGE, A. R. G. (2006) 'Natural' rivers, 'hydromorphological quality' and river restoration: a challenging new agenda for applied fluvial geomorphology. *Earth Surface Processes and Landforms,* 31**,** 1606-1624.
NOE, G. B. & HUPP, C. R. (2009) Retention of Riverine Sediment and Nutrient Loads by Coastal Plain Floodplains. *Ecosystems,* 12**,** 728-746.
NOIJ, I. G. A. M., HEINEN, M., HEESMANS, H. I. M., THISSEN, J. T. N. M. & GROENENDIJK, P. (2012) Effectiveness of Unfertilized Buffer Strips for Reducing Nitrogen Loads from Agricultural Lowland to Surface Waters. *J. Environ. Qual.,* 41**,** 322-333.
NOIJ, I. G. A. M., HEINEN, M., HEESMANS, H. I. M., THISSEN, J. T. N. M. & GROENENDIJK, P. (2013) Effectiveness of buffer strips without added fertilizer to reduce phosphorus loads from flat fields to surface waters. *Soil Use and Management,* 29**,** 162-174.
NSRI (2012) Soil Attribute Data. HORIZON fundamentals data and description. LandIS. www.landis.org.uk/data/datafamilies.cfm. Last accessed on 24th July 2013.
OCKENDEN, M. C., DEASY, C., QUINTON, J. N., BAILEY, A. P., SURRIDGE, B. & STOATE, C. (2012) Evaluation of field wetlands for mitigation of diffuse pollution from agriculture: Sediment retention, cost and effectiveness. *Environmental Science & Policy,* 24**,** 110-119.
OECD (2013) Agri-environmental indicators. www.oecd.org/greengrowth/sustainable-agriculture/agri-environmentalindicators.htm. Last accessed on 24th July 2013
OEURNG, C., SAUVAGE, S., COYNEL, A., MANEUX, E., ETCHEBER, H. & SANCHEZ-PEREZ, J.-M. (2011) Fluvial transport of suspended sediment and organic carbon during flood events in a large agricultural catchment in southwest France. *Hydrological Processes,* 25**,** 2365-2378.
OLIVER, D. M., HEATHWAITE, A. L., HODGSON, C. J. & CHADWICK, D. R. (2007) Mitigation and current management attempts to limit pathogen survival and movement within farmed grassland. *Advances in Agronomy, Vol 93*, 95*.* San Diego, Elsevier Academic Press Inc.
OLIVER, M. A. & WEBSTER, R. (1991) How geostatistics can help you. *Soil Use and Management,* 7**,** 206-217.
ORMEROD, S. J., DOBSON, M., HILDREW, A. G. & TOWNSEND, C. R. (2010) Multiple stressors in freshwater ecosystems. *Freshwater Biology,* 55**,** 1-4.
OWEN, G. J., PERKS, M. T., BENSKIN, C. M. H., WILKINSON, M. E., JONCZYK, J. & QUINN, P. F. (2012) Monitoring agricultural diffuse pollution through a dense monitoring network in the River Eden Demonstration Test Catchment, Cumbria, UK. *Area,* 44**,** 443-453.
OWENS, P. N., BATALLA, R. J., COLLINS, A. J., GOMEZ, B., HICKS, D. M., HOROWITZ, A. J., KONDOLF, G. M., MARDEN, M., PAGE, M. J., PEACOCK, D. H., PETTICREW, E. L., SALOMONS, W. & TRUSTRUM, N. A. (2005) Fine-grained sediment in river systems: Environmental significance and management issues. *River Research and Applications,* 21**,** 693-717.
OWENS, P. N., DUZANT, J. H., DEEKS, L. K., WOOD, G. A., MORGAN, R. P. C. & COLLINS, A. J. (2007) Evaluation of contrasting buffer features within an agricultural landscape for reducing sediment and sediment-

associated phosphorus delivery to surface waters. *Soil Use and Management,* 23**,** 165-175.
OWENS, P. N., WALLING, D. E., CARTON, J., MEHARG, A. A., WRIGHT, J. & LEEKS, G. J. L. (2001) Downstream changes in the transport and storage of sediment-associated contaminants (P, Cr and PCBs) in agricultural and industrialized drainage basins. *Science of the Total Environment,* 266**,** 177-186.
PAGE, T., HAYGARTH, P. M., BEVEN, K. J., JOYNES, A., BUTLER, T., KEELER, C., FREER, J., OWENS, P. N. & WOOD, G. A. (2005) Spatial Variability of Soil Phosphorus in Relation to the Topographic Index and Critical Source Areas: Sampling for Assessing Risk to Water Quality. *Journal of Environmental Quality,* 34**,** 2263-2277.
PAGE, T., HEATHWAITE, A. L., MOSS, B., REYNOLDS, C., BEVEN, K. J., POPE, L. & WILLOWS, R. (2012) Managing the impacts of nutrient enrichment on river systems: dealing with complex uncertainties in risk analyses. *Freshwater Biology,* 57**,** 108-123.
PALLANT, J. (2007) *SPSS Survival Manual*, Open University Press.
PAZ-GONZALEZ, A., VIEIRA, S. R. & CASTRO, M. T. T. (2000) The effect of cultivation on the spatial variability of selected properties of an umbric horizon. *Geoderma,* 97**,** 273-292.
PEACOCK, M., BURDEN, A., COOPER, M., DUNN, C., EVANS, C. D., FENNER, N., FREEMAN, C., GOUGH, R., HUGHES, D., HUGHES, S., JONES, S., LEBRON, I., WEST, M. & ZIELINSKI, P. (2013) Quantifying dissolved organic carbon concentrations in upland catchments using phenolic proxy measurements. *Journal of Hydrology,* 477**,** 251-260.
PEUKERT, S., BOL, R., ROBERTS, W., MACLEOD, C. J. A., MURRAY, P. J., DIXON, E. R. & BRAZIER, R. E. (2012) Understanding spatial variability of soil properties: a key step in establishing field- to farm-scale agro-ecosystem experiments. *Rapid Communications in Mass Spectrometry,* 26**,** 2413-2421.
PIERZYNSKI, G. M., SIMS, J. T. & VANCE, G. F. (2000) *Soils and Environmental Quality,* Boca Ratton, Florida, USA, CRC Press LLC, pp. 459.
PIIRSOO, K., VIIK, M., KOIV, T., KAIRO, K., LAAS, A., NOGES, T., PALL, P., SELBERG, A., TOOMSALU, L. & VILBASTE, S. (2012) Characterisitcs of dissolved organic matter in the inflows and the outflow of Lake Vortsjarv, Estonia. *Journal of Hydrology,* 475**,** 306-313.
POWLSON, D. S. (1998) Phosphorus, agriculture and water quality. *Soil Use and Management,* 14**,** 123.
PRICE, K., JACKSON, C. R. & PARKER, A. J. (2010) Variation of surficial soil hydraulic properties across land uses in the southern Blue Ridge Mountains, North Carolina, USA. *Journal of Hydrology,* 383**,** 256-268.
PRUDHOMME, C., YOUNG, A., WATTS, G., HAXTON, T., CROOKS, S., WILLIAMSON, J., DAVIES, H., DADSON, S. & ALLEN, S. (2012) The drying up of Britain? A national estimate of changes in seasonal river flows from 11 Regional Climate Model simulations. *Hydrological Processes,* 26**,** 1115-1118.
QUINTON, J. N., CATT, J. A., WOOD, G. A. & STEER, J. (2006) Soil carbon losses by water erosion: Experimentation and modeling at field and national scales in the UK. *Agriculture, Ecosystems and Environment,* 112**,** 87-102.

QUINTON, J. N., GOVERS, G., VAN OOST, K. & BARDGETT, R. D. (2010) The impact of agricultural soil erosion on biogeochemical cycling. *Nature Geoscience,* 3**,** 311-314.

RAMCHUNDER, S. J., BROWN, L. E. & HOLDEN, J. (2009) Environmental effects of drainage, drain-blocking and prescribed vegetation burning in UK upland peatlands. *Progress in Physical Geography,* 33**,** 49-79.

REANEY, S. M., LANE, S. N., HEATHWAITE, A. L. & DUGDALE, L. J. (2011) Risk-based modelling of diffuse land use impacts from rural landscapes upon salmonid fry abundance. *Ecological Modelling,* 222**,** 1016-1029.

RELYEA, C. D., MINSHALL, G. W. & DANEHY, R. J. (2012) Development and Validation of an Aquatic Fine Sediment Biotic Index. *Environmental Management,* 49**,** 242-252.

RIGA, A., VAN PRAAG, H. J. & BRIGODE, N. (1971) Rapport isotopique naturel de l'azote dans quelques sols forestiers et agricoles de Belgique soumis a divers traitements culturaux. *Geoderma,* 6**,** 213-222.

RIVERO, R. G., GRUNWALD, S., OSBORNE, T. Z., REDDY, K. R. & NEWMAN, S. (2007) Characterization of the spatial distribution of soil properties in water conservation area 2A, Everglades, Florida. *Soil Science,* 172**,** 149-166.

ROBERTS, W. M., STUTTER, M. I. & HAYGARTH, P. M. (2012) Phosphorus Retention and Remobilization in Vegetated Buffer Strips: A Review. *J. Environ. Qual.,* 41**,** 389-399.

ROTHAMSTED RESEARCH (2013) North Wyke Farm Platform. www.rothamsted.ac.uk/northwyke/FarmPlatform.html. Last accessed on 24th July 2013.

RUSSELL, M. A., WALLING, D. E. & HODGKINSON, R. A. (2001) Suspended sediment sources in two small lowland agricultural catchments in the UK. *Journal of Hydrology,* 252**,** 1-24.

SANDFORD, R. C., BOL, R. & WORSFOLD, P. J. (2010) In site determinantion of dissolved organic carbon in freshwater using a reagentless UV sensor. *Journal of Environmental Monitoring,* 12**,** 1678-1683.

SAUNDERS, W. M. H. & WILLIAMS, E. G. (1955) OBSERVATIONS ON THE DETERMINATION OF TOTAL ORGANIC PHOSPHORUS IN SOILS. *Journal of Soil Science,* 6**,** 254-267.

SCHLESINGER, W. H. (1997) *Biogeochemistry: An Analysis of Global Change*, Academic Press, pp. 588.

SCHOLEFIELD, P., HEATHWAITE, A. L., BRAZIER, R. E., PAGE, T., SCHÄRER, M., BEVEN, K., HODGKINSON, R., WITHERS, P., WALLING, D. & HAYGARTH, P. M. (2013) Estimating phosphorus delivery from land to water in headwater catchments using a fuzzy decision tree approach. *Soil Use and Management,* 29**,** 175-186.

SCHOLZ, M. (2007) Ecological effects of water retention in the River Rhine valley: a review assisting future retention basin classification. *International Journal of Environmental Studies,* 64**,** 171-187.

SCHULTE, R. P. O., MELLAND, A. R., FENTON, O., HERLIHY, M., RICHARDS, K. & JORDAN, P. (2010) Modelling soil phosphorus decline: Expectations of Water Framework Directive policies. *Environmental Science & Policy,* 13**,** 472-484.

SCHUMAN, G. E., HERRICK, J. E. & JANZEN, H. H. (2001) The Dynamic of Soil Carbon in Rangelands. In: FOLLETT, R. F., KIMBLE, J. M. & LAL, R. (Eds.) *The Potential of U.S. Grazing Lands to Sequester Carbon and*

Mitigate the Greenhouse Effect. Boca Raton, Boston, CRC Press, 267-290.

SENBAYRAM, M., DIXON, L., GOULDING, K. W. T. & BOL, R. (2008) Long-term influence of manure and mineral nitrogen applications on plant and soil N-15 and C-13 values from the Broadbalk Wheat Experiment. *Rapid Communications in Mass Spectrometry,* 22**,** 1735-1740.

SHARPLEY, A., KLEINMAN, P. J. A., FLATEN, D. & BUDA, A. (2010) Critical Source Area Management of Agricultural Phosphorus: Experiences, Challenges and Opportunities. In: VAN BOCHOVE, E., VANROLLEGHEM, P. A., CHAMBERS, P. A., THERIAULT, G., NOVOTNA, B. & BURKART, M. R. (Eds.) *Proceedings of the 14th International Conference, IWA Diffuse Pollution Specialist Group: Diffuse Pollution and Eutrophication.* Quebec, Canada, IWA, 18-26.

SHARPLEY, A. N., KLEINMAN, P. J. A., JORDAN, P., BERGSTROM, L. & ALLEN, A. L. (2009) Evaluating the Success of Phosphorus Management from Field to Watershed. *Journal of Environmental Quality,* 38**,** 1981-1988.

SHORE, M., MURPHY, P. N. C., JORDAN, P., MELLANDER, P. E., KELLY-QUINN, M., CUSHEN, M., MECHAN, S., SHINE, O. & MELLAND, A. R. (2013) Evaluation of a surface hydrological connectivity index in agricultural catchments. *Environmental Modelling & Software,* 47**,** 7-15.

SILGRAM, M., JACKSON, B., QUINTON, J. N. & STEVENS, C. J. (2006) Practical mitigation options for controlling phosphorus and sediment loss at hillslope scale. *Proceedings of the BHS 9th National Hydrology Symposium.* Durham, 103-107.

SLEUTEL, S., DENEVE, S., SINGIER, B. & HOFMAN, G. (2006) Organic C levels in intensively managed arable soils - long-term regional trends and characterization of fractions. *Soil Use and Management,* 22**,** 188-196.

SMILEY, P. C., JR. & DIBBLE, E. D. (2008) Influence of spatial resolution on assessing channelization impacts on fish and macroinvertebrate communities in a warmwater stream in the southeastern United States. *Environmental Monitoring and Assessment,* 138**,** 17-29.

SMITH, L., INMAN, A. & CHERRINGTON, R. (2012) The potential of land conservation agreements for protection of water resources. *Environmental Science & Policy,* 24**,** 92-100.

SOIL SURVEY OF ENGLAND AND WALES (1983) National Soil Map NATMAP Vector. National Soil Research Institute, Cranfield, UK.

SOULSBY, C., GIBBINS, C., WADE, A. J., SMART, R. & HELLIWELL, R. (2002) Water quality in the Scottish uplands: a hydrological perspective on catchment hydrochemistry. *The Science of the Total Environment,* 294**,** 73-94.

SOULSBY, C., TETZLAFF, D., RODGERS, P., DUNN, S. & WALDRON, S. (2006) Runoff processes, stream water residence times and controlling landscape characteristics in a mesoscale catchment: An initial evaluation. *Journal of Hydrology,* 325**,** 197-221.

SPACKMAN, E. (1993) Calculation and mapping of rainfall average for 1961-1990. *Proceedings of meeting of the BHS (British Hydrological Society), University of Salford, Manchester, 15th December 1993*.

STANLEY, E. H., POWERS, S. M., LOTTIG, N. R., BUFFAM, I. & CRAWFORD, J. T. (2011) Contemporary changes in dissolved organic carbon (DOC) in human-dominated rivers: is there a role for DOC management? *Freshwater Biology,* DOI: 10.1111/j.1365-2427.2011.02613.x.

STELZER, R. S., HEFFERNAN, J. & LIKENS, G. (2003) The influence of dissolved nutrients and particulate organic matter quality on microbial respiration and biomass in a forest stream. *Freshwater Biology,* 48**,** 1925-1937.
STEVENS, C. J. & QUINTON, J. N. (2009a) Diffuse Pollution Swapping in Arable Agricultural Systems. *Critical Reviews in Environmental Science and Technology,* 39**,** 478-520.
STEVENS, C. J. & QUINTON, J. N. (2009b) Policy implications of pollution swapping. *Physics and Chemistry of the Earth,* 34**,** 589-594.
STRAUSS, P., LEONE, A., RIPA, M. N., TURPIN, N., LESCOT, J. M. & LAPLANA, R. (2007) Using critical source areas for targeting cost-effective best management practices to mitigate phosphorus and sediment transfer at the watershed scale. *Soil Use and Management,* 23**,** 144-153.
STUTTER, M. I., CHARDON, W. J. & KRONVANG, B. (2012) Riparian Buffer Strips as a Multifunctional Management Tool in Agricultural Landscapes: Introduction. *J. Environ. Qual.,* 41**,** 297-303.
STUTTER, M. I., DEEKS, L. K., LOW, D. & BILLETT, M. F. (2006) Impact of soil and groundwater heterogeneity on surface water chemistry in an upland catchment. *Journal of Hydrology,* 318**,** 103-120.
STUTTER, M. I., LANGAN, S. J. & DEMARS, B. O. L. (2007) River sediments provide a link between catchment pressures and ecological status in a mixed land use Scottish River system. *Water Research,* 41**,** 2803-2815.
STUTTER, M. I., LUMSDON, D. G., BILLETT, M. F., LOW, D. & DEEKS, L. K. (2009) Spatial Variability in Properties Affecting Organic Horizon Carbon Storage in Upland Soils. *Soil Science Society of America Journal,* 73**,** 1724-1732.
TABACHNICK, B. G. & FIDELL, L. S. (2001) *Using Multivariate Statistics*, Allyn and Bacon, pp. 966.
TEAGASC (2013) Agricultural Catchments Programme. www.teagasc.ie/agcatchments. Last accessed on 24th July 2013
TETZLAFF, D., SOULSBY, C., WALDRON, S., MALCOLM, I. A., BACON, P. J., DUNN, S. M., LILLY, A. & YOUNGSON, A. F. (2007) Conceptualization of runoff processes using a geographical information system and tracers in a nested mesoscale catchment. *Hydrological Processes,* 21**,** 1289-1307.
TOMER, M. D. & LOCKE, M. A. (2010) The Challenge of Documenting Water Quality Benefits of Conservation Practices: A Review of USDA-ARS's Conservation Effects Assessment Project Watershed Studies. IN VAN BOCHOVE, E., VANROLLEGHEM, P. A., CHAMBERS, P. A., THERIAULT, G., NOVOTNA, B. & BURKART, M. R. (Eds.) *14th International Conference of the IWA Diffuse Pollution Specialist Group, DIPCON 2010.* Quebec, Canada, IWA.
TOWNSEND, C. R., UHLMAN, S. S. & MATTHAEI, C. D. (2008) Individual and combined reponses of stream ecosystems to multiple stressors. *Journal of Applied Ecology,* 45**,** 1810-9.
TRUMPER, K., BERTZKY, M., DICKSON, B., VAN DER HEIJDEN, G., JENKINS, M. & MANNING, P. (2009) The Natural Fix? The role of ecosystems in climate mitigation. A UNEP rapid response assessment. Cambridge, UK., United Nations Environment Programme, UNEP-WCMC.

TURNER, E. K., WORRALL, F. & BURT, T. P. (2013) The effect of drain blocking on the dissolved organic carbon (DOC) budget of an upland peat catchment in the UK. *Journal of Hydrology,* 479**,** 169-179.
TYRREL, S. F. & QUINTON, J. N. (2003) Overland flow transport of pathogens from agricultural land receiving faecal wastes. *Journal of Applied Microbiology,* 94**,** 87S-93S.
UK TAG (2008) UK Environmental Standards and Conditions (Phase 2). WFD UK TAG, pp. 84.
UK TAG (2012) A revised approach to setting Water Framework Directive phosphorus standards, pp. 35. www.wfduk.org. Last accessed on 28th February 2013.
UK NATIONAL ECOSYTEM ASSESSMENT (2011) The UK National Ecosystem Assessment: Synthesis of the Key Findings. UNEP-WCMC, pp. 87.
USDA (1999) Soil Taxonomy. A Basic System of Soil Classification for Making and Interpreting Soil Surveys. *Agriculture Handbook 436.* 2nd ed. USDA Natural Resources Conservation Service, pp. 871.
VAN DEN BERG, L. J. L., SHOTBOLT, L. & ASHMORE, M. R. (2012) Dissolved organic carbon (DOC) concentrations in UK soils and the influence of soil, vegetation type and seasonality. *Science of the Total Environment,* 427**,** 269-276.
VAN DER LEE, G. E. M., VENTERINK, H. O. & ASSELMAN, N. E. M. (2004) Nutrient retention in floodplains of the Rhine distributaries in The Netherlands. *River Research and Applications,* 20**,** 315-325.
VAN OOST, K., GOVERS, G., QUINE, T. A. & HECKRATH, G. (2004) Comment on "Managing Soil Carbon" (1). *Science,* 305**,** 1567b.
VANNOTE, R. L., MINSHALL, G. W., CUMMINS, K. W., SEDELL, J. R. & CUSHING, C. E. (1980) RIVER CONTINUUM CONCEPT. *Canadian Journal of Fisheries and Aquatic Sciences,* 37**,** 130-137.
VENTERINK, H. O., VERMAAT, J. E., PRONK, M., WIEGMAN, F., VAN DER LEE, G. E. M., VAN DEN HOORN, M. W., HIGLER, L. W. G. & VERHOEVEN, J. T. A. (2006) Importance of sediment deposition and denitrification for nutrient retention in floodplain wetlands. *Applied Vegetation Science,* 9**,** 163-174.
VIDON, P. (2010) Riparian zone management and environmental quality: a multi-contaminant challenge. *Hydrological Processes,* 24**,** 1532-1535.
VIDON, P., HUBBARD, L. E. & SOYEUX, E. (2009) Seasonal solute dynamics across land uses during storms in glaciated landscape of the US Midwest. *Journal of Hydrology,* 376**,** 34-47.
VIDON, P., WAGNER, L. E. & SOYEUX, E. (2008) Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses. *Biogeochemistry,* 88**,** 257-270.
WAGENHOFF, A., TOWNSEND, C. R. & MATTHAEI, C. D. (2012) Macroinvertebrate responses along broad stressor gradients of deposited fine sediment and dissolved nutrients: a stream mesocosm experiment. *Journal of Applied Ecology,* 49**,** 892-902.
WAGENHOFF, A., TOWNSEND, C. R., PHILLIPS, N. & MATTHAEI, C. D. (2011) Subsidy-stress and multiple-stressor effects along gradients of deposited fine sediment and dissolved nutrients in a regional set of streams and rivers. *Freshwater Biology,* 56**,** 1916-1936.
WALL, D., JORDAN, P., MELLAND, A. R., MELLANDER, P. E., BUCKLEY, C., REANEY, S. M. & SHORTIE, G. (2011) Using the nutrient transfer

continuum concept to evaluate the European Union Nitrates Directive National Action Programme. *Environmental Science & Policy,* 14**,** 664-674.
WALL, D. P., JORDAN, P., MELLAND, A. R., MELLANDER, P. E., MECHAN, S. & SHORTLE, G. (2013) Forecasting the decline of excess soil phosphorus in agricultural catchments. *Soil Use and Management,* 29**,** 147-154.
WALL, D. P., MURPHY, P. N. C., MELLAND, A. R., MECHAN, S., SHINE, O., BUCKLEY, C., MELLANDER, P. E., SHORTLE, G. & JORDAN, P. (2012) Evaluating nutrient source regulations at different scales in five agricultural catchments. *Environmental Science & Policy,* 24**,** 34-43.
WALLAGE, Z. E., HOLDEN, J. & MCDONALD, A. T. (2006) Drain blocking: An effective treatment for reducing dissolved organic carbon loss and water discolouration in a drained peatland. *Science of the Total Environment,* 367**,** 811-821.
WALLEY, W. J. & HAWKES, H. A. (1997) A computer-based development of the Biological Monitoring Working Party score system incorporating abundance rating, site type and indicator value. *Water Research,* 31**,** 201-210.
WALLING, D. E. (1999) Linking land use, erosion and sediment yields in river basins. *Hydrobiologia,* 410**,** 223-240.
WALLING, D. E. & OWENS, P. N. (2003) The role of overbank floodplain sedimentation in catchment contaminant budgets. *Hydrobiologia,* 494**,** 83-91.
WALLING, D. E., WEBB, B. & SHANAHAN, J. (2007) Investigations into the use of critical sediment yields for assessing and managing fine sediment inputs into freshwater ecosystems. Natural England, Sheffield, pp. 105.
WALLING, D. E. & WEBB, B. W. (1985) ESTIMATING THE DISCHARGE OF CONTAMINANTS TO COASTAL WATERS BY RIVERS - SOME CAUTIONARY COMMENTS. *Marine Pollution Bulletin,* 16**,** 488-492.
WALLING, D. E. & WEBB, B. W. (1986) Solutes in river systems. In: T., T. S. (Ed.) *Solute Processes.* Chichester, John Wiley & Sons Ltd., 251-327.
WALLING, D. E., WEBB, B. W. & RUSSELL, M. A. (1997) Sediment-associated nutrient transport in British Rivers. In: WEBB, B. W. (Ed.) *Freshwater Contamination (Proc. Rabat Symp., April 1997).* IAHS Press, Wallingford, UK, 69-81.
WANG, Z. M., SONG, K. S., ZHANG, B., LIU, D. W., LI, X. Y., REN, C. Y., ZHANG, S. M., LUO, L. & ZHANG, C. H. (2009) Spatial variability and affecting factors of soil nutrients in croplands of Northeast China: a case study in Dehui County. *Plant Soil and Environment,* 55**,** 110-120.
WARREN, N., ALLAN, I. J., CARTER, J. E., HOUSE, W. A. & PARKER, A. (2003) Pesticides and other micro-organic contaminants in freshwater sedimentary environments - a review. *Applied Geochemistry,* 18**,** 159-194.
WEBSTER, R. & OLIVER, M. A. (2001) *Geostatistics for Environmental Scientists.*, John Wiley & Sons, Ltd. Chichester, England, pp. 271.
WEISHAAR, J. L., AIKEN, G. R., BERGAMASCHI, B. A., FRAM, M. S., FUJII, R. & MOPPER, K. (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology,* 37**,** 4702-4708.
WEITMAN, D. (2010) Regulatory and Voluntary Programs to Control Nonpoint Source Pollution in the United States. IN VAN BOCHOVE, E.,

VANROLLEGHEM, P. A., CHAMBERS, P. A., THERIAULT, G., NOVOTNA, B. & BURKART, M. R. (Eds.) *Proceedings of the 14th International Conference of the IWAS Diffuse Pollution Specialist Group, DIPCON 2010.* Quebec, Canada, IWA, 262-267.

WHITEHEAD, P. G. & CROSSMAN, J. (2012) Macronutrient cycles and climate change: Key science areas and an international perspective. *Science of the Total Environment,* 434**,** 13-17.

WHITEHEAD, P. G., FUTTER, M. N. & WILBY, R. L. (2006) Impacts of climate change on hydrology, nitrogen and carbon in upland and lowland streams: assessment of adaptation strategies to meet Water Framework Directive Objectives. *Proceedings of the BHS 9th National Hydrology Symposium.* Durham, 129-134.

WHITEHEAD, P. G., WILBY, R. L., BATTARBEE, R. W., KERNAN, M. & WADE, A. J. (2009) A review of the potential impacts of climate change on surface water quality. *Hydrological Sciences Journal-Journal Des Sciences Hydrologiques,* 54**,** 101-123.

WILBY, R. L., ORR, H., WATTS, G., BATTARBEE, R. W., BERRY, P. M., CHADD, R., DUGDALE, S. J., DUNBAR, M. J., ELLIOTT, J. A., EXTENCE, C., HANNAH, D. M., HOLMES, N., JOHNSON, A. C., KNIGHTS, B., MILNER, N. J., ORMEROD, S. J., SOLOMON, D., TIMLETT, R., WHITEHEAD, P. J. & WOOD, P. J. (2010) Evidence needed to manage freshwater ecosystems in a changing climate: Turning adaptation principles into practice. *Science of the Total Environment,* 408**,** 4150-4164.

WILLIAMS, G. P. (1989) Sediment concentration versus water discharge during single hydrologic events in rivers. *Journal of Hydrology,* 111**,** 89-106.

WILSON, H. F. & XENOPOULOS, M. A. (2008) Ecosystem and seasonal control of stream dissolved organic carbon along a gradient of land use. *Ecosystems,* 11**,** 555-568.

WILSON, L., WILSON, J., HOLDEN, J., JOHNSTONE, I., ARMSTRONG, A. & MORRIS, M. (2010) Recovery of water tables in Welsh blanket bog after drain blocking: Discharge rates, time scales and the influence of local conditions. *Journal of Hydrology,* 391**,** 377-386.

WILSON, L., WILSON, J., HOLDEN, J., JOHNSTONE, I., ARMSTRONG, A. & MORRIS, M. (2011a) Ditch blocking, water chemistry and organic carbon flux: Evidence that blanket bog restoration reduces erosion and fluvial carbon loss. *Science of the Total Environment,* 409**,** 2010-2018.

WILSON, L., WILSON, J., HOLDEN, J., JOHNSTONE, I., ARMSTRONG, A. & MORRIS, M. (2011b) The impact of drain blocking on an upland blanket bog during storm and drought events, and the importance of sampling-scale. *Journal of Hydrology,* 404**,** 198-208.

WINDOLF, J., BLICHER-MATHIESEN, G., CARSTENSEN, J. & KRONVANG, B. (2012) Changes in nitrogen loads to estuaries following implementation of governmental action plans in Denmark: A paired catchment and estuary approach for analysing regional responses. *Environmental Science & Policy,* 24**,** 24-33.

WITHERS, P. & JARVIS, S. C. (1998) Mitigation options for diffuse phosphorus loss to water. *Soil Use and Management,* 14**,** 186-192.

WITHERS, P. J. A., MAY, L., JARVIE, H. P., JORDAN, P., DOODY, D., FOY, R. H., BECHMANN, M., COOKSLEY, S., DILS, R. & DEAL, N. (2012) Nutrient emissions to water from septic tank systems in rural catchments:

Uncertainties and implications for policy. *Environmental Science & Policy,* 24**,** 71-82.
WOOD, F. L., HEATHWAITE, A. L. & HAYGARTH, P. M. (2005a) Evaluating diffuse and point phosphorus contributions to river transfers at different scales in the Taw catchment, Devon, UK. *Journal of Hydrology,* 304**,** 118-138.
WOOD, P. J. & ARMITAGE, P. D. (1997) Biological effects of fine sediment in the lotic environment. *Environmental Management,* 21**,** 203-217.
WOOD, P. J. & ARMITAGE, P. D. (1999) Sediment deposition in a small lowland stream - Management implications. *Regulated Rivers-Research & Management,* 15**,** 199-210.
WOOD, P. J., PITCHER, A., MONK, W. A. & WORRALL, T. (2011) The influence of substratum composition on benthic invertebrates: Testing PSI, Report for the Environment Agency, Bristol, UK, pp. 25.
WOOD, P. J., TOONE, J., GREENWOOD, M. T. & ARMITAGE, P. D. (2005b) The response of four lotic macroinvertebrate taxa to burial by sediments. *Archiv Fur Hydrobiologie,* 163**,** 145-162.
WORRALL, F., ARMSTRONG, A. & HOLDEN, J. (2007) Short-term impact of peat drain-blocking on water colour, dissolved organic carbon concentration, and water table depth. *Journal of Hydrology,* 337**,** 315-325.
WORRALL, F. & BURT, T. P. (2007) Flux of dissolved organic carbon from UK rivers. *Global Biogeochemical Cycles,* 21.
WORRALL, F., HARRIMAN, R., EVANS, C. D., WATTS, C. D., ADAMSON, J., NEAL, C., TIPPING, E., BURT, T., GRIEVE, I., MONTEITH, D., NADEN, P. S., NISBET, T., REYNOLDS, B. & STEVENS, P. (2004) Trends in dissolved organic carbon in UK rivers and lakes. *Biogeochemistry,* 70**,** 369-402.
WORRALL, F., ROWSON, J. G., EVANS, M. G., PAWSON, R., DANIELS, S. & BONN, A. (2011) Carbon fluxes from eroding peatlands - the carbon benefit of revegetation following wildfire. *Earth Surface Processes and Landforms,* 36**,** 1487-1498.
WORRALL, F., SPENCER, E. & BURT, T. P. (2009) The effectiveness of nitrate vulnerable zones for limiting surface water nitrate concentrations. *Journal of Hydrology,* 370**,** 21-28.
WORSHAM, L., MARKEWITZ, D. & NIBBELINK, N. (2010) Incorporating spatial dependence into estimates of soil carbon contents under different land covers. *Soil Science Society of America Journal,* 74**,** 635-646.
WRIGHT, D. B. (2009) Modern regression techniques using R: a practical guide for students and researchers. London: SAGE. DOI: 10.4135/9780857024497
WRIGHT, J. F. (2000) An introduction to RIVPACS. In: WRIGHT, J. F., SUTCLIFFE, D. W. & FURSE, M. T. (Eds.) *Assessing the biological quality of freshwaters.* The Freshwater Biological Association, 1-23.
WWAP (2012) Managing Water under Uncertainty and Risk: The United Nations World Water Development Report 4. UNESCO Paris, pp. 909.
YALLOP, A. R. & CLUTTERBUCK, B. (2009) Land management as a factor controlling dissolved organic carbon release from upland peat soils 1: Spatial variation in DOC productivity. *Science of the Total Environment,* 407**,** 3803-3813.
YAN, B., FANG, N. F., ZHANG, P. C. & SHI, Z. H. (2013) Impacts of land use change on watershed streamflow and sediment yield: An assessment

using hydrologic modelling and partial least squares regression. *Journal of Hydrology,* 484**,** 26-37.

YATES, A. G., BAILEY, R. C. & SCHWINDT, J. A. (2007) Effectiveness of best management practices in improving stream ecosystem quality. *Hydrobiologia,* 583**,** 331-344.

YATES, A. G., BRUA, R. B., CORRIVEAU, J., CULP, J. M. & CHAMBERS, P. A. (2013) Seasonally driven variation in spatial relationships between agricultural land use and in-stream nutrient concentrations. *River Research and Applications*. DOI: 10.1002/rra.2646

YSI, S. (2009) Flow Tracker Hand Held ADV Technical Manual. Firmware Version 3.7. Software Version 2.30. SonTek YSI, pp. 126 .

ZHANG, J. B., ZHU, T. B., CAI, Z. C., QIN, S. W. & MUELLER, C. (2012) Effects of long-term repeated mineral and organic fertilizer applications on soil nitrogen transformations. *European Journal of Soil Science,* 63**,** 75-85.

ZHANG, S., LU, X. X., SUN, H. & HAN, J. (2011) Modeling catchment controls on organic carbon fluxes in a meso-scale mountainous river (Luodingjiang), China. *Quaternary International,* 244**,** 296-303.

ZWEIG, L. D. & RABENI, C. F. (2001) Biomonitoring for deposited sediment using benthic invertebrates: a test on 4 Missouri streams. *Journal of the North American Benthological Society,* 20**,** 643-657.